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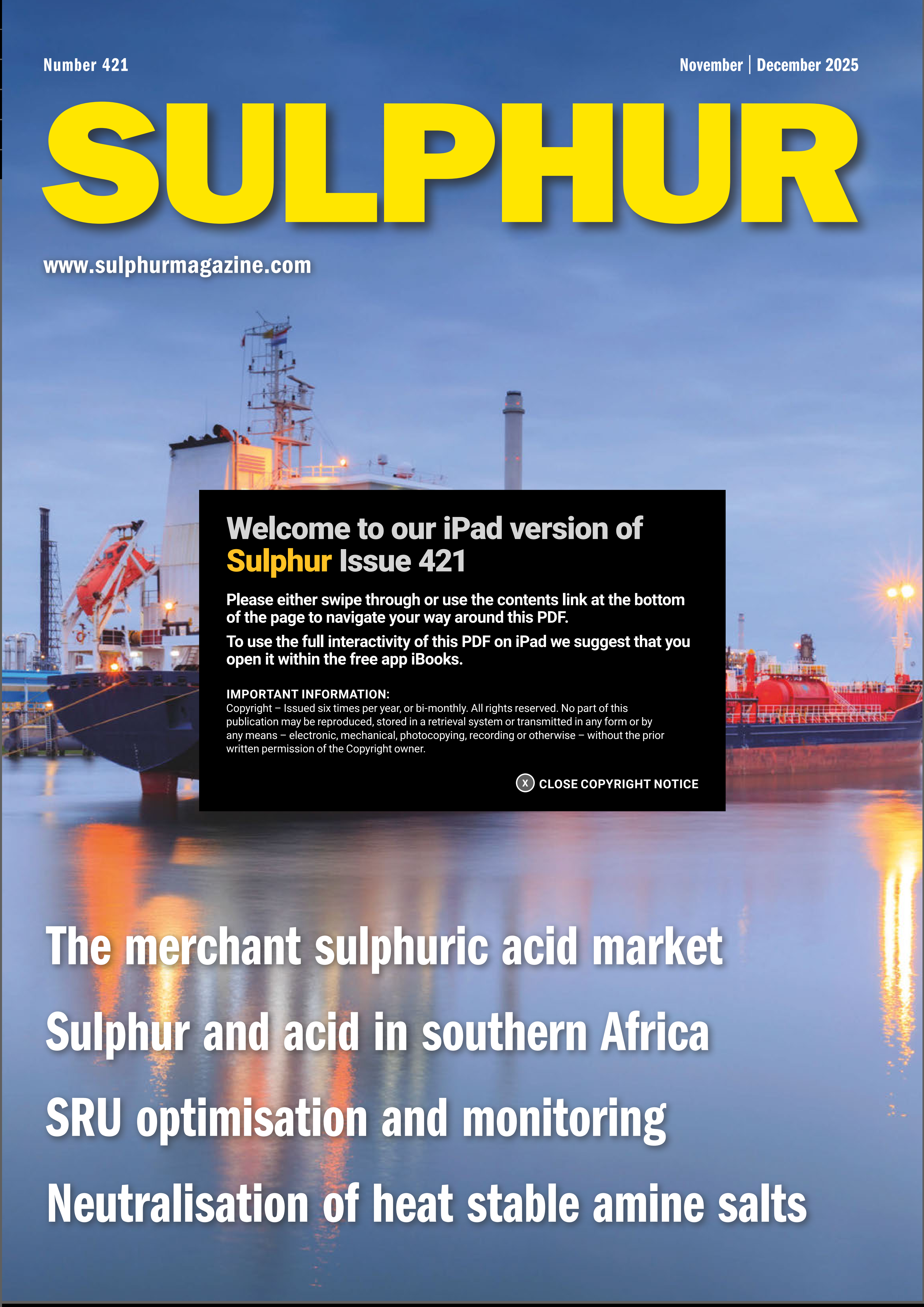

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The merchant sulphuric acid market

Sulphur and acid in southern Africa

SRU optimisation and monitoring

Neutralisation of heat stable amine salts

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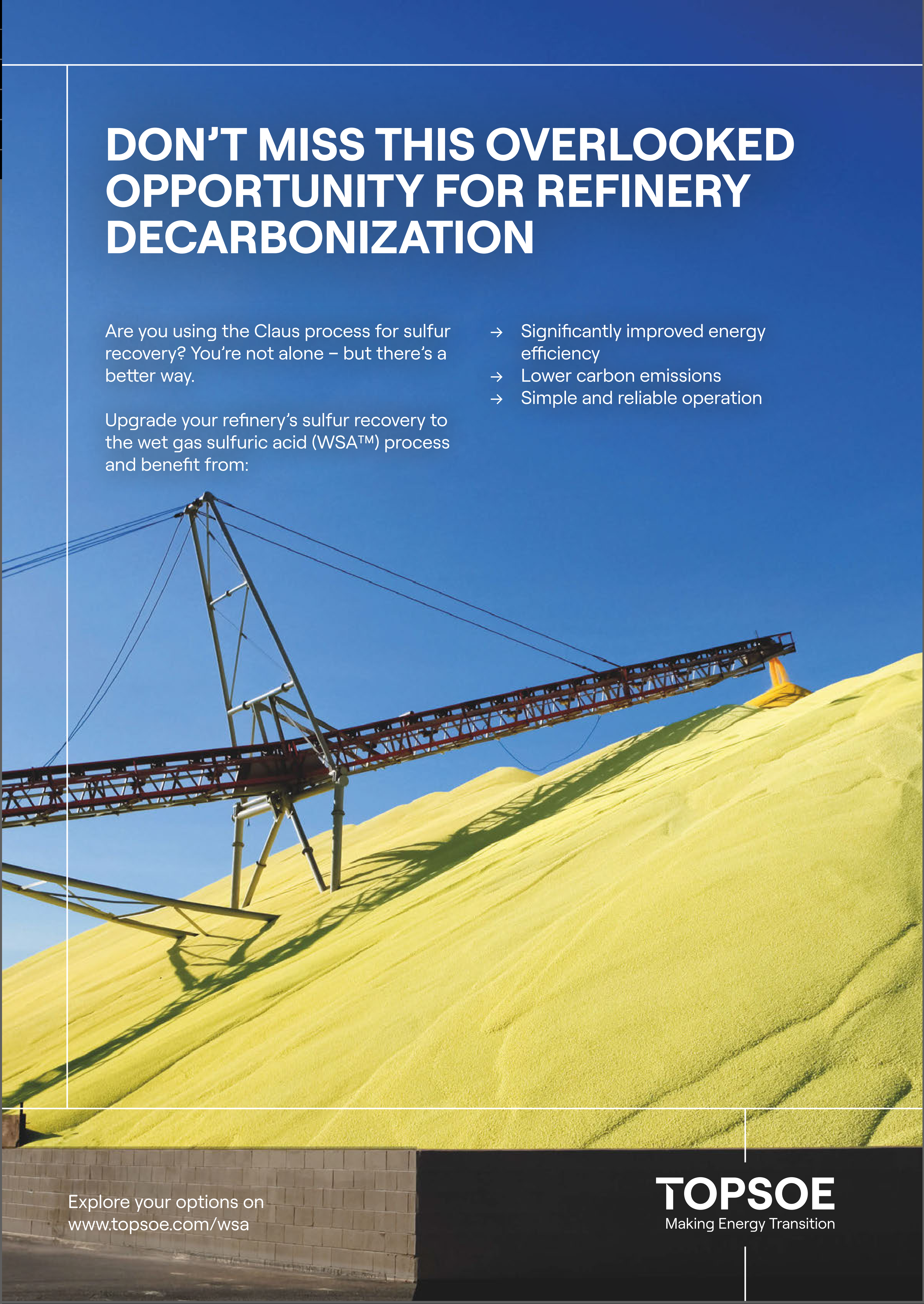

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Cover: *Tanker in the Tweede Petroleumhaven in Rotterdam. Photo: GAPS/ istockphoto.com*

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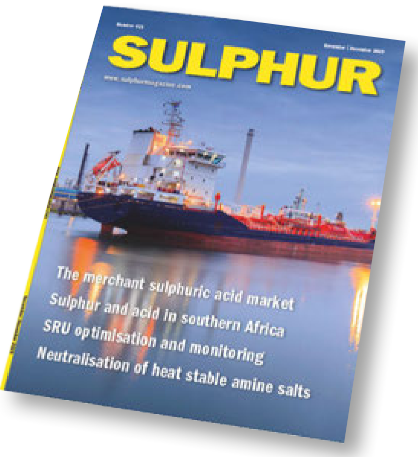
A cold wind from the east


SULPHUR

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> “The sulphuric acid market has also been affected by the surge in sulphur prices...”

Prices in sulphur markets have been climbing rapidly for several weeks now due to short supply, reaching their highest levels for early two and a half years, since July 2022. A major cause has been widening Ukrainian drone and missile strikes against Russian oil and gas facilities. In particular, drone strikes in September on the Astrakhan and Orenburg natural gas plants led to Russian sulphur exports being cut drastically, first from around 400,000 tonnes per month to only 100,000 tonnes in October, and then to zero from the 1st of November, as Russia implemented a ban on exports of sulphur used in fertilizer production which was projected to last at least until December 31st. “This decision will stabilise shipments of raw materials to the domestic market to maintain current mineral fertilizer production volumes and ensure the country’s food security,” the government’s press service reported. The restriction applies to the export of liquid, granulated, and lump sulphur. It remains to be seen whether exports of Kazakh material from Ust Luga will be affected, but some Kazakh sulphur is now being sold via Iran.

Particularly affected has been Indonesia. One of the key inputs for HPAL operations is sulphuric acid which accounted for 24% of HPAL processing costs in 2024, making it the second largest cost component after consumables. As a result, the large share of acid in processing costs leaves HPAL operations exposed to fluctuations in the sulphur price. Sulphur prices reached $420-430/t c.fr delivered into Indonesia at the end of October, more than $100/t up on June 2024. There is some temporary respite from increasing prices for cobalt, which is co-produced with the nickel, but Indonesian sulphur imports were up 52% year on year for the period from January to September, reaching 3.7 million tonnes, compared to 2.4 million tonnes (itself a record) for the same period of 2024.

The sulphuric acid market has also been affected by the surge in sulphur prices. As we note in our article in this issue, merchant sulphuric acid has increasingly come from sulphur burning acid plants, especially in China, and as high sulphur prices force some acid producers to shut down, so traders are increasingly looking for scarce smelter acid cargoes, themselves constrained by lack of copper concentrate availability. At the same time, fertilizer demand remains robust, though India may see some demand destruction from phosphate producers. Coupled with some refinery outages and logistics bottlenecks in sulphur supply, CRU expects sulphur prices to remain elevated through the fourth quarter of 2025. However, it is likely that Russia will return to the export market in Q1 2026, hopefully providing some much needed relief to the market. ■

Richard Hands, Editor

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Price Trends

SULPHUR

Sulphur prices advanced further in October, more than expected, supported by the supply towards the end of summer becoming restricted, with a number of non-mainstream sources facing logistical constraints.

Russian supply was cut due to drone strikes at the Astrakhan and Orenburg gas plants in early September. Exports of sulphur from Russian ports fell from around 400,000 tonnes per month to 100,000 tonnes in October. Bullish pricing prevailed, with higher benchmark prices from China and Indonesia.

Indonesian prices reached $420-430/t c.fr at the start of November, with offers heard up to $440/t c.fr. Upward price momentum is likely to continue with a number of buyers lacking the import licenses needed to shift from sulphur to sulphuric acid, according to market participants. As such, demand is expected to tick along throughout November.

Although the phosphate export window has now closed, the bullish sentiment also remains present in China with deals reaching as high as $420/t c.fr in the south. Additionally, a phosphate producer in southern China is said to have bought Canadian material at $408-410/t c.fr. Port spot prices are reported at rmb 3,350-3,360/t ($472-473/t), up $8/t compared with last week. This port price would indicate a delivered price of around $408/t c.fr. Sulphur port inventories in China decreased by 58,000 tonnes to around 2.299 million tonnes as of 29 October 2025. Stocks at Yangtze River ports rose by 34,000 tonnes to 1.036 million tonnes, while Dafeng port inventories declined by 30,000 tonnes to around 250,000 tonnes.

In the Middle East, the Qatar Sulphur Price (QSP) was set $76/t above October levels but other monthly contracts by KPC and ADNOC were yet to be released as of the time of writing. Still, the market has not seen benchmark prices at these levels since July 2022 at $428/t c.fr. This, along with higher Asian deals, pushed prices in the Middle East to $400-410/t f.o.b. The new QSP reflects delivered levels to China in the high $410s/t c.fr, and follows the QatarEnergy tender which is understood to have been awarded at around $412/t f.o.b. to another producer in the region.

The Brazilian market also saw an uptick in prices to $390-395t c.fr, based on higher global levels. The price was indicated higher in line with higher prices at origin locations with previous levels no longer considered viable by market sources. The market has seen limited activity after a single bid was presented in a CMOC tender at a level around $410-412/t c.fr. The tender was scrapped, and it is understood that negotiations post-tender also failed, according to market participants. Since then, offers into the market have been heard at around $410-420/t c.fr, but no transactions are understood to have taken place at these levels. The Brazilian market has most recently looked at Canadian material due to the risk of trade tariffs between Brazil and the US. Still, competition for Canadian material has increased with enquiries now reported from Brazil, India, China and Indonesia, according to industry participants.

In the Mediterranean, tight availability alongside persistent demand supported price increases in both f.o.b. and c.fr bases. The price is bullish and further increases are expected on any new business. Mediterranean sulphur prices were assessed up at $380-400/t f.o.b. and $410-425/t c.fr at the start of November.

In Africa, the main Tanzanian port of Dar Es Salaam was reported as closed, with operations halted until at least 31 October. The disruption comes after as civil unrest was reported following the general elections held in the country on 29 October. Operations are also being affected by a government-imposed internet blackout, according to industry sources. Dar Es Salaam is the largest port in the country and is considered essential for trade not only by Tanzania but also functioning as an entry point to a number of landlocked neighbouring countries. Sulphur imports into the port are estimated at around 1.2 million t/a but the country has most recently been building stock at port estimated at around 200,000 tonnes.

SULPHURIC ACID

Global sulphuric acid prices have seen steady declines from the peak of July this year, with the return of smelter supply

Price Indications

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

Cash equivalent	June	July	August	September	October
Sulphur, bulk ($/t)					
Adnoc monthly contract	290	265	265	285	324
China c.fr spot	280	280	285	334	415
Liquid sulphur ($/t)					
Tampa f.o.b. contract	252	252	252	252	310
NW Europe c.fr	274	290	290	290	240
Sulphuric acid ($/t)					
US Gulf spot	155	163	163	120	128

Source: various

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from maintenance, combined with weak demand. October saw a shift to a more bullish sulphuric acid market, driven primarily by a higher sulphur price environment (see above) combined with supply constraints due to limited Indonesian production. Demand also gained momentum. As a result, multiple sulphuric acid benchmarks climbed towards the end of the month, reflecting sustained bullish momentum driven by tighter availability, stronger sulphur pricing, and firmer December-loading indications.

Spot prices for sulphuric acid into the US Gulf were assessed at $125-140/t c.fr, with market sources indicating a number of transactions in the $130-140/t c.fr range. Sentiment is broadly bullish, supported by tightening supply in Europe and elevated sulphur prices.

The Chinese acid export market surged 103% year on year in January-September, with smelter material filling international gaps amid renewed demand from Saudi Arabia and Chile. In October sulphuric acid spot prices moved to $95-105/t f.o.b., the highest since July 2022. Offers as high as $120/t f.o.b. were reported, though these have not been confirmed. Producers have reportedly recently raised spot offers to around $110/t f.o.b. Again the market tone is bullish, with strength in sulphur prices supporting higher acid values. In Japan and South Korea, export prices moved up to $80-95/t f.o.b. despite limited liquidity, tracking higher levels in China and reflecting where cargoes would likely clear if moved.

India's acid market is trending up as sulphur-driven burner economics raise the floor. Trades at $137-145/t c.fr have reset benchmarks. Offers for 20,000 tonnes cluster at $140-150/t, while pricing for smaller lots is higher due to scarcity and freight. Near term, the bias is higher towards $150/t c.fr, with downside capped unless sulphur softens or Chinese availability improves. Paradeep Phosphates Limited (PPL) bought 20,000 tonnes from a trader at $137/t c.fr for equal discharge at Paradip and Mangalore, though several sources indicate the parcel will fully discharge at Paradip. The cargo, reportedly of Far East origin, likely Japan or South Korea, is due late November to early December. Separately, a 10,000 tonne parcel was sold to Mangalore Chemicals at $140-145/t c.fr for December loading, reportedly sourced from China via Torbert; the trader involvement remains unconfirmed. Local traders suggest PPL secured both parcels below prevailing indications. Fertilisers and Chemicals Travancore Limited (FACT) has closed a tender for two parcels of 10,000-14,000 tonnes each for discharge at Cochin. Three bidders participated - Hindalco, Hexagon, and Libra Alkalischemie Private Limited, a new entrant to India's acid supply chain. Market participants expect offers to reflect the firmer environment, likely $140–150/t c.fr. India's October acid imports were about 221,100 tonnes, up 38% year on year, according to Interocean vessel tracking, underscoring India's continued reliance on seaborne supply. Early November arrivals total roughly 48,000 tonnes, keeping inflows steady ahead of the Rabi season.

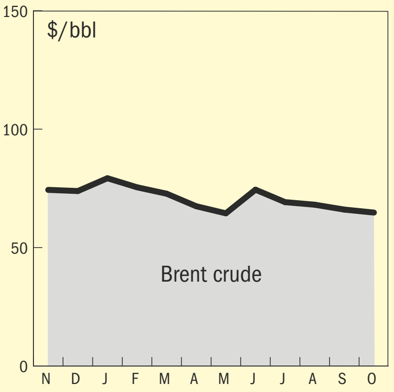
In October, the northwestern European f.o.b. level edged higher but still remained $37/t down from the peak seen in mid-June at $135/t f.o.b. Availability in the region has started to tighten up despite muted Moroccan demand, with December shipments now reported at $90-95/t f.o.b. Fresh spot interest is now centred on December and January loadings. For second-half December into early January, indications have been pegged as high as $100/t f.o.b., with near-term CFc.frR ideas around $105/t. Reported December loadings were $90–100/t f.o.b. Near-term sentiment is bullish, with tight spot supply supporting further gains.

Brazilian spot prices were steady, unchanged for a month amid limited market liquidity. In South America, attention centred on Chile, where initial ideas for annual contract negotiations were heard, with early indications in the $160s/t c.fr. That backdrop, together with firmer global f.o.b. levels, helped nudge Chilean spot indications to $150-160/t c.fr despite a lack of concluded sales. Prices are likely to keep trending higher in the region.

In Chile, the market has been quiet, with prices holding around $153/t c.fr for three consecutive weeks, and significant activity is unlikely to resume until Q2. Even so, a more bullish global backdrop should lend support despite limited demand. Average prices are forecast to firm from $152/t c.fr in October to a peak of $163/t c.fr in February, before drifting back to roughly $152/t c.fr by October 2026. ■

END OF MONTH SPOT PRICES

oil



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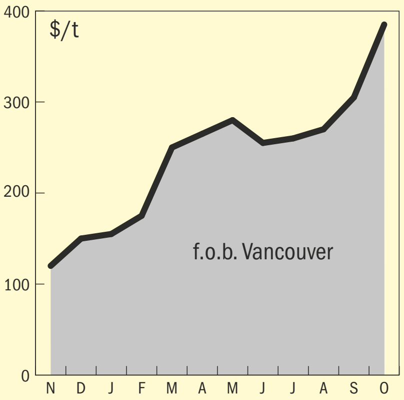
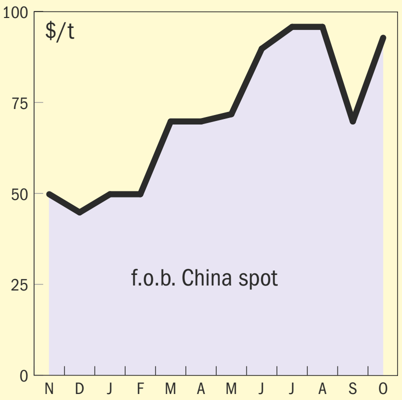
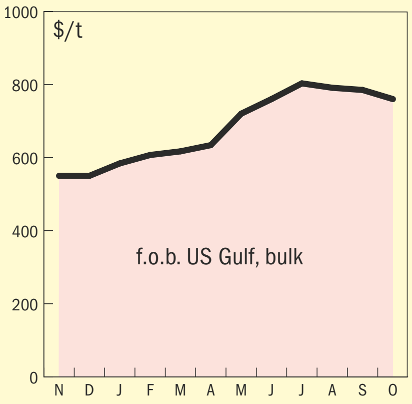


sulphuric acid



diammonium phosphate



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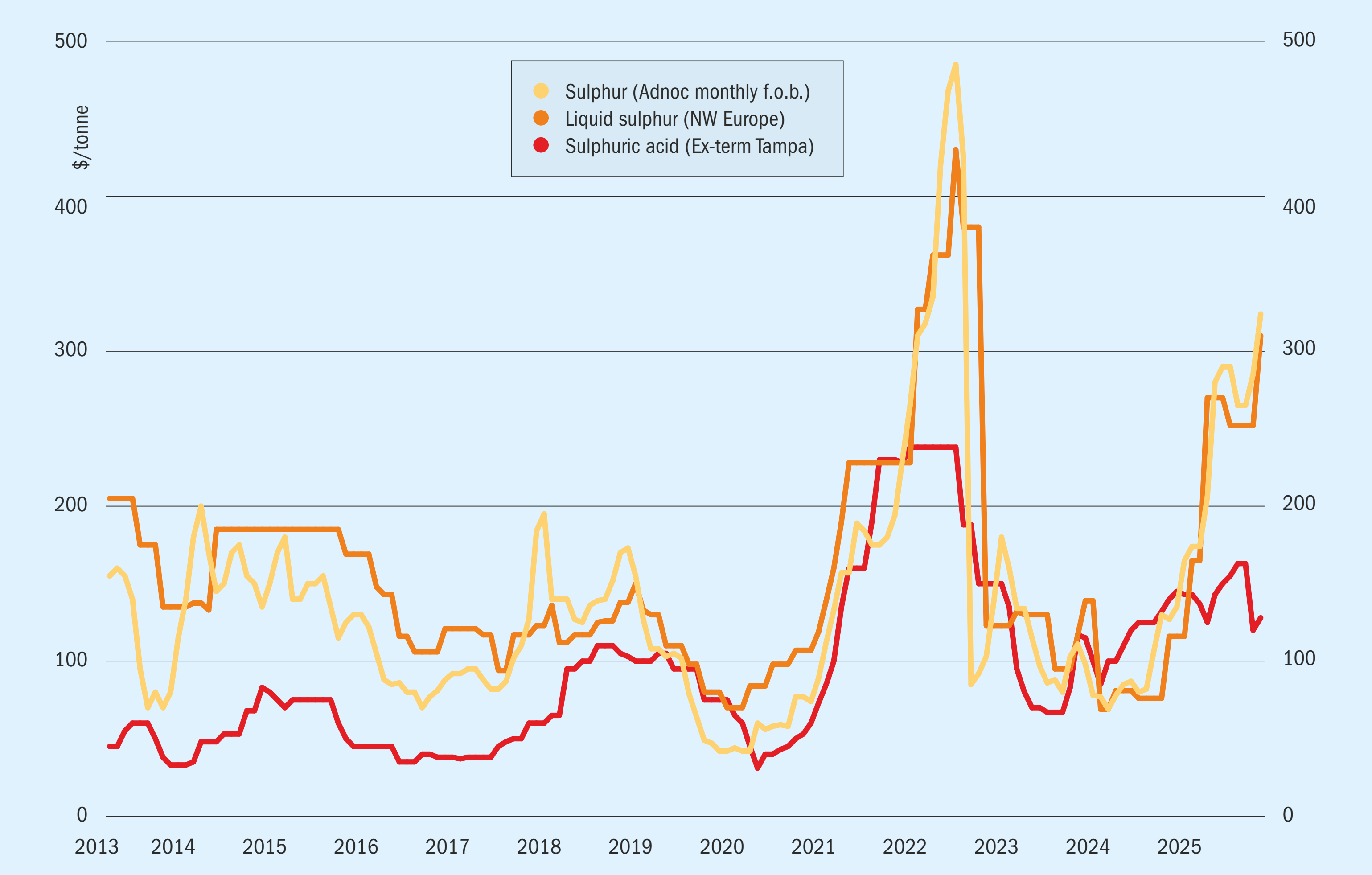
Market Outlook

Historical price trends $/tonne



Source: CRU

SULPHUR

- Russia is set to impose a temporary ban on sulphur exports, covering liquid, granulated, and lump material, to ensure domestic supply. The measure will be in effect until 31 December 2025. CRU expects Russia to return to the export market in 2026 Q1. On the other hand, exports from Iranian ports are set to come back not only for Iranian production but also for Turkmenistan.
- Sulphur spot prices in the Middle are set to peak at $430/t f.o.b. in December-January before steadily declining to a low of $268/t f.o.b. in October 2026.
- Average Canadian prices moved to $385/t f.o.b., supported by the latest Asian transactions. Prices are set to trend similarly to other key markets, peaking at a forecast price of $420/t f.o.b. in January 2026 before falling to a low of $262/t f.o.b. in October 2026.
- Demand in Asia has been a highlight, with Indonesia particularly active. In the Chinese phosphate sector, sulphur has become chronically unaffordable, with the share of phosphate price already at around 84%, poised to surpass the 2022 peak of 92%. This implies crisis-level cost pressure for consumers. Prices are set to rise until January and then decline through 2026. Unlike 2022, normalisation is less likely to come quickly from the supply side; near-term adjustment will need to come from demand rationing or substitution.
- European sulphur prices are expected to peak in January before correcting lower thereafter. With northern hemisphere winter exports typically subdued, demand will need to soften to pull prices down. The 2026 Q1 decline will be driven largely by increased Russian and Iranian supply and slower Chinese consumption after the New Year holiday.

SULPHURIC ACID

- NW Europe prices are likely to continue higher to an average peak of $92/t f.o.b. in January, then trend lower through the year to a low near $72/t f.o.b. by October 2026. Morocco will likely step back into the market in 2026 Q1 for cargoes, which should help support the European FOB level.
- Chinese demand is likely to be even stronger from Saudi Arabia and from Indonesia in 2026. Higher sulphur prices have encouraged a shift from sulphur burning to importing acid, with Indonesia already taking Chinese cargoes. The price divergence between sulphur and sulphuric acid is incentivising increased acid imports, particularly in Indonesia and India. This should more rapidly absorb any surplus in the market.
- Acid premiums have compressed sharply, with India and China briefly in negative territory, weakening sulphur-burner economics. In the near term, firm sulphur prices and constrained Asian smelter availability should keep imports elevated and support sulphuric acid prices into early 2026.
- Overall, prices are expected to rebound in November-December and remain supported through much of Q1, aided by limited Asian smelter availability due to seasonal maintenance and a likely pickup in Chilean procurement ■

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KUWAIT

SRU contract awarded for gas sweetening facility

India's Megha Engineering and Infrastructures Limited (MEIL) has won a $225.5 million contract from the Kuwait Oil Company (KOC) for setting up a new gas sweetening and sulphur recovery facility at West Kuwait oilfields. The project, to be developed on a build-own-operate basis with a buyback option for KOC, includes design, construction, operation and maintenance. It will be completed in two years, followed by a five-year operation and maintenance phase.

A senior MEIL official said the sulphur recovery unit (SRU) will have two trains of 100 t/d capacity each, achieving about 99.9% sulphur recovery. The facility will treat sour gas with up to 4% hydrogen sulphide and 10% carbon dioxide, processing 120 million scf/d. The purified gas will be sent through KOC's pipeline network to the LPG plant at Mina Ahmadi Refinery for further processing.

"This project reflects MEIL's commitment to world-class energy infrastructure that enhances environmental safety and operational efficiency," said P Doraiah, director, MEIL. ■

UNITED KINGDOM

NextChem to conduct study on SAF plant

NextChem subsidiary MyRechemical has been awarded an engineering study contract by Altalto Ltd. for a sustainable aviation fuel (SAF) plant in Immingham, Lincolnshire, based on its proprietary NX CircularTM gasification and NX CPOTM technologies. Altalto is a company set up by Velocys to develop SAF projects in the UK. The plant is expected to be operational in 2030. Initial targets include the production of 23,000 t/a of SAF for the UK market. Feedstock will be sourced from residual municipal solid waste (MSW) and commercial and industrial waste. The project has been awarded a grant from the UK Department for Transport's Advanced Fuels Fund to progress basic engineering design. MyRechemical will operate as a technology provider and as coordinator for other technological partners. It will also supply engineering services.

NX Circular gasification technology allows the plant to convert waste by generating syngas, which is subsequently transformed to syncrude through Velocys' Fischer-Tropsch technology and upgraded to high-quality sustainable fuels. NX CPO technology produces synthesis gas via controlled partial oxidation through a very fast reaction, is contributing to maximising overall yield while minimising carbon intensity of the product.

NIGERIA

Dangote cleared of breaching fuel sulphur limits

A UK–based energy watchdog, the Impact Investigators Platform (IIP), has dismissed allegations that the Dangote Petroleum Refinery imported substandard gasoline into Nigeria, describing the claims as "technically inaccurate, commercially implausible, and unsupported by verifiable evidence." The IIP said its independent assessment of shipping data, customs declarations, and refinery process documentation found no indication that the refinery imported or sold Premium Motor Spirit (PMS) with sulphur levels above Nigeria's approved limit of 50 parts per million (ppm). The investigation followed media reports alleging that a vessel had delivered high-sulphur gasoline to the Dangote Refinery under the guise of locally refined products. However, the IIP clarified that the cargo in question was an intermediate feedstock,a raw material used for refining and not finished gasoline meant for retail.

RUSSIA

Fuel exports suspended following drone attacks

Ukraine has mounted several strikes on the Russian Black Sea port of Tuapse, hitting oil infrastructure with airborne and seagoing drones and missiles. Tuapse is a tanker loading terminal, one of two main oil export facilities on Russia's Black Sea coast, with the capacity to transship around 17 million t/a of oil products. A raid on November 2nd reportedly damaged two tankers, halted fuel exports and refinery operations for days, caused an oil spill and forced tankers to abandon the port. Russia's national rail company has halted rail shipments to Tuapse port, citing insufficient train car handling capacity.

Ukrainian drones also hit rail infrastructure in the Russian port city Rostov, on the north-eastern shore of the adjacent Sea of Azov. The strikes are part of a coordinated Ukrainian campaign which began in July targeting Russian oil processing and transport capacity, and later expanding to rail infrastructure and power grid nodes, with the official objective of reducing Russian state income from overseas oil sales. Independent estimates of total Russian oil processing capacity lost so far amount to around 20-40% of total national capacity.

CANADA

Start-up for Albright gas plant

CSV Midstream Solutions says that it has successfully completed commissioning and commenced operations at its Albright gas plant in northern Alberta, tapping into the Montney shale gas field. The new 150 million scf/d sour gas plant with associated sulphur recovery represents the first of its kind to be built in Alberta in more than a generation.

"The successful completion of the Albright plant marks an important achievement for CSV and provides an essential service to our producer partners," said Chris Dutcher, Vice President, Corporate and Business Development. "With LNG Canada ramping up, combined with the high sulphur prices we have today, there is a growing need for projects that focus on natural gas processing and sulphur recovery. This facility sets a new benchmark in sulphur recovery efficiency, positioning us to replicate this solution at our Gold Creek development and other locations under consideration," adds Dutcher.

The similarly sized Gold Creek gas plant received regulatory approval last year and will be built modelling the Albright design. Discussions with producers for Gold Creek are ongoing. CSV has also secured regulatory approval for its 150 million scf/d Valhalla 2 plant, a new greenfield sour gas processing facility adjacent to its existing Valhalla plant. Valhalla 2 will feature a similar gas processing design, utilising acid

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PHOTO: CSV MIDSTREAM SOLUTIONS

The Albright gas plant, Alberta.

gas reinjection in lieu of sulphur recovery.

"We have a strong pipeline of greenfield projects and brownfield expansions that will allow us to continue to grow our midstream platform in partnership with our producers," said Daniel Clarke, CEO. "With gas processing services available at Albright, Gold Creek, and Valhalla we are in a strong position to meet the area's growing demand for critical sour gas processing services."

UNITED ARAB EMIRATES

Sultech to supply micronised sulphur technology

Sultech Global Innovation Corp., a Canadian agricultural technology company, has signed a memorandum of understanding (MoU) with ADNOC Sour Gas for its micronised elemental sulphur technology. Under the MoU, the companies will conduct a feasibility study and pilot production program to establish the UAE's first commercial micronised sulphur manufacturing facility. The initiative will integrate Sultech's patented micronisation process within ADNOC's sulphur granulation at the Shah Gas Plant, the world's largest ultra-sour gas operation.

"Sultech is proud to see Canadian innovation taking its place on the world stage through our partnership with ADNOC Sour Gas. Our micronised sulphur technology represents a major leap forward in sustainable agriculture, transforming a by-product into a breakthrough that supports farmers, food security, and the environment," said Murray MacKinnon, CEO of Sultech Global. "As we position for rapid growth, Sultech is advancing plans for a new manufacturing facility in Alberta, strategically integrated with the natural gas sector. This expansion will strengthen our production capacity and establish a North American hub for sustainable sulphur-based solutions."

Founded in 2014 and headquartered in Alberta, Canada, Sultech' proprietary process converts elemental sulphur into an ultra-fine suspension, branded as SulGro™65, which claims to deliver faster oxidation of sulphur to a plant usable form and greater nutrient availability, as well as lower greenhouse gas emissions compared to traditional fertilizers. Micronised sulphur addresses widespread sulphur deficiencies in global soils, improving crop yields, protein content, and fertilizer efficiency while reducing nutrient losses to waterways.

In parallel with the UAE initiative, Sultech says that it is finalising plans for a new facility in Alberta, co-located with the natural gas sector to minimise sulphur disposal, cut emissions, and advance circular economy practices. The project was made possible with the support of Emissions Reduction Alberta (ERA), through a C$5 million investment awarded under the Emerging Innovators Challenge. The site will serve as a North American manufacturing and export hub, leveraging Canada's expertise in responsible resource development and agricultural innovation.

First production from Ghasha "within months"

First gas from Abu Dhabi's 1.5 billion cfd Ghasha sour gas concession will be reached in early 2026, according to project partner PTTEP. The gas will come from the first phase 340 million cfd Dalma development. The Ghasha project is being developed by ADNOC (70%), Eni (10%), Thailand's PTTEP (10%) and Russia's Lukoil (10%). The outlook, published in PTTEP's Q3 results, is a more cautious assessment than that provided by Eni in its own Q3 results. Eni said it was optimistic that the development would start up by the end of 2025.

Tenders for Ruwais sulphur terminal expansion

ADNOC has received bids for its Ruwais Sulphur Terminal expansion. The project aims to expand the existing sulphur handling terminal facilities, SHT-1 and SHT-2, located in Ruwais, Abu Dhabi. The purpose of the expansion is to increase the capacity of the Ruwais sulphur handling terminal to accommodate an additional 10,600 t/d of liquid sulphur from the Hail and Ghasha offshore sour gas field development. ■

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Sulphuric Acid News

UNITED STATES

Travertine starts operation of demonstration plant

PHOTO: TRAVERTINE TECHNOLOGIES

The Travertine Technologies demonstration plant, Rochester, New York.

Travertine Technologies, Inc., has began operations at its demonstration plant in New York state. The core Travertine process demonstrated at this plant combines three major unit operations: salt-splitting electrolysis, caustic direct air capture, and mineralisation. This process produces sulphuric acid, calcium carbonate, and green hydrogen from waste gypsum and carbon dioxide captured directly from the air. The demonstration plant will produce 125 t/a of sulfuric acid, 125 t/a of calcium carbonate, and 55 t/a of carbon dioxide sequestration. The plant will supply sustainable sulphuric acid for local partner Sabin Metal Corporation's precious metals recycling and refining business.

"This demo plant is an exciting next step as we scale up the core Travertine process. Our process can be used for a number of vital industrial applications, including using our sulphuric acid to produce phosphoric acid for the fertilizer and LFP battery industries with our proprietary phosphoric acid production process," said Laura Lammers, PhD, founder and CEO of Travertine. "What is unique about Travertine is that we enable carbon-negative critical chemical production without making mineral byproducts that need to be landfilled."

"Sabin Metal has long been committed to precious metals recycling with a focus on chemical reuse, sustainable procurement, and minimizing byproducts. We are pleased to partner with Travertine to incorporate their sustainable sulphuric acid into our process and continue the legacy of innovation in the Rochester area," said Brent Vesa, technical director at Sabin Metal Corporation.

Aurubis looking at new US smelter

Aurubis says that it is in discussions with the US government about possible financial support for the construction of a new copper smelter. Reuters reports comments from Aurubis CEO Toralf Haag during LME Week that there had been a positive response from the Trump administration. The US is currently only able to supply about half of its refined copper demand of 1.7 million t/a from domestic production, and the gap may widen as demand increases.

The move comes in the wake of the start-up of Aurubis' new multi-metal recycling facility in the state of Georgia. The $860 million investment will ramp up to an annual output of 70,000 t/a of copper. CEO Dr. Toralf Haag commented: "The commissioning of our facility in Richmond marks a milestone in Aurubis' growth journey. We are first movers and have built the first greenfield smelter in the US in over a century. Our timely entry into the US market and our unique set of capabilities coupled with a supportive funding environment are a strong foundation for further growth in one of the most attractive metal markets in the world.".

SENEGAL

Indorama to boost phosphate fertilizer production

Singapore-based Indorama Group, through its Senegalese subsidiary Industries Chimiques du Sénégal (ICS), has signed a memorandum of understanding with Senegal's Investment and Major Projects Promotion Agency (APIX) to launch a major $210 million investment, aiming to boost Senegal's phosphate and fertilizer production capacity, reinforcing the country's strategic role in the regional agricultural input market.

The investment will focus on modernizing and expanding ICS's production facilities. At the Mbao fertilizer plant, the company will increase NPK and DAP output from 250,000 to 400,000 t/a. It also plans to build a new single superphosphate (SSP) unit with a capacity of 350,000 t/a. Meanwhile, production of phosphoric acid at Darou will rise to 660,000 t/a year, supported by a new sulphuric acid plant capable of producing 700 t/d. These projects represent a significant scaling up of ICS's operations and are expected to give Indorama a stronger foothold in Senegal's growing fertilizer market.

AUSTRALIA

Kalgoorlie secures major project status renewal

Ardea Resources says that its Kalgoorlie Nickel Project in Western Australia has secured a crucial renewal of its major project status from the federal government for another three years, underscoring the project's strategic importance, granting it streamlined approvals and direct access to the country's major project facilitation agency. Located 80 km from Kalgoorlie, the project hosts what Ardea says is the world's largest undeveloped nickel-cobalt resource, containing 854 million tonnes averaging 0.71% (6.1 million tonnes) of nickel and 0.045% (386,000 tonnes) of cobalt.

The company is currently working towards publishing a definitive feasibility study over the project, which is fully funded by Ardea's heavyweight Japanese partners Sumitomo Metal Mining and Mitsubishi Corporation. A 2023 pre-feasibility study envisages producing 30,000 t/a of nickel over a 40 year project lifespan, using high-pressure acid leach (HPAL) technology. Partnership deals are in place for 75% of the project offtake, for use in electric vehicle (EV) battery and stainless steel markets.

Managing Director and CEO Andrew Penkethman said: "On behalf of Ardea, I extend my sincere thanks to the Australian Federal Government and the Major Projects Facilitation Agency for renewing Major Project Status for the KNP. This renewal reaffirms the strategic and economic importance of the Kalgoorlie Nickel Project. It ensures continued support in streamlining regulatory pathways, enhancing approvals coordination, and maintaining access to project-enabling funding avenues."

Mining licence approved for Ammaroo phosphate project

Austrlai's Northern Territories Government has approved a mining licence for Verdant Minerals' Ammaroo phosphate project. The approval follows the granting of two mineral leases in March and represents a critical step towards construction and mining operations at one of the world's largest phosphate resources. Verdant estimates the value of production over the life of the mine to exceed $15 billion. Verdant says that securing the mining licence puts the project firmly on track to reach a final investment decision and commence construction as early as mid-2027. Located 200 kilometres south-east of Tennant Creek, the Ammaroo phosphate deposit contains more than one billion tonnes of phosphate ore.

Verdant Minerals Managing Director Chris Tziolis said: "Mining approval from the NT Government is a major milestone for Ammaroo and clears the way for Verdant Minerals to advance the process of project financing to enable the construction of the first stage of the project, delivering local jobs, contracting opportunities, and long-term economic benefits across the NT. Ammaroo will help strengthen regional phosphate rock supply at a time of global uncertainty. We're ready to move from planning to execution and create a reliable, NT-made phosphate rock product for regional agriculture."

JORDAN

Sulphuric acid leak at Aqaba

At least 43 people were injured after sulphuric acid fumes leaked from a chemical storage at the port of Aqaba in October, according to local press reports. Two of the injured were admitted to intensive care and another six were held in hospital. The remaining cases were described as mild and were treated either on-site or in nearby hospitals. Jordan's Public Security Directorate (PSD) said emergency teams from the Aqaba Civil Defence Department, supported by the Aqaba Support Group, responded immediately to reports of a sulphuric acid vapour leak which created a fume cloud roughly 400 square metres in size. The operating company's technical team managed to stop the leak before specialised hazardous materials units from the Civil Defence took over, implementing safety procedures in line with approved protocols. Investigations are under way to determine the cause of the leak, in coordination with the Public Security Directorate and other relevant agencies. Three years ago a sulphuric acid leak from a storage tank at Aqaba killed 13 and injured several hundred people.

INDIA

Paradeep plans additional phosphoric acid capacity

Paradeep Phosphates Ltd (PPL) has announced a $400 million capacity expansion program, following its October 13th merger with Mangalore Chemicals & Fertilizers Limited (MCFL). This company says that the move aims to strengthen PPL's market position and enhance its production capabilities. The investment will involve increasing granulation capacity by 1.0 million t/a at the Paradeep site, as well as an additional 250,000 t/a of phosphoric acid and 750,000 t/a of sulphuric acid capacity at the company's new Mangalore site. The expansion is expected to be completed within three years, according to PPL, and is expected to ensure 100% backward integration for fertilizer production, reduce import dependency, and enhance operational capabilities and profitability.

CANADA

Arianne to use Travertine technology

Arianne Phosphates has signed a memorandum of understanding with Travertine Technologies Inc.for the production of purified phosphoric acid using Travertine's proprietary process on high-purity phosphate concentrate from Arianne's planned Lac à Paul project in Quebec Province.

Travertine's phosphate process produces PPA from phosphate concentrate using recycled sulphuric acid, eliminating a substantial cost associated with PPA production, as well as avoiding phosphogypsum waste, while producing carbon-neutral or carbon-negative materials for cements. Arianne says that its phosphate concentrate is a perfect feedstock for this process given its high-purity, low-contaminant nature. Current work is on-going to advance engineering on a Phase 1 small commercial facility expected to produce PPA for use in lithium iron phosphate (LFP) cathode active materials production.

"We are excited to be working with Travertine on this venture," said Brian Ostroff, Arianne's head of Strategic and Business Initiatives. "This partnership plays directly into Arianne's strategy of not only being a miner of phosphate but in also being a producer of purified phosphoric acid thus capturing the opportunity and unlocking the substantial economic benefits. Arianne has concluded on this as a first step in its goal of partnering with players that have technologies and operations that will allow the Company to benefit directly from the growing demand for purified phosphoric acid, a necessity for the LFP battery. Deals like this will allow Arianne and its partners to aid in the West's requirement for a secure supply of battery materials."

"The global energy transition is driving huge demand growth for critical elements such as phosphorus," said Laura Lammers, PhD, founder and CEO of Travertine. "Partnering with Arianne is an important step toward our goal of building a new circular economy at scale for the next generation of phosphates production."

Lac à Paul is claimed to be the world's largest greenfield phosphate deposit. Due to the phosphate deposit being igneous, and thus geologically rare, Arianne can produce a very high-purity,

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low-contaminant phosphate concentrate that allows for easy conversion into purified phosphoric acid. The company has spent over C$100 million advancing the project and has received funding and investment from the Quebec Government.

Nutrien considering phosphate sell-off

Nutrien said in its 3Q results that it has initiated a review of strategic alternatives for its phosphate business, which could include reconfiguring operations, strategic partnerships or a potential sale. A final decision on the future of the phosphate business will be taken in 2026, according to the company .

The phosphate division, reportedly valued at about $2.4 billion, is the smallest of Nutrien's four business units. It generated $384 million in adjusted EBITDA in 2024. Nutrien said in its 3Q results that phosphate markets continue to be tight due to limited supply, including from Chinese export restrictions. Global shipments in 2025 have been constrained by supply availability and weaker affordability for phosphate fertilizer has impacted demand.

"We continue to progress our strategic initiatives and take actions to simplify our portfolio," president and chief executive officer Ken Seitz said in a statement. He added that the changes aim to "enhance earnings quality, improve cash conversion and support growth in free cash flow per share over the long term."

INDONESIA

Government to limit new nickel projects

The Indonesian government has moved to limit new licenses for nickel projects in an attempt to correct overdevelopment of the industry and the subsequent crash in global nickel prices. The permit restriction applies to new nickel processing companies that produce intermediate products, both with pyrometallurgical (RKEF) and hydrometallurgical (HPAL) technologies. Currently, Indonesia already has 54 nickel processing plants operating, 38 in the construction stage, and 45 are still under planning.

Manyar smelter faces supply issues

Freeport Indonesia may be forced to suspend operations at its Manyar smelter at the end of October due to a lack of copper concentrate, according to local press reports. The news follows the mudslide at the Grasberg mine in September, which killed seven workers. Grasberg, which represents almost 3% of global copper mine production, has halted production and Freeport says that it may not return to pre-accident operating rates until 2027. Stocks of copper concentrate at Grasberg were estimated to be only sufficient to operate the Manyar smelter until the end of October. The $3.7 billion Manyar smelter only resumed operations in May after a fire broke out in October last year, damaging the plant.

CHILE

Permit agreed for smelter revamp

Chile's state-run mining company Enami says that it has received an environmental permit for a new $1.7 billion copper smelter, as part of the modernization of its Hernan Videla Lira smelting facility in the northern Atacama region. The new facility will process up to 850,000 t/a of copper concentrate, and its electrolytic refinery will produce up to 240,000 t/a of copper cathodes for use in electronics, construction and renewable vehicles. Enami says that the modernisation will "ensure profitable and sustainable operations, and practically triple the capacity of the old smelter."

Metso expands technical service centre

Metso has completed the expansion of its service centre in Antofagasta, Chile, adding an additional 1,200 m² of operational capacity, totalling 4,800 m² of technical workspace. Strategically located in the La Negra industrial district, at the heart of northern Chile's mining area, the service centre has tripled its technical-commercial agreements in recent years, becoming a key strategic partner for major mining companies in the country. Following the expansion, the centre can now repair and refurbish large-scale equipment including HRC™ and high pressure grinding roll units, Vertimill® grinding technology, and mills for mining customers. It also supports beneficiation and dewatering technologies, such as filter plate pack service offerings. In addition, the centre provides service capabilities for mining crushers, grinding mills, screens, and car dumpers.

Within the expansion scope, Metso has installed an overhead crane with a lifting capacity of up to 140 tonnes and a high-precision vertical lathe capable of handling parts up to 5 meters in diameter. The crane, which is among the largest in South America, will be used alongside the vertical lathe to minimize equipment transport needs, decrease turnaround times, and support local service operations.

"Our service centre in Antofagasta, which has been operational since 2013, has become a benchmark in technical support for large-scale mining in northern Chile. The expansion enables us to work on multiple critical pieces of equipment, reduce lead times and improve availability for our customers. The investment, which was announced in 2023, is a testament to our commitment to staying close to our customers and providing concrete solutions to the address the mining industry's needs," said Leonardo Osorio, Vice President, Services Project Delivery, South America, Metso.

SMAC to list on Toronto stock exchange

Queensland-based SMAC (Strategic:Minerals:Acid:Critical) Developments says that it plans to list on the Toronto Stock Exchange in December to raise $1.3 million to fund a final feasibility study. The company is attempting to develop sulphuric acid production in northern Queensland to supply local industries. The company plans to initially build a 180,000 t/a sulphur burning acid plant at a site at Cloncurry, followed by a second phase which would involve developing a pyrite roasting plant to generate 550-600,000 t/a of sulphuric acid.

Queensland faces a shortage of acid if the Glencore Mount Isa copper smelter closes down. Mount Isa produces around 1 million t/a of acid. Glencore says that the smelter is losing tens of millions of dollars per month, and in spite of an A$600 million bridging loan from the Queensland government, it is slated to close in 2028. The smelter is the main supplier of acid to Dyno Nobel's Phosphate Hill facility, which uses up to 1.2 million t/a of acid. Aside from the Mount Isa supply, the balance comes from Sun Metals zinc smelter in Townsville. More acid could be required by the expanding vanadium industry in the state and copper leaching operations. Explosives company Dyno Nobel has said that it may cease operations at its fertiliser plant in September 2026 if a buyer is unable to be secured by March next year.

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People

Jeanne Johns, non-executive director, Worley.

Worley has announced changes to its Group Executive team to "simplify its structure, streamline governance and accelerate the company's transition to an AI-enabled organization". Effective from November 1, 2025, **Laura Leonard** will take up the role of Chief AI and Enterprise Services Officer bringing together a number of corporate functions including Digital, Transformation, Risk, Sustainability, and Corporate Affairs, with three existing Group Executive members moving to report to Laura. This consolidates resources that support operations and reduces the size of Worley's Group Executive team from twelve to nine.

"AI and Enterprise Services reflects the critical role AI will play in enabling our strategy," said CEO Chris Ashton. "Beyond their enterprise roles, this team is charged with leading our transformation into a digitally enabled company with AI-supported full project delivery capability. For two years we have been laying a strong foundation for AI – these organisational changes accelerate the next stage of our digital transformation."

Worley had previously announced the retirement of non-executive director **Sharon Warburton** from the company board, effective 31 August 2025. Sharon joined the board in February 2019, bringing extensive business experience and expertise in strategy, finance and risk management. Sharon served as Chair of the Audit and Risk Committee from February 2023 to August 2024, providing strong leadership and oversight throughout her tenure.

Chair of Worley John Grill said: "We thank Sharon for her significant contribution to Worley over the past six and a half years. The Board has benefited greatly from her insights, skills and experience and we wish her the very best."

Her replacement as an independent non-executive director of the Worley board is **Jeanne Johns**. Her appointment follows her career as an international executive in refining, petrochemicals, oil and gas, civil explosives and agricultural fertilizers. She served as Chief Executive Officer and Managing Director of Incitec Pivot Ltd from November 2017 until June 2023. Prior to joining Incitec, Johns held several executive leadership roles in the US, UK/Europe and Asia/China during her 30 years with BP plc. She brings a global perspective and insights from working in diverse business environments along with technical expertise in HSE, operations, projects and engineering. Johns is also a non-executive director of HF Sinclair.

Chair of Worley, John Grill, said: "We are delighted that Jeanne has agreed to join the Worley Board. Jeanne's breadth of experience in Worley's key markets in Australia and overseas enhances our existing abilities. We look forward to Jeanne's contribution."

TotalEnergies has announced the appointment of **Nicola Mavilla** as Senior Vice President Exploration, with effect from 1st November 2025. Nicola Mavilla is replacing **Kevin McLachlan**, who held this position since 2015. Mavilla has 25 years of experience in the oil and gas industry and a strong track record in leading successful exploration activities. He joined Eni in 2002 and served as exploration manager in Libya and Norway, VP exploration for West Africa, VP exploration for Americas and Northern Europe and managing director of Eni Ivory Coast. Since 2024, he was Head of Exploration Projects of Eni. He holds a PhD in Geology from the University of Bordeaux.

Freeport has named **A. Cory Stevens** as President and Chief Operating Officer of Freeport Americas, effective December 1, 2025. Stevens joined Freeport in 1997 and has held multiple leadership roles at the company's North and South America operations and most recently led the team responsible for developing Freeport's smelter project in Indonesia. He currently leads FCX's centralized technical organization, with responsibility for a broad range of technical support functions across the company, including engineering and construction activities, growth projects, including the high-impact innovative leach initiative, operational support and research and development. Under the new structure, Stevens' role will be expanded to include responsibility for Freeport's Americas operations. ■

Calendar 2025/2026

NOVEMBER

12-13
ESA General Assembly, CATANIA, Italy
Contact: Katija Baljevic, European Sulphuric Acid Association (ESA)
Tel: +32 490 447 484
Email: kba@cefic.be

FEBRUARY 2026

5-6
SulGas Conference, MUMBAI, India
Contact: Three Ten Initiative Technologies LLP
Tel: +91 96766 11950
Email: admin@sulgasconference.com
Web: sulgasconference.com

17-20
Laurance Reid Annual Gas Conditioning Conference, NORMAN, Oklahoma, USA
Contact: Lily Martinez, Program Director
Tel: +1 405 325 4414
Email: lmartinez@ou.edu

APRIL

13-15
CRU Phosphates+Potash Expoconference, PARIS, France
Contact: CRU Events
Tel: +44 (0) 20 7903 2444
Email: conferences@crugroup.com

13-15
World Copper Summit, SANTIAGO, Chile
Contact: CRU Events
Tel: +44 (0) 20 7903 2444
Email: conferences@crugroup.com

28-30
TSI Sulphur World Symposium 2026, VANCOUVER, Canada
Contact: The Sulphur Institute, Washington D.C., USA
Tel: +1 202 331 9660
Email: sulphur@sulphurinstitute.org

27 – MAY 1
RefComm Expoconference, GALVESTON, Texas, USA
Contact: CRU Events
Tel: +44 (0) 20 7903 2444
Email: conferences@crugroup.com

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Recent developments in sulphuric acid markets

Smelter outages and tight concentrate markets ease an oversupplied market.

This year is set to be a transitional year for the global sulphuric acid market, with local supply additions set to increase overall availability, but ongoing smelter outages and tight concentrate markets somewhat muting the scale and timing of any price declines.

Supply

The near-term supply increase through 2025 is expected to be led by additional sulphur-burning capacity, notably in Morocco, India, and Indonesia, and by new or restarted smelter capacity (e.g., Adani's smelter in India, Amman Mineral and expanded Freeport capacity in Indonesia). However, smelter supply growth is currently constrained by the availability of copper concentrate: persistent concentrate shortages are forcing smelters to run at lower utilisation rates, and therefore are likely to limit smelter acid output in some regions, especially China. This concentrates market tightness could persist into 2026, necessitating further smelter cuts or project delays. Pyrite-roaster contributions (e.g., Merdeka AIM in Indonesia) add incremental volumes of acid, as noted in our article elsewhere in this issue on the pyrite sector, but the dominant growth contributor in 2025 remains sulphur-burning expansion.

There has been a fundamental structural change in China's export mix: exports are shifting away from sulphur-burnt acid toward smelter-derived acid. Whereas sulphur-burnt supply accounted for over 75% of China's exports in 2018, it is expected to be roughly one-third by 2025. This shift makes the market's response to import declines more complex; smelter acid behaves differently from sulphur-burnt acid because smelter output depends on concentrate availability and smelter operating rates; when concentrate flows tighten, smelter acid can fall back quickly. Nevertheless, that China's domestic market has remained supportive, with domestic prices rising strongly in 2025 and narrowing the incentive for exporters to offload volumes. As a result, China is positioned to increase market share in traded acid through 2025, particularly where smelter volumes can step into gaps left by outages elsewhere.

Looking to the medium term, by 2029, the market trajectory is toward greater overall supply abundance, with the sulphur-burnt sector still central in regions like Indonesia and Morocco, while smelter-derived acid recovers where concentrate availability allows.

Demand

Overall global demand is forecast to grow from about 306 million t/a in 2024 to roughly 355 million t/a by 2029, driven primarily by a recovery in phosphate fertilizer demand, particularly in Morocco, and a rapid expansion in metals-related demand - notably nickel for battery feedstocks - concentrated in Indonesia. Phosphate-based demand remains the single largest end-use and the primary driver of long-term acid demand growth. Recovery in phosphoric acid production (for DAP and other fertilizers), including higher operating rates in Morocco and rebounding US phosphate activity is central to a medium-term demand recovery.

Metals-based consumption is forecast to grow rapidly, with nickel-related demand (nickel sulphate/Li-ion battery feedstocks) experiencing the fastest percentage gains, particularly in Indonesia where massive nickel-leaching projects are ramping up. By 2029 nickel-related demand share is forecast to rise materially from 2024 levels. Other incremental demand sources include ammonium sulphate, uranium, titanium dioxide, manganese, and emerging lithium-linked acid consumption tied to battery supply chains. Demand growth is geographically concentrated: Indonesia leads metals-based increases, Morocco drives phosphate demand, and China shows mixed trends with some sectors (ammonium sulphate) growing while phosphate declines slightly this year due to export allocation policy changes.

Regional highlights

- **China**: Domestic prices surged in 2025 to their highest levels since 2022, supporting exports even as domestic smelter availability improved. China is expected to ramp up smelter acid supply in 2025 and increase exports by nearly 1 million t/a, though phosphate-policy adjustments via export quotas are creating downward pressure on local phosphate-based demand. The shift from sulphur-burnt to smelter-based exports makes China both a stabiliser (able to fill demand gaps) and a potential source of oversupply if domestic markets do not absorb volumes.
- **Indonesia**: The single largest geographic change in the outlook is that Indonesia's total acid production and consumption will grow rapidly through 2029, driven by new nickel-leaching operations and sulphur-burner projects. Smelter commissions (e.g., Amman Mineral, Freeport expansions) and pyrite-based roasters (e.g., Merdeka AIM) substantially raise local supply, which reduces import dependence from 2025 onward. Nevertheless, Indonesia's own nickel-driven demand rises substantially, possibly consuming much of the new smelter output domestically.
- **Morocco**: A material increase in on-site sulphur-burning capacity (at OCP's

PHOTO: CHEMTRADE AS

A sulphuric acid tanker at the port of Rotterdam.

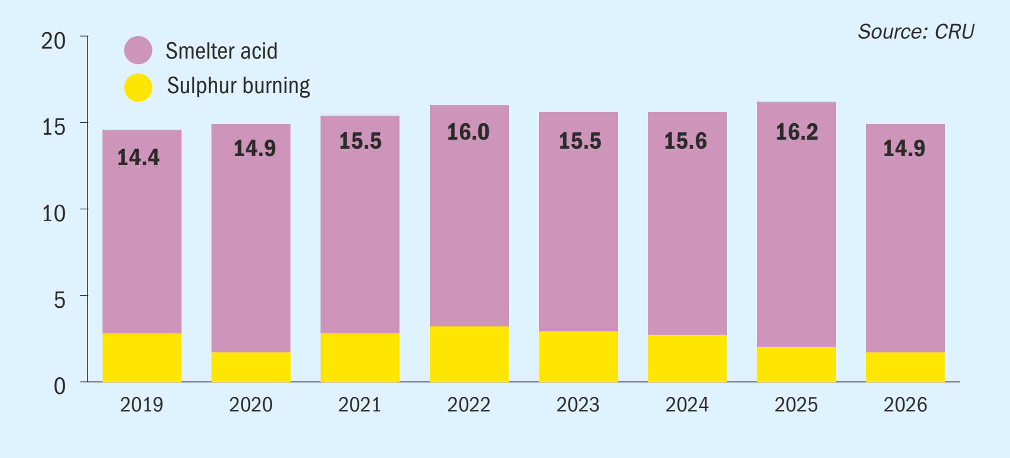
Jorf Lasfar and related sites) is set to sharply reduce import reliance; imports are forecast to decline towards about 1.2 million t/a in 2025. Moroccan phosphate demand recovery in 2024–25 underpins higher domestic sulphur-burnt production.

- **Chile and Peru**: Unplanned smelter outages in Chile (e.g., Altonorte, Potrerillos) in 2025 have raised import requirements substantially in 2025 Q2 and Q3. Consequently, China and other exporters are expected to supply larger long-distance cargoes into the Pacific. Peru's domestic demand will rise from projects such as Tia Maria (if commissioned as expected), reducing Peruvian exportability by 2028–29.
- **India**: Local smelter capacity (notably Adani) and new sulphur burners (e.g., Paradeep Phosphates Limited, plus other projects) will increase domestic supply, but early-stage start-up delays could maintain elevated import needs in 2025. Over time, increased local production should reduce India's dependence on seaborne acid.
- **United States**: Demand rebounds in 2025 after a weak 2024, driven by phosphate and, later on in the outlook, from lithium projects. The US will continue to structurally rely on imports of around 3 million t/a, because sulphur-burner capacity additions are lagging consumption growth. Tariff dynamics and project timelines (e.g., new burners) shape near-term import patterns.
- **Europe**: Smelter acid production has been influenced by maintenance and outages but is projected to recover from 2026 as recent maintenance pressures ease and some new capacity comes online. However, exports from Europe are falling as a greater share of production is absorbed domestically.

Seaborne trade

Traded acid flows are projected to remain elevated in 2025 as import needs rise in specific markets such as Chile, Saudi Arabia, and Peru, while import demand falls in places where sulphur-burner capacity is added (for example Morocco, India, and Indonesia) and where domestic integration increases. Global seaborne acid trade was relatively stable in 2024 at 15.6 million t/a, and is forecast to rise to 16.2 million t/a in 2025 as import needs grow where smelter supply is weak. The makeup of seaborne exports is evolving: smelter acid accounted for 83% of traded acid in 2024 with sulphur-burnt supply contributing the remainder. By 2025 the share is shifting but sulphur-burnt costs will still heavily influence price-setting. Export volumes from Europe, Japan/South Korea, and other traditional suppliers are expected to decline in 2025 by a combined drop of about 800,000 t/a, while China's exports are forecast to grow by nearly 1.0 million t/a as it fills gaps in supply, particularly to Chile and Saudi Arabia. Despite growth in producer-side integration (more burners and smelters), long-distance supply, especially Pacific trade flows, remains important due to new demand additions in Chile and Peru.

Fig. 1: **Total seaborne sulphuric acid trade, 2019-2026**



Prices

Prices have been at elevated levels following supply tightening in Europe and East Asia; the premium of acid cost over the equivalent volume of sulphur rose sharply in 2024 and stayed high into 2025. However, it is expected that acid prices will soften in the second half of 2025 and into 2026 as smelter supply recovers and newly commissioned sulphur burner capacity begins to displace some imports. That said, the price decline is expected to be more muted than earlier anticipated because unplanned smelter outages (notably in Chile, the Philippines, and Namibia) have removed material volumes from the market and because strong domestic pricing in China will offer a floor under international spot levels. The acid-to-sulphur margin and the acid share of downstream product prices (e.g., DAP, copper, nickel) are key affordability metrics: DAP affordability currently looks favourable due to a surge in DAP prices, while metal-sector affordability has weakened as copper and nickel prices rise and acid costs remain firm.

Conclusion

The market is entering a phase where structural supply additions - mainly sulphur-burners and some smelter start-ups - increase overall capacity, but the full price impact is likely to be dampened by smelter outages and ongoing copper concentrate constraints. Traded acid volumes will remain significant through 2025 as China steps in to supply shortfalls and as new importers (notably Saudi Arabia and Chile) raise demand. By 2026–2029, CRU foresees a return toward a more balanced market with slower price trajectories, provided copper concentrate availability improves and planned burner capacities come online as scheduled. Market participants should therefore plan for volatility through 2025 and early 2026 while monitoring concentrate flows, smelter operational status, and sulphur feedstock pricing closely.

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Pyrite-based acid production

While sulphuric acid production is dominated by sulphur burning or metallurgical acid routes, pyrite roasting remains a niche sector, particularly in China.

PHOTO: MERKEDA BATTERY MATERIALS

Construction work at the Merkeda pyrite plant, Indonesia.

Iron pyrite (FeS_2) has a long history as a feedstock for producing sulphuric acid, but today it occupies a niche position in a market dominated by other sulphur sources. Roasting pyrites produces sulphur dioxide (SO_2), which can be converted to sulphur trioxide (SO_3) in the Contact process and then turned into sulphuric acid (commonly via the oleum route). Technically the route is straightforward, but economic and environmental realities have reshaped where and when it is used.

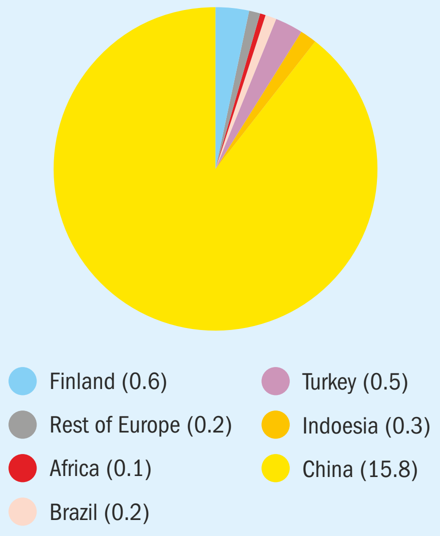
Global sulphuric acid production from pyrites reached peaked at around 30 million t/a in the 1970s, at which time it represented 22% of sulphur production in all forms. However, it has been in long-term decline since then, and was down to only 6% of total sulphuric acid production in 2024. Production of pyrite-based acid has gradually stopped in most of the world. It ended in the United States in 1988, Brazil and Bulgaria in the 1990s, India in 2003, Russia in 2007, and Zimbabwe in 2008 with the closure of the Iron Duke mine. Finland's main pyrite mine is no longer operational and acid production is due to end soon. Nevertheless, some production continues in Brazil, Turkey, and particularly China (see Fig. 1), which now represents 89% of world pyrite roasting acid production, and there is also new production in Indonesia.

Process economics

The recovery of large volumes of sulphur from oil and gas as a by-product and the recovery of sulphur rich off-gases from copper and other base metal smelting have collectively largely undercut the economics of pyrite mining for acid production, hence its gradual discontinuing in many of the countries that formerly used it, as noted above. Pyrite rock tends to be cheaper than elemental sulphur as a raw material, and the operating costs for a pyrite based acid plant can be lower or comparable, but the lower capital cost of a sulphur burning acid plant makes for faster payback in the medium term. Some pyrite plants can be more profitable in the long term, but this depends on the price of sulphur, the ore grade, local availability, transport costs, and the cost of gas-cleaning and waste handling.

The solid iron cinder produced in the process contains around 30-60% iron. The production of 1 tonne of sulphuric acid usually results in the creation of 0.8–1.5 tonnes of iron cinder. The cinder is not very valuable, and sometimes is merely disposed of as tailings, but it can be used in the manufacture of cement or as ballast in road construction, and it can also be used a source of iron in steel manufacture, which has had particular application in China. China makes around 55% of the world's steel, and the country imports large quantities of iron ore in order to do so. The iron calcine from pyrite manufacture can be used in lower grade

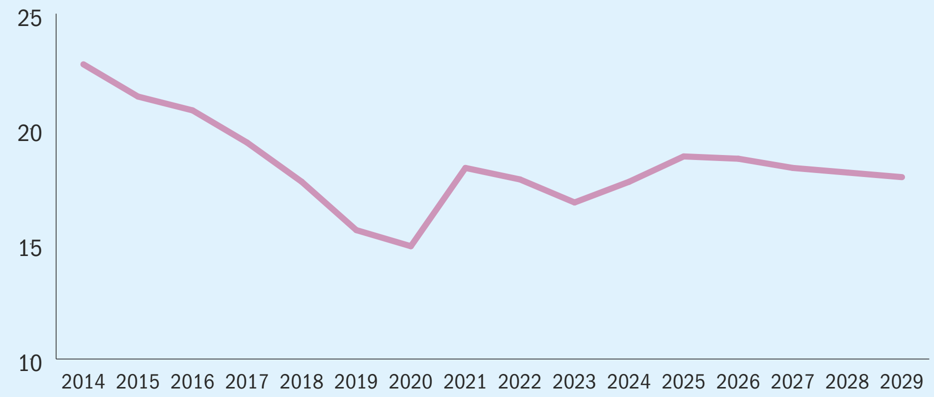
Fig. 1: **Production of acid from pyrites by country/region, 2024**



Total: 17.7 million t/a

Source: CRU

Fig. 2: **Pyrite-based acid production, 2014-2029, million t/a**



Source: CRU

steel manufacture and helps offset the process economics via an iron credit. In addition, there are also often trace 'impurities' such as copper and gold in the calcine, and recovery of these minerals can also assist with the economics of the process.

However, there are also considerable problems with pyrite roasting. Pyrites commonly contain arsenic, selenium and other trace metals. These can complicate gas cleaning, and even poison catalysts such as vanadium oxide, commonly used for sulphuric acid production. This makes feeds from elemental sulphur combustion or smelter off-gases cleaner, easier to treat, and cheaper to process at scale. Roasting also generates particulate matter and acid gases; poor control risks air pollution and acid deposition. Exposed tailings can also lead to acid mine drainage, a persistent environmental problem. Robust off-gas cleaning, tailings management, and catalyst protection increase capital and operating costs relative to cleaner sulphur feeds.

In general, pyrite roasting tends to make economic sense at mines with abundant low-value sulphide material where roasting is already part of ore processing and capturing SO_2 adds value, and/or locations with restricted access to cheaper sulphur sources where local acid demand and regulatory frameworks make onsite production attractive. Integrated metallurgical plants that roast multiple sulphide minerals and can centralise gas treatment and acid production can also make pyrite roasting an attractive option.

Acid production

After its long slow decline from its peak in the 1970s, global pyrite production has actually been at a fairly stable level over the past two decades. In 2024 it accounted for just under 18 million t/a of acid production worldwide (see Fig. 2). While production in several countries has been declining or ceasing, Chinese production was actually on an upward trend in 1990s and 2000s, with many of the smaller producers – there were over 350 producers of pyrite based acid in 2006 – closing at the same time that larger, more efficient and lower cost plants were completed. In 2006 Outotec completed the world's largest pyrites roaster at Tongling Nonferrous Metals, which produces 400,000 t/a of sulphuric acid, and Hunan Hengyang started up a 300,000 t/a acid plant based on pyrites in 2008. Some pyrite roasters have converted their acid plants to sulphur burning, though the sulphur price spike of 2008 and continuing strong demand for both sulphuric acid and iron, continue to make pyrites roasting economical in parts of China. Much of China's sulphuric acid output is concentrated in Hubei and Yunnan provinces, with significant production also in Guizhou, Sichuan, Shandong and Anhui.

There have been predictions of the demise of China's pyrite roasting acid industry for many years now, but the industry was kept alive via demand for iron and the burgeoning phosphate industry in China, which required ever-increasing amounts of sulphuric acid. In spite of increased competition from smelter-based acid production, a number of pyrite roasting plants continue to operate, and while some closures are forecast over the next few years, China will likely continue to maintain its pyrite roasting acid sector.

Rest of the world

Outside of China, the next largest producer of acid from pyrites in 2024 was Finland. Finland's pyrites have mainly come from First Quantum Minerals (FQM) Pyhasalmi mine, the deepest in Europe at 1.45 km, which produces the bulk of Finland's pyrites. However, underground mining at the site ended in 2022, and since then FQM has been processing pyrite-rich mine tailings to produce 330-350,000 t/a of pyrite for acid production. The tailings are expected to be exhausted late this year or early next, at which time FQM says that the mine will be closed "in accordance with best practice". Turkey is also a significant producer of pyrites, consuming some domestically, as well as exporting to Uzbekistan and other countries.

However, the largest new source of pyrite-based acid is Indonesia. Merkeda Battery Materials (MBMA) started operations at a new pyrite plant in 2024. Pyrite is a by-product generated by copper mining at the company's Wetar mine, and efforts to add value to the pyrite have been part of the company's plans since 2019. The smelting process at the Wetar mine previously only yielded copper, leaving by-products that could not be further processed. The new AIM (Acid Iron Metals) plant is designed to process pyrite ore at a nominal rate of 1.0 million t/a, and consists of four interconnected processing facilities. The second phase, comprising the sulphuric acid plant, started production in April 2024. Both trains of the roaster/acid plant are now in operation with post-commissioning debottleneck modifications conducted. This year the plant is expected to generate about 1 million t/a of sulphuric acid, moving Indonesia into second place in pyrite acid production. ■

Sulphur and sulphuric acid in southern Africa

While north Africa's sulphur demand is dominated by its phosphate industry, south of the Sahara it is copper, cobalt and uranium mining, leaching and smelting that hold sway over acid production and demand.

Sulphur

There is very little domestic sulphur production in the region, and what there is comes from a relatively small refinery sector. Refining capacity in sub-Saharan Africa is also uneven: there are a few larger, higher-complexity installations, and several small or lower-complexity refineries, where capacity and reliability are often constrained by ageing equipment, feedstock logistics, and underinvestment. Many countries import refined products despite having refineries because of outages or limited runs. The region produces around 5.5% of the world's oil, but has only 1.5% of its refining capacity.

Significant sulphur production only comes from South Africa and Nigeria. South Africa had six refineries at the start of 2020, four of which processed imported crude. However, during 2020-22 three of the six closed down – Sapref and Engen in Durban and the PetroSA gas to liquids plant at Mossel Bay, while a fourth – Astron in Cape Town – was shut for a considerable period after an explosion. The outcome is that South Africa has become a massive importer of refined petroleum. The US Energy Information Administration estimates that South Africa produces only 20% of its domestic fuel requirements and is forced to import the rest. The problem was the cost of installing new treatment sections at the country's ageing facilities to be able to meet a proposed 10 ppm sulphur fuel content. The country's Central Energy Fund has bought the idled Sapref refinery, with 180,000 bbl/d of capacity, for a token sum, but a planned investment programme for it has failed to materialise. This leaves Astron, Natref at Sasolburg, and Sasol's Secunda synthetic fuel complex as the last producers in the country. In 2024, South Africa produced around 350,000 tonnes of sulphur from these facilities.

Table 1: **Sulphuric acid consumption in sub-Saharan Africa, 2024, million t/a**

Country	**Consumption for:**				
	Copper	**Nickel**	**Uranium**	**Phosphate**	**Total**
Dem Rep Congo	5.8	-	-	-	5.8
Madagascar	-	1.4	-	-	1.4
Namibia	-	-	0.5	-	0.5
Niger	-	-	0.1	-	0.1
Nigeria	-	-	-	-	0.1
Senegal	-	-	-	1.5	1.5
South Africa	-	-	0.1	1.3	1.6
Zambia	0.8	-	-	-	1.0
Zimbabwe	-	-	-	-	0.1
Total	**6.4**	**1.4**	**0.7**	**2.8**	**12.0**

Source: CRU

In Nigeria, there are older refineries at Warri and Kaduna, but the largest and most modern refinery belongs to Dangote, and started up in 2023, with a capacity of 650,000 bbl/d. However, in spite of its size, the Dangote refinery produces only 30,000 t/a of sulphur at capacity, as Nigerian oil is relatively sweet and local fuel standards are fairly forgiving of sulphur content.

Mining and metals

Conversely, while the refining sector remains relatively stunted, the region's metal mining operations continue to expand. Globally, copper supply comes mainly from Latin America (Chile, 23% and Peru, 10%), but Africa is second, with the DRC responsible for 14% of production, and Zambia at 4%. Copper production comes mainly from the central African Copper Belt, which stretches across the DRC and into Zambia. This belt is considered to be the largest mineralised sediment-hosted copper province in the world. There is also a secondary, less explored deposit in the Kalahari, across Botswana and into Namibia.

The copper belt also produces cobalt, increasingly important for battery production. Global cobalt production was 300,000 t/a in 2024, 80% of which came from the DRC. Other acid consuming industries include uranium and zinc mining as well as phosphates, and nickel leaching in Madagascar. While there is some industrial consumption, particularly in South Africa, as Table 1 shows, Copper, nickel, uranium and phosphate extraction together represent 95% of all sulphuric acid demand in the region, with consumption concentrated in just five countries: the DRC, Madagascar, Senegal, South Africa and Zambia.

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PHOTO: IVANHOE

The Kamoa-Konkola copper complex, DRC

DRC

Although the copper industry in the DRC is more recent than that in neighbouring Zambia, it has been the hot ticket for new copper discoveries and developments in recent years, much of it high grade ores with copper content of 3-5%, as compared to a typical 0.6-0.8% elsewhere. Almost two thirds of new copper reserves identified worldwide were in the DRC's Katanga Basin, according to S&P. The largest development has been at Kamoa-Kakula, run by Ivanoe, which has expanded production to 600,000 t/a of finished copper, following the completion of a third concentrator last year. Kakula is estimated to be the world's highest grade major copper mine, with an initial mining rate of 3.8 million t/a at an estimated average feed grade of more than 6.0% copper over the first five years of operations.

Other major operations in the country include Glencore's Mutanda Mining (MUMI) and Kamoto Copper (KCC); CMOC's Tenke Fungurume; ERG's Comide and Frontier mines; China Molybdenum's Tenke Fungurume Mine (TFM); and MMG's Kinsevere mine. High copper grades have been amenable to leaching via solvent extraction/electrowinning (SX/EW), with consequent higher consumption of sulphuric acid. As Table 1 shows, the

Table 2: **Sulphuric acid production in sub-Saharan Africa, 2024, million t/a**

Country	Consumption for:			
	Sulphur burning	Smelter acid	Pyrites	Total
Dem Rep Congo	3.2	0.3	-	3.6
Madagascar	1.4	-	-	1.4
Namibia	0.3	0.2	-	0.5
Niger	0.1	-	-	0.1
Nigeria	0.1	-	-	0.1
Senegal	1.5	-	-	1.5
South Africa	1.3	0.4	-	1.7
Zambia	0.3	3.0	0.1	3.4
Zimbabwe	-	-	-	0.0
Total	**8.1**	**3.9**	**0.1**	**12.1**

Source: CRU

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DRC's copper industry consumed nearly 6 million tonnes of acid in 2024, almost half of the region's total demand.

Acid to feed production initially came from smelters across the border in neighbouring Zambia. However, as Table 2 shows, there has been an increasing number of sulphur burning acid plants built in the DRC, and the need for domestic capacity in the DRC became more acute after disputes with Zambia over taxes on copper concentrates which led to the loss of smelter acid production in Zambia. There are now sulphur burning acid plants at Sicomines, Gecamines, and Tenke Fungurume. China's Huyaou Dongfang has a 4,000 t/d plant and Shalina Resources has 600 t/d of capacity in two plants.

Madagascar

Madagascar's acid demand comes solely from the Ambatovy high pressure acid leach (HPAL) nickel facility, with a nameplate 60,000 t/a of nickel capacity, which started production in 2012. The plant has had operating issues which saw Sheritt withdraw from the project, and it currently runs at around 50% of nameplate capacity, operated jointly by Sumitomo and Korea's KOMIR. Sulphuric acid consumption is about 1.3 million t/a, requiring sulphur imports of 450,000 t/a to feed the sulphur burning acid plant at the site.

Senegal

Senegal imports around 3-400,000 t/a of sulphur to generate acid for its phosphate production at Industries Chimique du Senegal, owned by Indorama since 2014. ICS is the largest producer of phosphate fertilizer in sub-Saharan Africa. Phosphate mining has been conducted since 1960, with phosphoric acid capacity added in the 1980s. The phosphoric acid plants are located in Darou and have a production capacity of 600,000 t/a. The downstream 250,000 t/a fertilizer plant is located in Mbao, which is close to the capital Dakar. ICS exports the majority of its phosphoric acid to India, while it sells its fertilizer products in West Africa and international markets.

South Africa

As well as being the only significant regional sulphur producer, South Africa also produces acid from the ageing Palabora copper smelter in Limpopo province, which produces around 60,000 t/a of copper and 180,000 t/a of acid. Anglo American's Polokwane platinum smelter also generates 55,000 t/a of acid from a wet sulphuric acid (WSA) plant installed in 2018, and the Implats platinum smelter at Rustenburg has another 65,000 t/a of production. Sulphur burning acid capacity is mainly dominated by phosphate fertilizer production. DAP and phosphoric acid producer Foskor buys in acid from local smelters as well as operating sulphur burning acid capacity in three large trains at Richards Bay. Sasol also produces sulphuric acid at its Secunda CTL plant.

Zambia

Zambia was once the largest copper producer in Africa but has seen itself eclipsed in recent years by the DRC. Copper production actually fell to 700,000 t/a in 2023, the lowest level for 14 years. The government has ambitious plans to reverse this decline, and there are large new investments planned. Zambia has focused on copper smelting. Copper smelters operational in Zambia include Chambishi Copper at Chambishi, with 660,000 t/a of acid capacity, First Quantum Minerals at Kansanshi (1.0 million t/a), Glencore's Mopani Copper at Kitwe and Mufulira, with a total of 760,000 t/a of capacity, ZCCM at Chambishi (90,000 t/a) and Vedanta's subsidiary KCM at Nchanga and Nkana (total ca 1.0 million t/a of capacity). There are also sulphur burning acid plants at Solwezi (FQM)and Kitwe (Metorex), with a combined 300,000 t/a of capacity. All told this brings Zambian acid capacity to 3.9 million t/a, far in excess of its approximately 1 million t/a of consumption. While excess acid is exported, mainly to the DRC, its requirement was only about 2.2 million t/a in 2024, which means that not all of the smelters can operate at capacity.

New copper mine capacity is planned in Zamnbia. Barrick's $2 billion expansion at Lumwana will see production grow from 118,000 t/a to 240,000 t/a in 2028. In 2022, FQM also announced a $1.25 billion expansion at Kansanshi, which would expand the life of mine until 2040. The Canadian miner accounts for most of Zambia's copper production – its Sentinel mine produces over 200,000 t/a and Kanshansi over 130,000 t/a. The Kansanshi expansion includes additional capacity at the smelter, which began operating in August 2025. Vedanta also wants to restart the Konkola underground mine, where operations had halted through a long legal battle with the previous government, and has announced a major refurbishment of its smelter.

Other consumers

Namibia is home to the region's main uranium mining activities, at Roessing and Husab. Roessing takes sulphuric acid from the Tsumeb metal smelter to dissolve uranium ores, occasionally buying import tonnages via Walvis Bay. At peak production consumption is up to 260,000 t/a of sulphuric acid, although it is typically lower. Huseb has its own dedicated 1,500 t/d sulphur burning acid plant.

Namibia's other sulphuric acid plants are operated by Vedanta Zinc, which runs the Skorpion Zinc mine and NamZinc processing facility, and Dundee Precious Metals, which runs the Tsumeb copper smelter.

Infrastructure issues

One of the major issues that the region faces is lack of transport infrastructure, which can lead to long lead times for sulphur or acid transport and high end user prices. Sulphur has to be brought in from out of the region via ports at Dar es Salaam in Tanzania, Beira in Mozambique, Richard's Bay near Durban in South Africa, Walvis Bay in Namibia, and Lobito in Angola. However, as Figure 1 shows, these are 1,600 – 3,000 km from the copper belt along poor roads and crossing several borders, often involving long queues and bureaucracy, tolls and bandits. Even so, taking sulphur on an outward trip and copper cathode or cobalt hydroxide on the return is proving to be a profitable operation for regional trucking companies. The DRC alone now imports over 500,000 t/a of sulphur. And with the world's appetite for copper seemingly endless and copper demand projected to rise from 21 million t/a to 25.5 million t/a by 2030, leading to a potential shortfall of up to 6 million t/a from existing projects, it seems likely that Africa will be seeing more acid production and more sulphur demand over the coming years. ■

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The Sulphur Institute at 65

The Sulphur Institute celebrates its 65th anniversary this year. In this article the organisation describes its lasting legacy and global impact.

On a spring day in 1960, four visionaries; Russell Coleman, Claude Stephens of Texas Gulf Sulphur, Harry Webb of Pan American Sulphur, and Charles Wight, signed articles of incorporation that gave birth to The Sulphur Institute (TSI). Their vision was simple yet profound: to create an organisation that would promote and expand the use of sulphur in all its forms, uniting an industry that was beginning to shape the modern world.

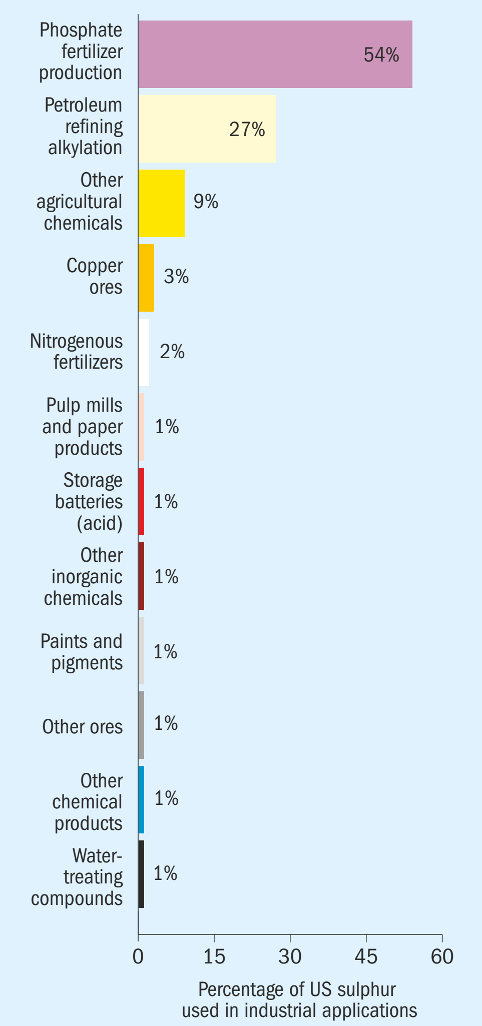
Sixty-five years later, TSI remains the global association for sulphur and sulphuric acid professionals. Its membership spans more than 60 companies worldwide, connecting producers, consumers, traders, researchers, agronomists and transporters across the value chain.

Changing industry, constant mission

At the time of TSI's founding, elemental sulphur came largely from Frasch mining, a process that melted deposits underground with superheated water. But as oil and gas refining expanded in the 1970s and 1980s, sulphur recovery from hydrogen sulphide through the Claus process surpassed mining as the dominant production method. This fundamental shift transformed the industry, and TSI adapted, expanding its membership to include multinational energy companies.

From 1970 to 2023, global sulphur production climbed from under 30 million t/a to more than 82 million t/a. As production methods and markets evolved, TSI never wavered from its core mission: to advocate for sulphur's benefits, promote safe and sustainable practices, advocate it as the 4th major crop nutrient and connect the industry on a global scale.

Fig. 1: **Sulphur use by sector, USA**



Source: USGS

Landmark contributions

Transforming sulphur's value perception – Once dismissed as a low-value byproduct, sulphur is now recognised as an essential raw material. TSI has championed its role in agriculture, chemicals, construction, and environmental management, helping elevate sulphur into a globally significant commodity.

Advancing research and innovation – By funding and coordinating research, TSI has driven breakthroughs in sulphur processing, utilisation, and fertilizer development. Its support of agronomic research has highlighted the importance of sulphur nutrition, where it is often described as the 'fourth major nutrient'.

Facilitating industry collaboration – Through international conferences like the Sulphur World Symposium and specialised working groups, TSI has brought together producers, marketers, agronomists, and policymakers. These gatherings have created neutral spaces for dialogue, best practice sharing, and new partnerships.

Establishing safety and environmental standards – TSI has led efforts to improve workplace safety and environmental stewardship. Its guidelines have informed responsible handling, transportation, and processing of sulphur, while supporting industry adaptation to tightening global regulations.

Education and workforce development – Training programs, technical publications, and outreach efforts have strengthened the skills of industry professionals. By fostering continuous learning, TSI has helped ensure operational excellence across generations.

Looking ahead

As TSI celebrates its 65th anniversary, it is not only reflecting on its past but also embracing the future. With sustainability, carbon management, and responsible supply chains now at the forefront, sulphur continues to play a vital role in feeding the world and fuelling industry.

The founders' vision in 1960 – to build a global forum that advances sulphur for the benefit of society – remains alive and well today. TSI's legacy is not only written in history but also in the future it is helping shape. ■

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SRU optimisation through continuous monitoring

Continuous monitoring of sulphur recovery units (SRUs) has proven to be an excellent tool for energy optimisation and emissions reduction, yielding financial incentives in the form of CO_2 credits and sustainability. Even in markets with limited CO_2 credits, significant economic benefits can still be realised through reduction in utility consumption, as demonstrated by a recent collaboration between Worley Comprimo and PRefChem in Malaysia.

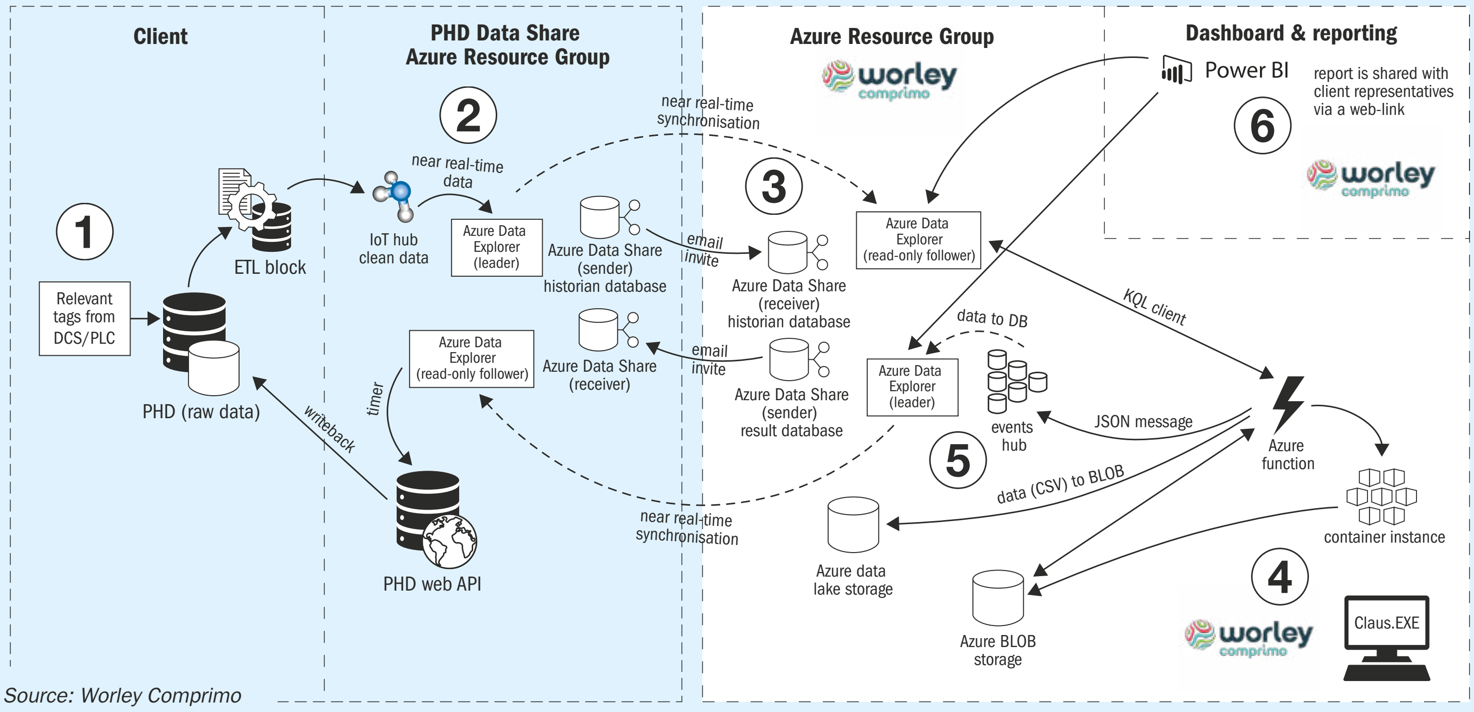
**Claudia Guarino (Comprimo)
and Gokul Sundaramoorthy (PRefChem)**

Energy optimisation and greenhouse gas (GHG) emissions reduction are increasingly important as global efforts intensify to combat climate change.

These efforts have triggered actions by the industry to either implement greener technologies or energy-optimise existing process configurations. In the latter case, continuous monitoring services such as Comprimo Insight, play a key role by providing a deeper operational insight, allowing for timely adjustments to reduce the plant energy footprint and operating cost.

This article summarises the use of Comprimo Insight to enable monitoring services in a sulphur recovery unit (SRU) at PRefChem in Malaysia to enhance energy efficiency while meeting sustainability and environmental requirements. The Comprimo Insight tool is a near real-time monitoring system that allows visualisation of plant performance and trends in KPIs tailored specifically to the needs of PRefChem. This capability allows for rapid evaluation and implementation of guidance from technology specialists. As a result, the SRU utility performance has been significantly improved, with incremental high-pressure steam (HPS) export and reduced fuel gas (FG) consumption, while maintaining all environmental targets.

Fig. 1: **Generic example of data transferring architecture between the plant and the monitoring system**



Source: Worley Comprimo

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Implementation of the monitoring system

To be successful, a monitoring service must be cost-efficient, allowing for seamless and timely automated data transfer, and providing quick, actionable feedback to plant operations.

The data transferring architecture between the plant and the monitoring system can be concisely described, as follows, and as illustrated in Fig. 1:

1. Relevant tags in the SRU are identified.
2. Data from identified tags are uploaded to the client's cyber secured cloud environment from the client's historian database.
3. Through a secured protocol, the data are then transferred into the monitoring system's historian database, located also in a secured cloud environment.
4. Once new data are available, they are processed through calculations and simulations specifically tailored to the plant configuration and design specifics using proprietary software, using selected plant data as input, and generating results that represent the expected plant performance.
5. These results populate a result database located in the monitoring system.
6. The results are then passed back to the client, also via a secured protocol and in the form of a visualisation dashboard, providing the most recent values and operational trends over long periods of time.

Technology specialists with access to this data can then provide insightful recommendations to prevent potential failures, provide guidance on potential catalyst replacements, improve plant efficiency, and reduce operating costs in an opportune manner.

Data are transferred continuously in one-minute average values. There is a delay of 10 to 25 minutes, depending on the client's setup, between data collection and dashboard availability. In the general example presented in Fig. 1, Azure Data Explorer is used for both, the client, and the monitoring system.

Collaboration between PRefChem and Worley Comprimo

PRefChem is a refinery and the largest petrochemical complex in Malaysia, part of the Pengerang Integrated Complex (PIC) in the southern state of Johor. It has three identical SRU trains using the SUPERCLAUS® technology.

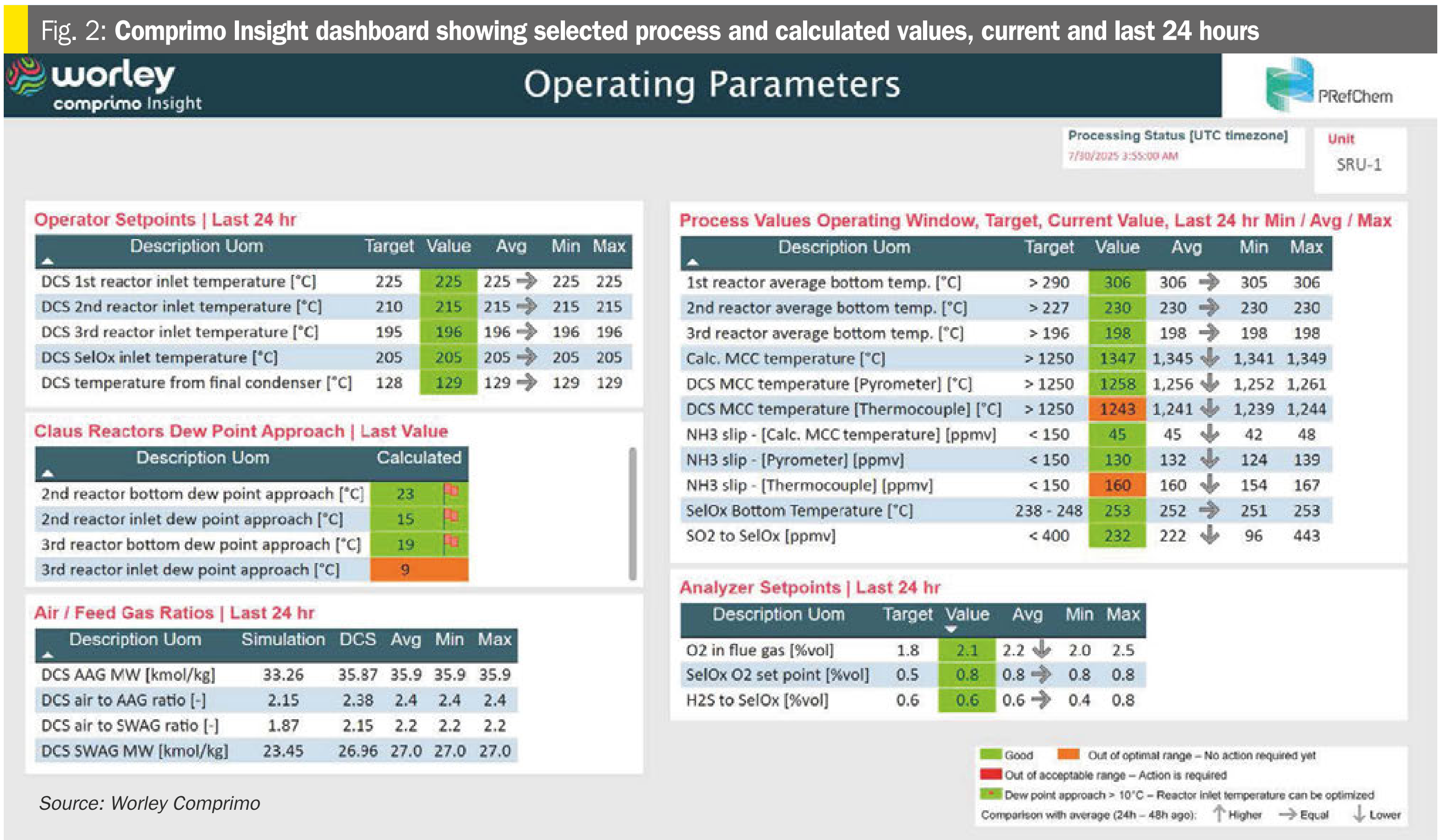
In 2023 PRefChem requested Worley Comprimo to provide ongoing technical assistance to optimise its SRUs and minimise emissions. By the third quarter of 2024, Comprimo Insight started continuously monitoring PRefChem units, collecting and analysing data, and providing recommendations to improve plant performance, and reduce both utility consumption and operating cost.

Several KPIs were developed to monitor the operation of the PRefChem SRUs, including the Claus sulphur recovery, SO_2 and H_2S concentrations at the stack, and other key parameters. Additionally, virtual analysers, (software tools that analyse calculated values based on other measurments), were also used to assess plant performance. Examples of virtual analysers for PRefChem include:

- Tail gas H_2S to selective oxidation (SelOx) reactor: the temperature rise across the SelOx reactor is a direct measure of the H_2S concentration at the SelOx reactor inlet and therefore a check of the H_2S value given by the tail gas analyser.
- Main combustion chamber temperature: the temperature in the main combustion chamber is calculated based on feed gas flow rates and assumed composition.

Fig. 2 presents selected distributed control system (DCS) process parameters, calculated values as well as visual analysers that are continuously monitored by Comprimo Insight.

Fig. 2: **Comprimo Insight dashboard showing selected process and calculated values, current and last 24 hours**



Operating Parameters

Processing Status [UTC timezone]
7/30/2025 3:55:00 AM

Unit
SRU-1

Operator Setpoints | Last 24 hr

Description Uom	Target	Value	Avg	Min	Max
DCS 1st reactor inlet temperature [°C]	225	225	225 →	225	225
DCS 2nd reactor inlet temperature [°C]	210	215	215 →	215	215
DCS 3rd reactor inlet temperature [°C]	195	196	196 →	196	196
DCS SelOx inlet temperature [°C]	205	205	205 →	205	205
DCS temperature from final condenser [°C]	128	129	129 →	129	129

Claus Reactors Dew Point Approach | Last Value

Description Uom	Calculated
2nd reactor bottom dew point approach [°C]	23 🚩
2nd reactor inlet dew point approach [°C]	15 🚩
3rd reactor bottom dew point approach [°C]	19 🚩
3rd reactor inlet dew point approach [°C]	9

Air / Feed Gas Ratios | Last 24 hr

Description Uom	Simulation	DCS	Avg	Min	Max
DCS AAG MW [kmol/kg]	33.26	35.87	35.9	35.9	35.9
DCS air to AAG ratio [-]	2.15	2.38	2.4	2.4	2.4
DCS air to SWAG ratio [-]	1.87	2.15	2.2	2.2	2.2
DCS SWAG MW [kmol/kg]	23.45	26.96	27.0	27.0	27.0

Process Values Operating Window, Target, Current Value, Last 24 hr Min / Avg / Max

Description Uom	Target	Value	Avg	Min	Max
1st reactor average bottom temp. [°C]	> 290	306	306 →	305	306
2nd reactor average bottom temp. [°C]	> 227	230	230 →	230	230
3rd reactor average bottom temp. [°C]	> 196	198	198 →	198	198
Calc. MCC temperature [°C]	> 1250	1347	1,345 ↓	1,341	1,349
DCS MCC temperature [Pyrometer] [°C]	> 1250	1258	1,256 ↓	1,252	1,261
DCS MCC temperature [Thermocouple] [°C]	> 1250	1243	1,241 ↓	1,239	1,244
NH3 slip - [Calc. MCC temperature] [ppmv]	< 150	45	45 ↓	42	48
NH3 slip - [Pyrometer] [ppmv]	< 150	130	132 ↓	124	139
NH3 slip - [Thermocouple] [ppmv]	< 150	160	160 ↓	154	167
SelOx Bottom Temperature [°C]	238 - 248	253	252 →	251	253
SO2 to SelOx [ppmv]	< 400	232	222 ↓	96	443

Analyzer Setpoints | Last 24 hr

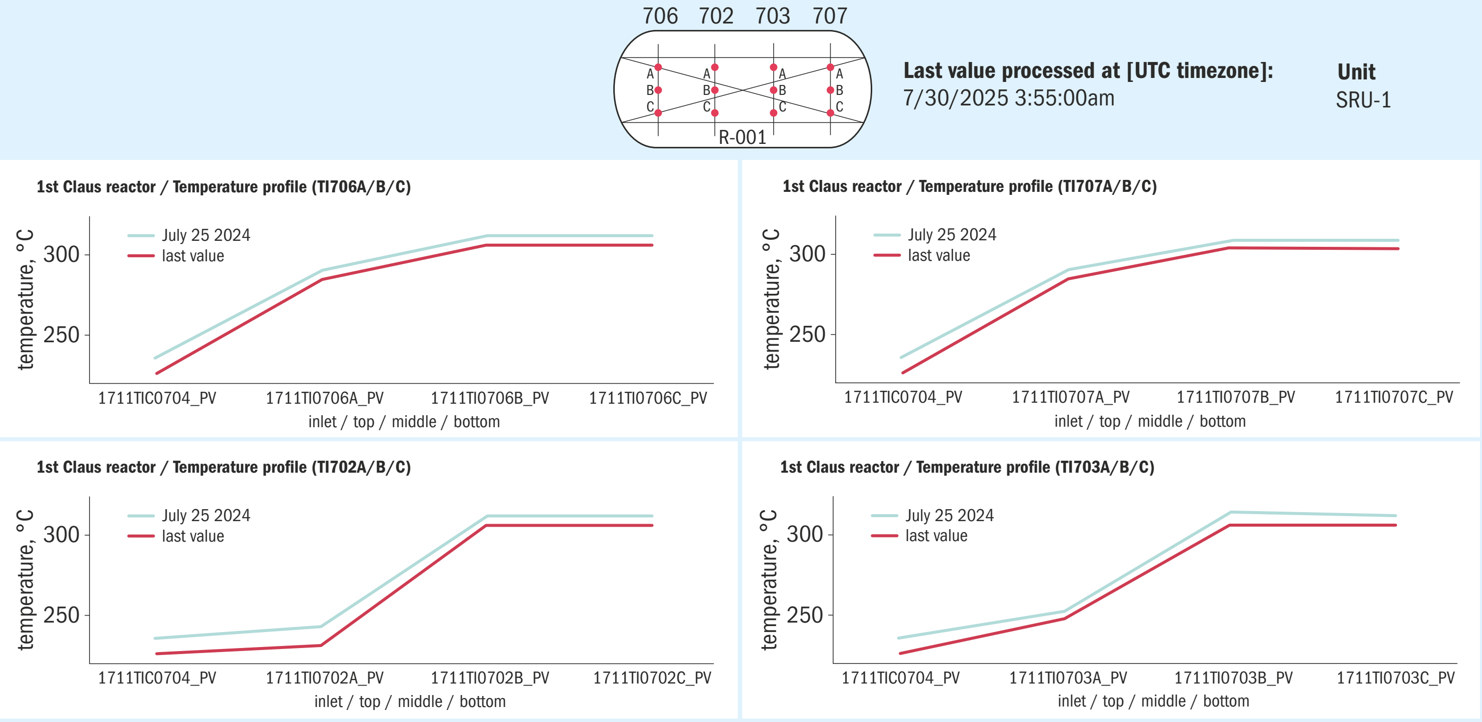
Description Uom	Target	Value	Avg	Min	Max
O2 in flue gas [%vol]	1.8	2.1	2.2 ↓	2.0	2.5
SelOx O2 set point [%vol]	0.5	0.8	0.8 →	0.8	0.8
H2S to SelOx [%vol]	0.6	0.6	0.6 →	0.4	0.8

🟩 Good 🟧 Out of optimal range – No action required yet
🟥 Out of acceptable range – Action is required
🚩 Dew point approach > 10°C – Reactor inlet temperature can be optimized
Comparison with average (24h – 48h ago): ↑ Higher → Equal ↓ Lower

Source: Worley Comprimo

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

Fig. 3: **Comprimo Insight dashboard with temperature profile across the 1st Claus reactor catalyst bed for plant SRU-1, actual values compared to fresh catalyst**

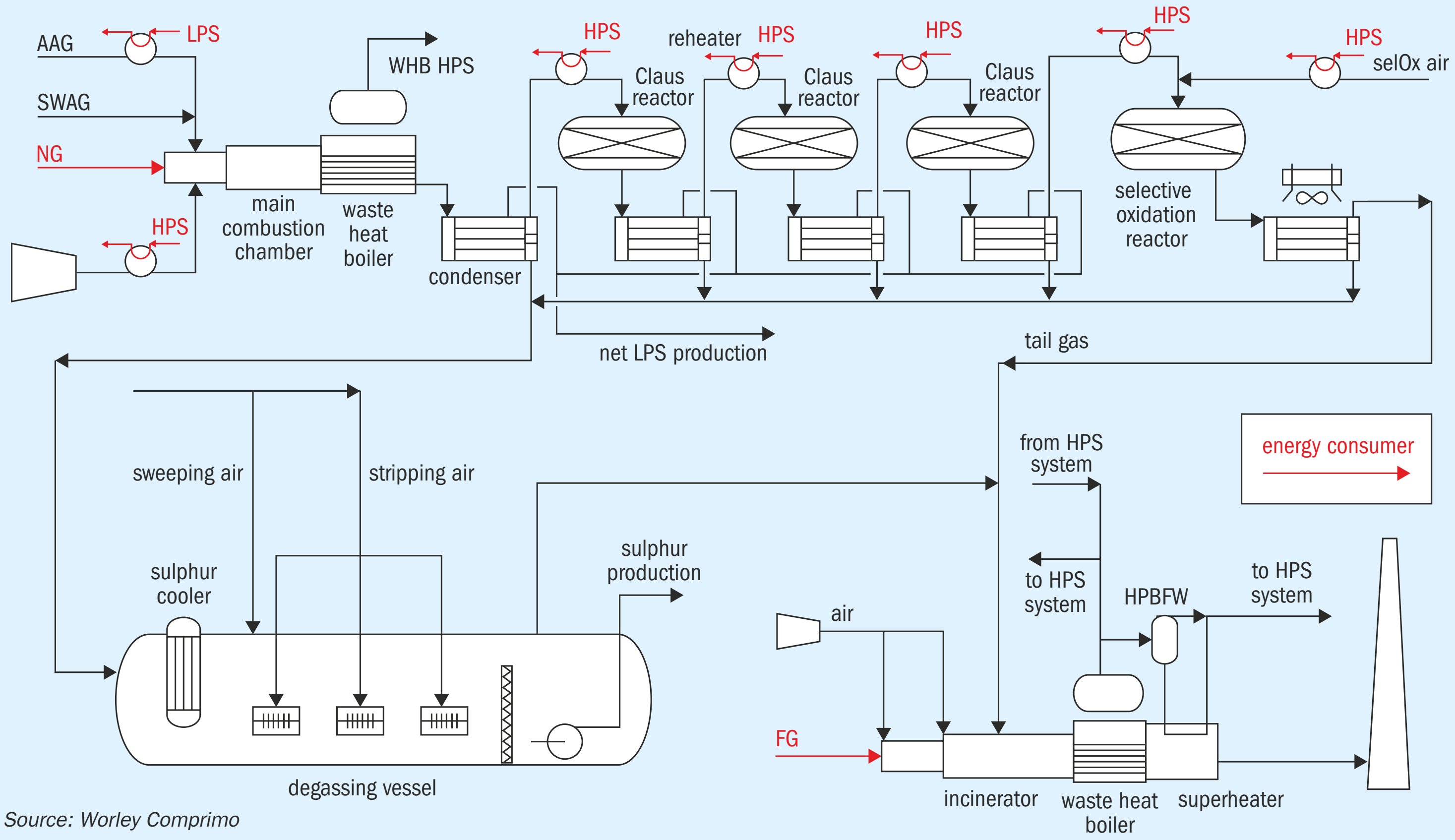


Source: Worley Comprimo

Reactor temperature profiles are also closely tracked and compared against historical data to identify potential signs of catalyst deactivation or other operational anomalies, as illustrated in Fig. 3.

Fig. 4 shows a representative process flow diagram for an SRU configured with three Claus reactors, followed by a single SelOx reactor. Analysis of the available operational data revealed optimisation opportunities in both the Claus reactor section and incinerator operation.

Fig. 4: **Typical process flow diagram of an SRU featuring a 3 Claus + 1 SelOx reactor configuration, indicating major energy-consuming equipment**



Source: Worley Comprimo

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- Dr. Eric Roisin, *Worley Comprimo*
- Hari Vamsi Duggirala, *310i*
- Jochen Geiger, *Ametek Process Instruments*
- Mayank Ranjan, *ONGC*
- Mohd Firdaus Sabturani, *PETRONAS*
- Mounica Manda, *Jord International*
- Nirmalya Nandi, *BPCL*
- Pranay Singh, *Fluor*
- Prasenjit Saha, *EIL*
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Reactor operation optimisation

By continuously monitoring temperature profiles across the catalyst beds through the Claus and SelOx reactors and estimating the dew points of process gas streams using proprietary process simulation tools, the operating conditions of the reactors are systematically assessed to identify opportunities for process optimisation and energy reduction.

For example, although the reactor inlet temperatures (RIT) are typically specified by the process licensor to meet the desired plant performance, careful evaluation can reduce energy consumption in the reheaters, without adversely affecting operational efficiency.

1st reactor optimisation

In addition to the Claus reaction, COS and CS_2 destruction happens in the 1st Claus reactor, requiring an outlet temperature of at least 290°C. Table 1 shows outlet temperatures for the 1st Claus reactors for all units typically around 310 to 312°C, giving around 20°C margin from the minimum bottom temperature required.

2nd and 3rd reactor optimisation

The 2nd and 3rd Claus reactors are operated so that the inlet and outlet temperatures are above the sulphur dew point to prevent sulphur condensation on the catalyst. Based on the data shown in Table 1, the dew point approach in the 2nd reactor is above 20°C, which is much higher than the industry standard of 10°C.

SelOx reactor optimisation

The SelOx RIT is maintained at 210 °C to ensure optimal yield. In the PRefChem 3+1 SUPERCLAUS® configuration, the typical H_2S tail gas setpoint is 0.5 mol-%. Because PRefChem H_2S setpoint is 0.6 mol-%, enough heat generation is expected, potentially permitting a 5°C reduction in the RIT while maintaining comparable reactor performance.

Based on the reactors operating conditions, it was suggested to decrease the RIT by 10°C in the 1st Claus reactor, and by 5°C in both the 2nd Claus and SelOx reactors to reduce HPS consumption in the reheaters, while assessing the plant performance. The 3rd reactor outlet already operates close enough to the sulphur dewpoint.

PRefChem carried out a test, decreasing the RIT in the reactors for all three units as shown in Fig. 5, and it was demonstrated that the plant performance was maintained.

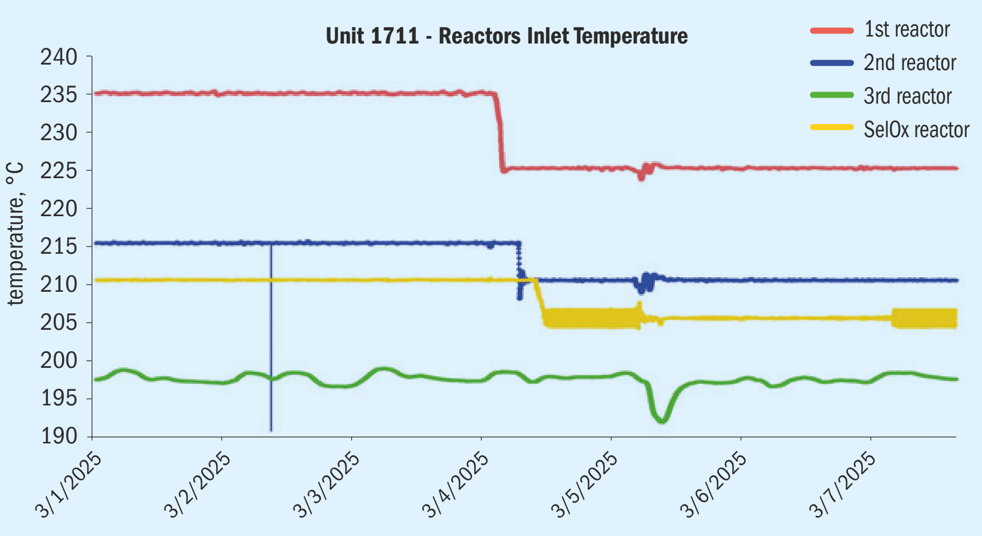
Table 1: **Operating conditions for Claus and SelOx reactors for SRU-1, SRU-2 and SRU-3**

Parameter	**Target**	**SRU-1**	**SRU-2**	**SRU-3**
1st reactor bottom temperature, °C	290 – 300	312	310	312
2nd reactor in/outlet temperature, °C	215/>220	215/231	215/229	215/232
2nd reactor dew point temperature, °C				
Inlet approach	10	22	20	22
Outlet approach	10	18	16	19
3rd reactor in/outlet temperature, °C	195/>195	195/198	195/195	195/196
3rd reactor dew point temperature, °C				
Inlet approach	10	15	14	15
Outlet approach	10	7	7	6
SelOx reactor in/outlet temperature, °C	210/ 240 – 260	209/255	206/246	209/251
H_2S tail gas analyser, mol-%				
DCS	0.6	0.59	0.44	0.60
Calculated based on SelOx ΔT		0.67	0.46	0.59

Source: Worley Comprimo

Note: Data collected between 16 October 2024 (00:00) - 08 January 2025 (23:59)

Fig. 5: **Adjustment for RITs for 1st, 2nd Claus reactors and SelOx reactor for SRU-1. Data collected between 01 March (00:00) - 07 March 2025 (23:59)**



Source: Worley Comprimo

Table 2: **HPS consumption reduction in affected reheaters after reducing RITs for all units**

Parameter	**SRU-1**	**SRU-2**	**SRU-3**
Plant load, %	48	43	55
Revenue increase at given plant load, USD/year	215,000	194,000	222,000
Revenue increase at 100% plant load, USD/year	448,000	450,000	403,000

Source: Worley Comprimo

Note 1: Steam consumption for the 1st, 2nd and 4th reheaters. 3% blowdown assumed.

Note 2: Temperatures around the 3rd Reheater (upstream 3rd Reactor) and the SelOx Air Preheater did not change significantly during the RITs adjustment.

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The savings in HPS consumption in the reheaters upstream the 1st, 2nd, and SelOx reactors (1st, 2nd, and 4th reheaters respectively) was estimated based on the actual DCS inlet and outlet temperature values of the process gas through these reheaters, before and after the adjustment in the RITs. These savings are presented in Table 2.

Incinerator optimisation

The incinerator is among the largest energy consumers in an SRU, making it a key candidate for optimisation efforts. The SRU incinerator is followed by a waste heat boiler (WHB) and a superheater for each train, providing superheated steam to steam turbines in the refinery complex.

Data analysis revealed inconsistent performance across the three SRUs under similar plant loads, as shown in Fig. 6.

SRU-3 consistently consumed more fuel gas than SRU-1 and SRU-2. Additionally, a fuel gas consumption ceiling for SRU-3 at plant throughputs exceeding 70% was observed, demonstrating that the maximum flow rate for fuel gas had already been reached. Further investigation revealed inadequate control of the combustion air flow rate to the incinerator caused by sticky valves, leading to increased fuel gas consumption to maintain the required incinerator temperature.

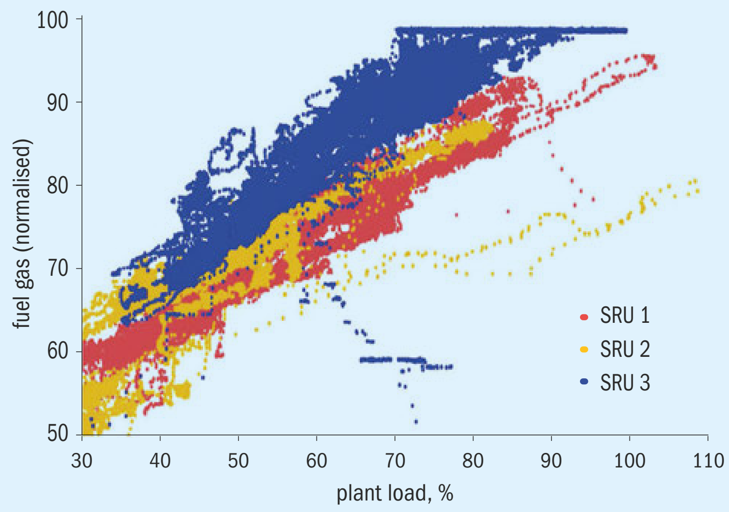
Incinerator flue gas temperatures averaged 750°C to 760°C with flue gas oxygen concentrations typically above 5 vol-%, the latter a result of the insufficient control of combustion air flow. Optimising the high oxygen concentration in the stack will lead to reduced fuel gas consumption and, consequently, lower operating cost.

Despite the sticky valves on the primary and staged air system, which challenge precise control of oxygen levels in the flue gas, an optimisation exercise conducted by PRefChem demonstrated notable energy savings opportunities.

The primary and staged air flows were manipulated to reduce the oxygen content in the flue gas while maintaining the incinerator temperature, without compromising the emission levels at the stack.

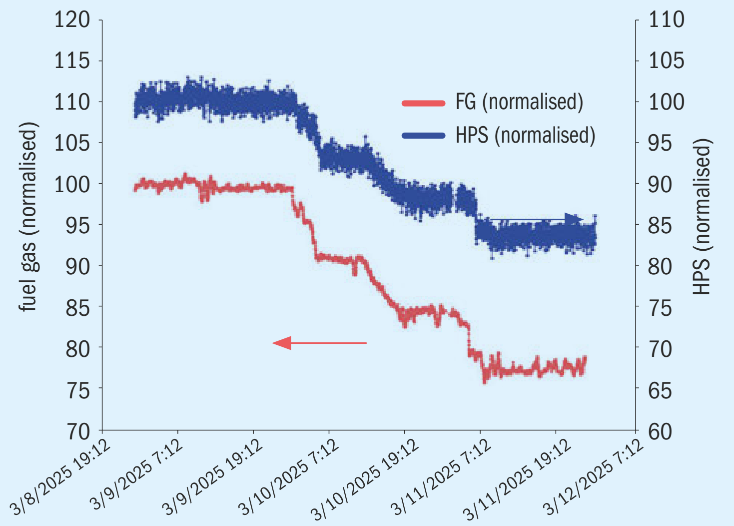
Figs 7 through 9 illustrate the impact on fuel gas consumption and high-pressure steam production in the WHB as primary and staged air flows to the incinerator were gradually lowered during the optimisation test performed for SRU-1.

Fig. 6: **Generic example of data transferring architecture between plant and monitoring system**



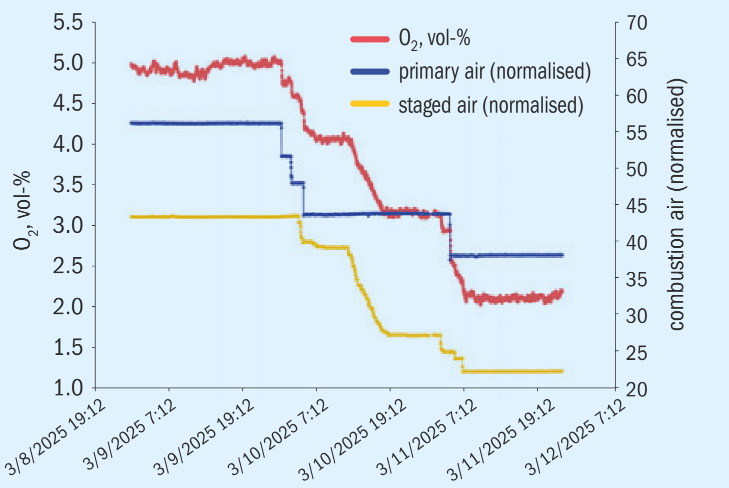
Source: Worley Comprimo

Fig. 7: **Incinerator fuel gas consumption and WHB high-pressure steam production in SRU-1**



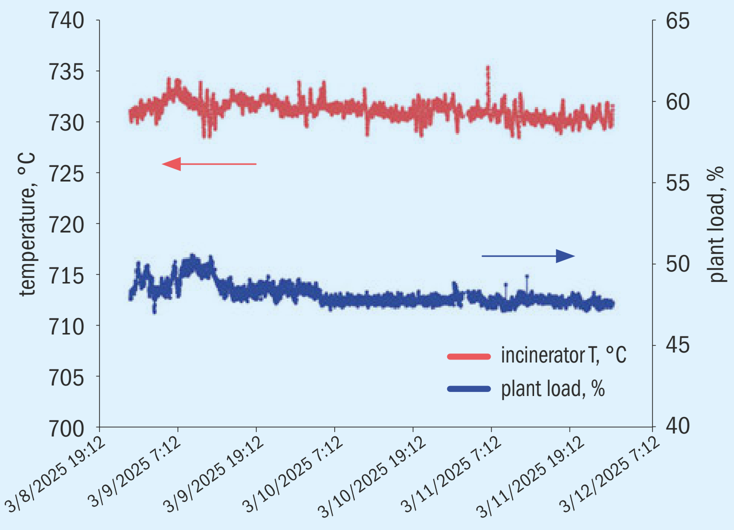
Source: Worley Comprimo

Fig. 8: **Incinerator primary and staged air flows and flue gas oxygen concentration in SRU-1**



Source: Worley Comprimo

Fig. 9: **Incinerator temperature and plant load in SRU-1**



Source: Worley Comprimo

Table 3: **Impact on incinerator operating cost for SRU-1 when reducing O_2 content in flue gas**

Operational parameters	**Before adjustment**	**After adjustment**
O_2 in flue gas, vol-%	4.95 +/- 0.06	2.13 +/- 0.03
Fuel gas consumption, normalised	100%	76.9%
HPS production in WHB, normalised	100%	83.5%
Incinerator temperature, °C	731 +/- 0.8	729 +/- 0.7
Plant load, %	49 +/- 0.6	48 +/- 0.2
Operational expenses (opex)		
Fuel gas cost, USD/year	4,313,000	3,316,000
HPS revenue, USD/year	5,390,000	4,499,000
Overall revenue, USD/year	1,077,000	1,182,000
Revenue after adjustment at ~50 % plant load, USD/year		**106,000**
Revenue after adjustment at 100% plant load, USD/year		**212,000**
CO_2 emission reduction		
CO_2 emission reduction at ~50% plant load, ton/year		**4,700**
CO_2 emission reduction at 100% plant load, ton/year		**9,400**

Source: Worley Comprimo

Note: Data collected between 09 March (00:00) - 11 March 2025 (23:59) – Data reported as average +/- standard deviation.

Table 4: **Impact on incinerator operating cost for SRU-2 when reducing O_2 content in flue gas**

Operational parameters	**Before adjustment**	**After adjustment**
O_2 in flue gas, vol-%	4.12 +/- 0.58	2.27 +/- 0.24
Fuel gas consumption, normalised	100%	76.3%
HPS production in WHB, normalised	100%	81.5%
Incinerator temperature, °C	746 +/- 0.7	745 +/- 0.4
Plant load, %	55 +/- 1.4	52 +/- 0.4
Operational expenses (opex)		
Fuel gas cost, USD/year	4,684,000	3,575,000
HPS revenue, USD/year	5,707,000	4,650,000
Overall revenue, USD/year	1,023,000	1,075,000
Revenue after adjustment at ~50 % plant load, USD/year		**52,000**
Revenue after adjustment at 100% plant load, USD/year		**98,000**
CO_2 emission reduction		
CO_2 emission reduction at ~50% plant load, ton/year		**5,200**
CO_2 emission reduction at 100% plant load, ton/year		**9,800**

Source: Worley Comprimo

Note: Data collected between 12 March (17:00) - 13 March 2025 (23:59) – Data reported as average +/- standard deviation.

The same optimisation exercise was carried out for SRU-2 and SRU-3. Tables 3 through 5 summarises the resulting impact on utility consumption, steam production, and operating costs for the incinerator and waste heat boiler following flue gas oxygen level optimisation.

Annual cost savings between $52,000 and $106,000 per train were achieved by optimising flue gas oxygen concentration at approximately 50% plant load. The range in savings reflects variability in oxygen concentration adjustments across units, as well as operational challenges associated with precise air valve modulation. PRefChem plans to replace the air valves during the next turnaround to enable more precise air control and deeper optimisation.

In addition to fuel gas savings, a reduction in CO_2 emissions is also realised through improved combustion efficiency. This environmental benefit may translate into further economic gains in markets where CO_2 emission credits or carbon trading mechanisms are in place.

Conclusions

Implementing advanced monitoring services in SRUs enables proactive performance management and optimisation. By leveraging real-time KPIs, virtual analysers, and data-driven insights from technology specialists, plant engineers and operators can identify inefficiencies, adjust operating conditions, and maintain compliance with environmental requirements.

Multiple energy and operating cost saving opportunities were identified for PRefChem:

- An estimated annual cost savings of approximately $1,300,000 for all three trains combined (at 100% plant load) can be realised by lowering the reactor inlet temperature in the 1st and 2nd Claus reactors as well as the selective oxidation (SelOx) reactor.
- An estimated annual cost savings of around $500,000 for the three trains combined (at 100% plant load) can be obtained by minimising flue gas oxygen levels in the incinerator. It is possible that even higher savings could be realised once the incinerator combustion air valves are replaced, and a more precise air control is possible.

It is remarkable that these significant savings can be accomplished without any additional investment or changes to the process configuration, and only by adjusting the operating parameters of the plant. This demonstrates the value of assertive and timely technical assistance, and the importance of having a service, such as Comprimo Insight, that enables rapid testing and implementation of such a guidance.

With ongoing data collection and analysis, and growing operational trends over longer periods of time, it is expected that other savings opportunities will be identified in the future.

Future initiatives

Looking ahead, continuous monitoring will explore integration with AI and specifically machine learning to enable predictive analytics, anomaly detection, and automatic performance optimisation. Additionally,

Table 5: **Impact on incinerator operating cost for SRU-3 when reducing O_2 content in flue gas**

Operational parameters	**Before adjustment**	**After adjustment**
O_2 in flue gas, vol-%	4.36 +/- 0.06	1.94 +/- 0.13
Fuel gas consumption, normalised	100%	84.9%
HPS production in WHB, normalised	100%	89.0%
Incinerator temperature, °C	714 +/- 1.4	719 +/- 1.3
Plant load, %	50 +/- 0.6	52 +/- 0.4
Operational expenses (opex)		
Fuel gas cost, USD/year	4,968,000	4,217,000
HPS revenue, USD/year	5,912,000	5,259,000
Overall revenue, USD/year	943,000	1,042,000
Revenue after adjustment at ~50 % plant load, USD/year		**99,000**
Revenue after adjustment at 100% plant load, USD/year		**198,000**
CO_2 emission reduction		
CO_2 emission reduction at ~50% plant load, ton/year		**3,500**
CO_2 emission reduction at 100% plant load, ton/year		**7,000**

Source: Worley Comprimo

Note: Data collected between 06 March (00:00) - 09 March 2025 (23:59) – Data reported as average +/- standard deviation.

remote monitoring and cloud-based environments allow centralised oversight of multiple units across different locations.

With the increasing availability of operational data from different plants and unit configurations, standardised benchmarks for key performance indicators and energy consumption are being established, facilitating more effective optimisation of plant operations.

Continuous monitoring services will become a vital component of a proactive strategy for environmental compliance and energy optimisation in SRU plants, as regulations tighten, and efficiency demands grow.

Reference

CRU Sulphur + Sulphuric Acid 2024 – Barcelona 2024, article and presentation, "Energy and Cost Optimisation Opportunities in an SRU", by Jan-Willem Hennipman and Martin Gensor, Worley Comprimo and Slovnaft.

Acknowledgment

Worley Comprimo would like to thank PRefChem for sharing and allowing the use of their plant data in the preparation of this collaborative work. Worley Comprimo also thanks Gokul Sundaramoorthy, Technical Specialist II, in the Sulphur Complex and Acid Gas Treating, Pengerang Refining Company Sdn Bhd (PrefChem Refining) for acting as reviewer and co-author of this article.

Analysing COS and CS_2 in a modern SRU

Maximising sulphur recovery in a modified Claus SRU/TGTU requires controlling and monitoring COS and CS_2. Leveraging decades of monitoring experience, AMETEK Process Instruments discusses the formation, impact and monitoring of COS and CS_2.

Rod Merz, Michael Gaura, Harry Burton, Nirav Patel (AMETEK Process Instruments)

For refineries, natural gas processing plants, coke producers and chemical plants, maximising the conversion efficiency of hydrogen sulphide (H_2S) to elemental sulphur is a critical path to meeting modern emission standards. To achieve this, the modified Claus sulphur recovery unit (SRU) combined with an amine-based tail gas treatment unit (TGTU) is a common configuration with a proven track record in obtaining a high level (>99.9% and better) of sulphur recovery efficiency.

Both carbonyl sulphide (COS) and carbon disulphide (CS_2) are well known reactants formed in the initial thermal reaction stage of the SRU. These compounds have been identified as contributing to elevated sulphur (as SO_2 primarily) emission levels. In a modified Claus SRU without tail gas treatment, it has been demonstrated in extreme cases that COS and CS_2 formation can result in H_2S conversion efficiency losses as high as 10%[1,2]. While extreme cases such as this are not the norm, any COS and CS_2 that makes it past the SRU's first converter stage ultimately end up as emissions. The addition of an amine-based TGTU provides a second opportunity to convert residual COS and CS_2 from the SRU to further reduce these compounds before they are sent to an incinerator.

The measurement of COS and CS_2 can provide valuable insights into the performance of both the SRU and the TGTU as well as explain increases in emissions when COS and CS_2 levels are elevated due to abnormal operation of the SRU and TGTU.

AMETEK Process Instruments has a background of over 50 years in sulphur recovery and combined global sales of over 2400 analysers into modified Claus plants and amine-based tail gas treater units from which much of the content presented is based upon.

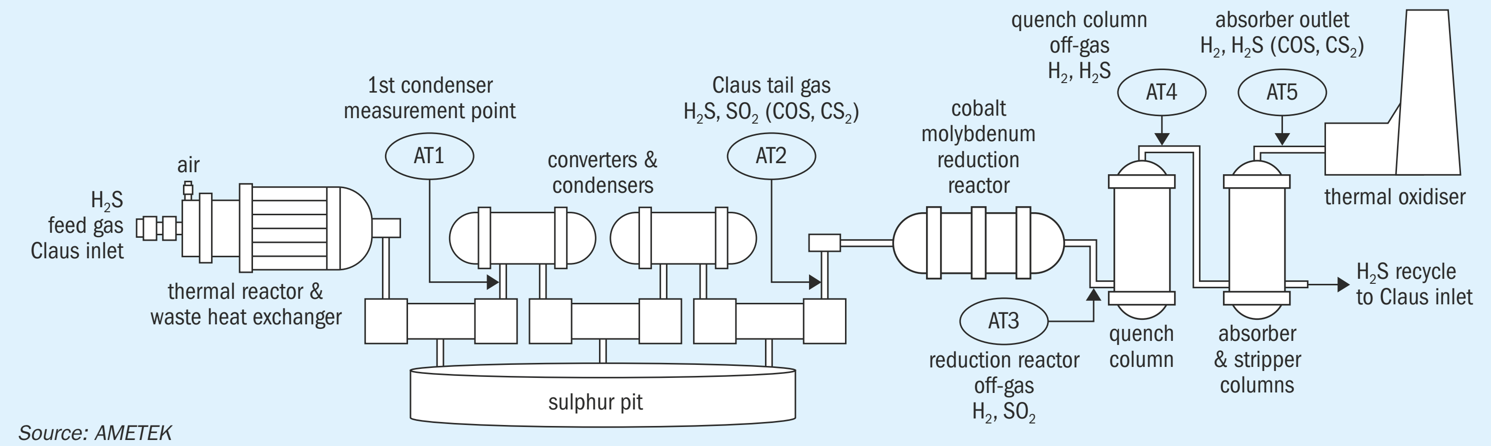
Modified Claus SRU and amine-based TGTU layout

The modified Claus SRU illustrated in Fig. 1 consists of five essential components, the thermal reactor, a waste heat exchanger, an initial condenser, and then typically multiple stages of gas reheaters, catalytic beds and condenser segments. Amine-based TGTUs will also have a catalytic converter section that utilises a cobalt (Co) molybdenum (Mo) catalyst. It may also have a reducing gas generator (RGG) in front of it, or another means of supplying additional hydrogen (H_2). The CoMo catalyst bed is typically followed by a quench tower with an amine absorber and amine regenerator section at the end. There are additional components, but these will not be relevant to the topic.

Modified Claus chemistry of COS and CS_2 in the SRU

For both refineries and sour gas plants, acid gas feed streams contain several components other than H_2S. Refineries will usually have an additional stream of sour water stripper gas (SWSG) added to the inlet of the SRU. In both cases, various hydrocarbons (HC), carbon dioxide (CO_2),

Fig. 1: **SRU and TGTU layout. The tags AT1 through AT5 indicate potential measurement locations in the SRU and TGTU**



Source: AMETEK

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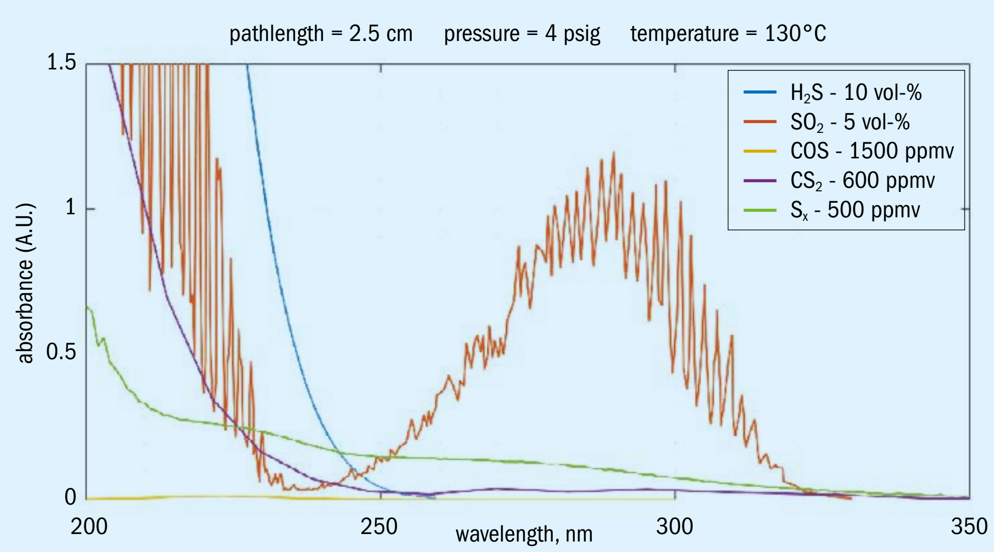
Fig. 2: **Sulphur absorbances at first condenser outlet**



Source: AMETEK

water (H_2O), and ammonia (NH_3) are part of the acid gas and SWSG feeds into the reaction furnace. These additional components are involved in many side reactions during the thermal reactor stage of the SRU.

Most of the important chemistry for the modified Claus reaction occurs in the thermal reactor stage where the goal is to utilise the modified Claus reaction and convert 1/3 of the H_2S to SO_2 in the thermal reactor stage to further react again to produce elemental sulphur (equation 1). The reaction between SO_2 and H_2S to form sulphur is equilibrium limited and to move the reaction forward, the sulphur produced must be removed.

$$3H_2S + {}^3/_2O_2 \rightarrow SO_2 + 2H_2S + H_2O \rightleftharpoons {}^3/_x Sx + 2H_2O \qquad (1)$$

The first condenser removes the produced sulphur allowing the same reaction to move forward again in the first and subsequent catalyst beds; however, there are many side reactions that occur as well. Much of the formation of COS and CS_2 also occurs in the thermal reactor where CO_2 and HCs are participants in these side reactions.

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad (2)$$

$$CO + ½S_2 \rightarrow COS \qquad (3)$$

Equations 2 and 3 show the initial formation of CO from CO_2. The CO is then converted to COS by reacting with the elemental sulphur produced as part of the Claus reaction.

$$CH_4 + 4S \rightleftharpoons CS_2 + 2H_2S \qquad (4)$$

Equation 4 illustrates the formation of CS_2 from sulphur reacting with methane, although any other hydrocarbon species present can be substituted for methane in the reaction.

After the formation of COS and CS_2 in the thermal reactor, the SRU first converter bed is a significant opportunity to have these compounds undergo hydrolysis as shown in equations 5 and 6.

$$CS_2 + H_2O \rightarrow CO_2 + H_2S \qquad (5)$$

$$COS + 2H_2O \rightarrow CO_2 + 2H_2S \qquad (6)$$

These hydrolysis reactions are favoured by higher temperatures in the first converter bed which is why the first converter bed is typically operated at a higher temperature than subsequent converter beds[1,2].

Once COS and CS_2 make it past the first converter bed, the last significant line of defence is the CoMo catalyst bed in the TGTU. The CoMo catalyst bed will allow a final opportunity for the hydrolysis reactions shown in equations 5 and 6. After the CoMo catalyst bed, any remaining COS and CS_2 will end up in the incinerator and contribute to the plant's emissions.

Measurement opportunities for COS and CS_2 in the SRU

There are five potential locations where COS and CS_2 can be measured in an SRU with an amine-based TGTU:

- the initial thermal reaction products found at the outlet of the first condenser (AT1 in Fig. 1);
- the post SRU remaining gas constituents measured at the outlet of the final condenser (AT2);
- the reaction products exiting the TGTU's cobalt molybdenum reduction reactor with a measurement point in front of the quench tower (AT3);
- the quench tower outlet (AT4);
- the remaining products exiting the top of the TGTU absorber (AT5).

While the possibility exists to measure COS and CS_2 after the SRU first condenser (AT1), the spectroscopic interference from concentrations of sulphur vapour, H_2S and SO_2 are substantial. Fig. 2 shows an example of the spectroscopic interferences at typical concentrations found after the first condenser.

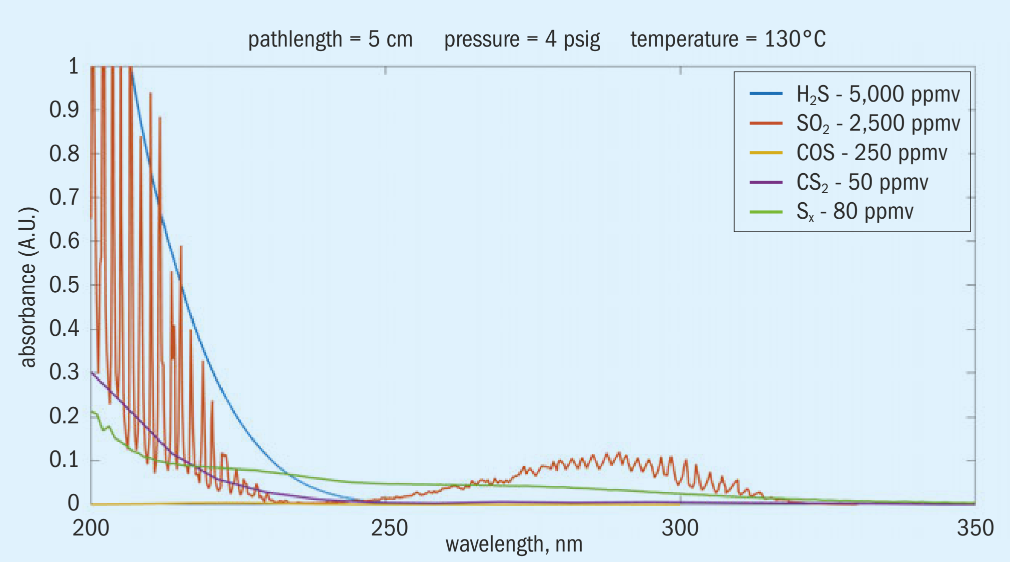
This location would normally be considered a compromised sample point with high concentrations of sulphur vapour still present that can easily overwhelm a sample conditioning system under adverse conditions. Also, the hydrolysis reactions that take place in the first converter bed have not occurred, so the only information obtained will be an indication what has occurred in the thermal reactor regarding COS and CS_2 formation. With little to no economic or functional gain to be had from this information, it has not been requested by industry.

The first converter bed does most of the work in performing the hydrolysis reaction for COS and CS_2. It is operated at elevated temperatures to facilitate the reaction in equations 5 and 6 and maximise the hydrolysis reaction for COS and CS_2[1,2]. The addition of a layer of titania catalyst in the first converter may also be used to maximise the conversion of COS and CS_2. Subsequent converters are operated at lower temperatures to maximise the Claus reaction and have a significantly smaller hydrolysis conversion rate. A measurement for COS and CS_2 is possible after the first converter but the spectroscopic limitations for minimum detectable levels will still be worse than the measurement at the final condenser due to elevated H_2S and SO_2 compared to the final condenser location. The COS and CS_2 are not expected to appreciably change after the first converter, so waiting to make the measurement after the final condenser makes more sense if there is a useful reason for the measurement at this point.

The SRU final condenser's air demand analyser sample location (AT2) is the only effective place in the SRU where COS and CS_2 measurements can be made. As such, this has traditionally been the

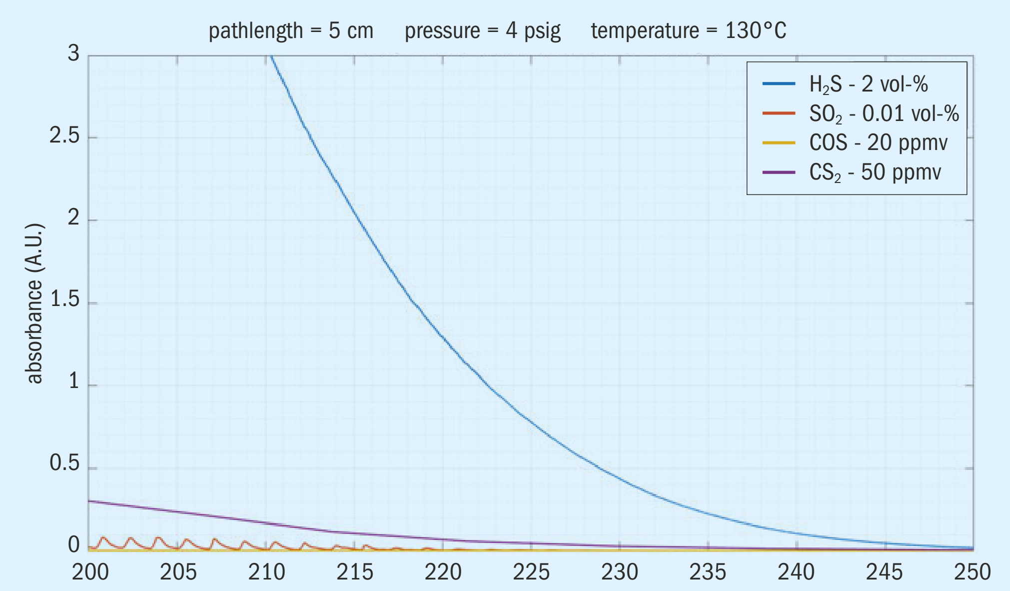
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52

Fig. 3: **Sulphur absorbances at final condenser outlet**



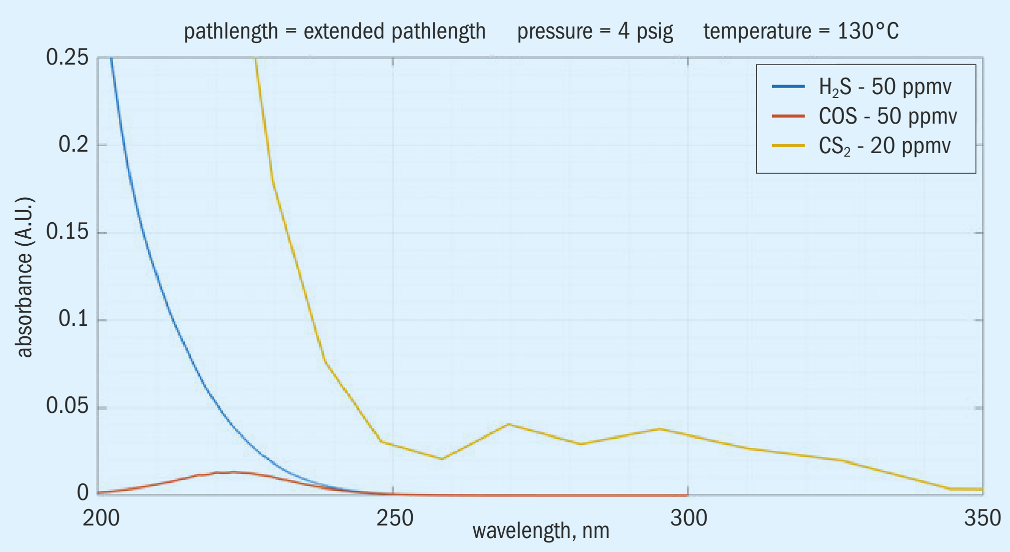
Source: AMETEK

Fig. 4: **Sulphur absorbances at quench tower inlet**



Source: AMETEK

Fig. 5: **Sulphur absorbances at TGTU absorber outlet**



Source: AMETEK

location where any measurement of COS and CS_2 is made. H_2S, SO_2, and sulphur vapour are at their lowest concentrations in the Claus unit at this point. While they will still provide some spectroscopic interference with the measurement of COS and CS_2, this is the only potentially useful location in the Claus unit. The COS and CS_2 measurements in this location are typically used to determine a loss in catalyst activity in the first converter bed. Measurements here have also been used to indicate significant variations of CO_2 or hydrocarbons in the SRU feed gas concentrations that have passed through the thermal reactor and modified Claus unit. For the former, proper temperature profiling will give a good indication of catalyst activity in the first converter bed. For the latter, a feed forward analyser will be much more useful in dealing with changes in the SRU feed gas HC content. It should be noted that in situations where co-firing with natural gas is utilised, elevated levels of COS and CS_2 will also be noticed; however, they should not fluctuate significantly over the co-firing period unless other events as mentioned above are occurring. There is little during SRU operation that can be done for significant changes in CO_2 content in the acid gas feed that leads to higher COS formation other than to examine the upstream processes feeding the SRU.

As shown in the Fig. 3, the interference from the remaining H_2S and SO_2 content in the tail gas can still result in a decrease in sensitivity for the COS and CS_2 measurement. At this point, the noise floor for COS can be in the order of 200 ppm to 500 ppm depending on the final H_2S and SO_2 concentration. At levels of 5,000 ppm and 2,500 ppm for the H_2S and SO_2 respectively, this level of noise compromises the value of the measurement.

There are three opportunities to measure COS and CS_2 within the TGTU:

- the quench tower inlet (AT3);
- the quench tower outlet (AT4);
- and the absorber (stripper) outlet (AT5).

At the quench tower inlet (AT3), there is a significant reduction in COS and CS_2 concentrations from the hydrolysis reaction in the CoMo catalyst bed. At the same time there is an increase in H_2S with nearly all the SO_2 having been converted to H_2S.

COS and CS_2 will be at their lowest concentrations in this location and H_2S

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

interference will be even more exaggerated compared to the final condenser measurement point (Fig. 4). In addition, the gas stream will have an elevated temperature. Any gas analyser installed at this location must have the ability to keep the sample in a gas phase, as any liquid formation would damage the analyser. Although some users have attempted to use sample coolers or chillers in this location, these tend to require more maintenance than the value any measurement would provide. From Ametek's experience, the only measurements that are done at the quench inlet are for hydrogen (H_2) and SO_2. Any indication of residual SO_2 will mean that the CoMo catalyst bed is not functioning properly and amine damage will occur. Hydrogen can be measured at any point after the CoMo catalyst bed, so unless the SO_2 measurement is needed, it is best to measure H_2 after the quench tower.

Measuring COS and CS_2 at the quench tower outlet (AT4) would require much less sample conditioning, as the sample is now cooled, and any liquids or particulates should be removed and no longer present. Unfortunately, the concentration of H_2S is still expected to be within a range of 0.5 to 5%, once again, resulting in the same spectral interference on the measurement of COS and CS_2 as found at the quench inlet.

Which brings us to the final measurement point for COS and CS_2; the measurement after the TGTU amine scrubber (AT5). This is the ideal location, as the sample will contain low ppm amounts of H_2S with no SO_2 or sulphur vapour. Here you will see the maximum resolution of the COS and CS_2 measurements in the SRU and TGTU.

At this location the measurement COS, CS_2 and H_2S will directly indicate what is going to the incinerator or thermal oxidiser and end up as emissions (Fig. 5). These values should directly correlate to the emission measurements with the caveat that there may be other streams also going to the incinerator such as the sulphur pit gas sweep or other process streams that can increase the final SO_2 measurements if the incinerator is shared with other operating units. As mentioned above, H_2 can also be measured here as well since the concentration will not change downstream of the CoMo catalyst bed.

Summary

Measuring COS and CS_2 in a modified Claus SRU/TGTU can provide useful information for determining the conversion activity of the first converter bed, the efficacy of the CoMo catalyst bed, and provide an indication of what the plants emissions will be; however, there are also limitations based on the measurement point location and the spectroscopic interferences observed from H_2S, SO_2, and sulphur vapour concentrations. Unless there is a specific need, the favoured location for the best resolution is at the absorber outlet (AT5). Any significant changes in the measurement of COS and CS_2 here typically only have a few potential causes, feedstock gas composition changes, catalyst bed temperature changes, or catalyst activity changes. ■

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Platinum-catalysed conversion of sulphur species

Platinum-promoted honeycomb catalyst bricks offer lower pressure drop, higher activity, reduced toxicity, and function as total oxidation catalysts that convert all oxidisable species under appropriate temperature and oxygen conditions. A case is presented for a sulphur-resistant total oxidation catalyst processing a gas stream bearing high amounts of H_2S – relevant to the fibre industry, Claus off-gas treatment, and other chemical sectors. Proper parameter settings enable conversion of H_2S to SO_3 for concentrated sulphuric acid production. Additional applications for the total oxidation catalyst include metallurgical off-gas treatment, VOC abatement, and CO abatement under harsh conditions.

Johannes Hofer, Alexander Sigg, Michael Felsberger and Paul Piantino (P&P Industries AG)

Platinum-promoted honeycomb (PPH) catalysts developed by P&P Industries AG (see Fig. 1) represent a significant technological progress compared to conventional bulk catalysts traditionally used in industrial oxidation processes of sulphurous species such as H_2S or SO_2. Their structured monolithic geometry enables low pressure drop – even at high gas flow rates. At the same time, the highly dispersed platinum active phase provides superior catalytic activity and thermal stability. Unlike almost all state-of-the-art oxidation catalysts applied in sulphuric acid manufacturing, which are typically based on vanadium pentoxide (V_2O_5), the VividOx PPH catalyst provided by P&P Industries shows lower toxicity and extended operational lifetime. The combination of these factors together with its high catalyst poison resistance, underlines its high suitability for the typically challenging industrial environment.

A distinguishing characteristic of the PPH catalysts is their total oxidation capability. Under appropriate operating conditions – specifically, sufficient temperature and controlled oxygen availability – these catalysts are capable of oxidising virtually all oxidisable components in a process gas stream making them a highly versatile tool in multipollutant environments.

The presented study focuses on the turnover behaviour specifically for the oxidation of hydrogen sulphide (H_2S), a species that poses health, safety and environmental hazards while being present in the tail gas of numerous industrial processes. High H_2S loadings are a typical challenge in fibre production facilities, Claus tail gas treatment units, and a range of chemical process industries. Due to its toxicity and corrosive nature, H_2S must be converted efficiently and be reliably removed from the respective gas stream before being released or further processed.

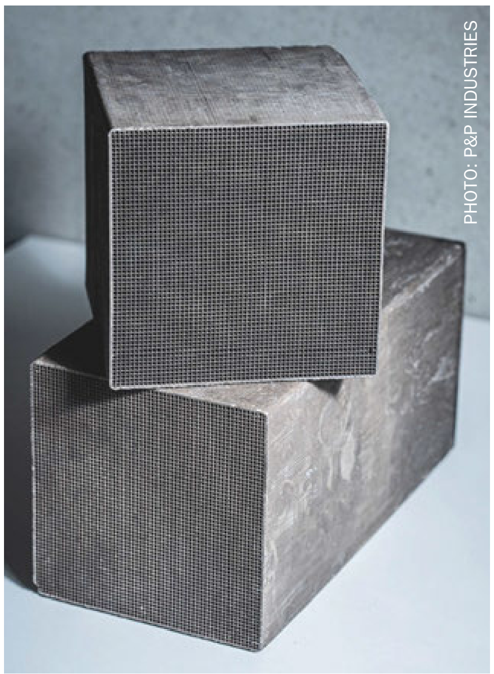


PHOTO: P&P INDUSTRIES

Fig. 1: PPH catalyst for total oxidation tasks in sulphur bearing gases developed by P&P Industries AG.

The catalytic oxidation using total oxidation catalysts like P&Ps VividOx PPH catalyst presents a robust solution to this challenge. The primary oxidation of H_2S to sulphur dioxide (SO_2) proceeds via a strongly exothermic reaction pathway, with high conversion achievable due to the reaction equilibrium which is strongly in favour of the products (see equation 1). Modulating oxygen concentration, temperature and residence time accordingly, SO_2 can subsequently be oxidised further to yield sulphur trioxide (SO_3) as indicated in equation 2. The integration of such a catalyst into an acid production loop offers opportunities to transform H_2S-rich off gas into valuable downstream products, resulting in both environmental and economic advantages.

$$H_2S + 1.5\ O_2 \rightarrow SO_2 + H_2O \qquad (1)$$

$$SO_2 + 0.5\ O_2 \rightarrow +\ SO_3 \qquad (2)$$

The experimental study performed on the P&P catalyst performance unit shows clearly the superior catalytic behaviour proposed earlier (see Fig. 2). The ignition temperature for H_2S oxidation using a PPH catalyst was found to be below 200°C. H_2S conversion yields up to 100% with increasing temperature forming SO_2 which is the dominant sulphurous species between 250°C and 375°C. With further increase of the reaction temperature the reaction proceeds to SO_3 with expected thermodynamic limitations as the reduced SO_2 conversion at higher temperatures indicates.

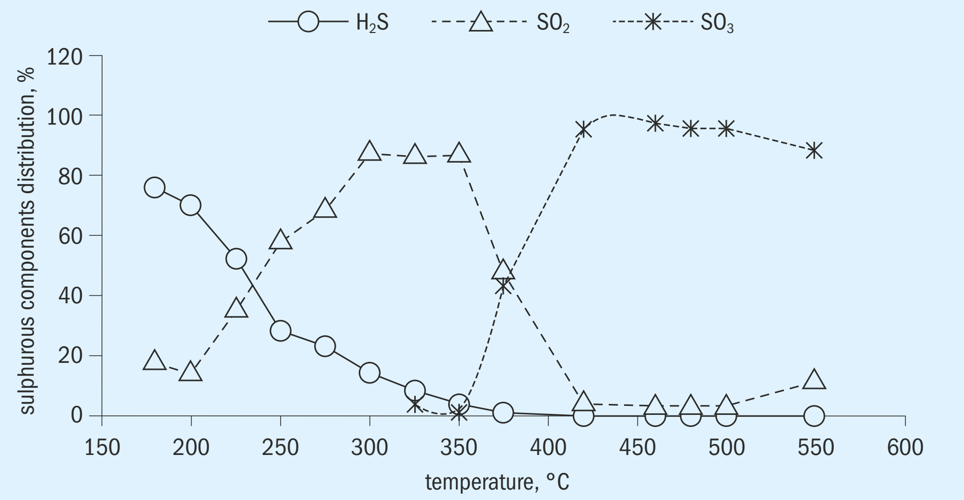
The sulphur tolerance of the examined PPH catalysts allows stable long-term operation even at elevated H_2S concentrations, avoiding the rapid deactivation observed for other oxidation catalysts. The honeycomb design ensures minimal pressure losses, making it feasible to retrofit the system into existing industrial gas lines without significant requirements for flow or construction adaptations (see Fig. 3). PPH catalysts have been in service for over a decade across more than 30 sulphuric acid and other industrial plants worldwide.

In addition to their superior catalytic performance in oxidising sulphurous species, PPH catalysts also excel in the total oxidation of carbon monoxide (CO) and volatile organic compounds (VOCs) in gas streams. For this challenging task, P&P Industries developed a highly robust total oxidation catalyst named AeroClear. The AeroClear PPH catalyst is characterised by an ignition temperature below 120°C and the capability of yielding 99.9% conversion (Fig. 4). For gas streams containing sulphurous compounds or heavy metals, specialised PPH catalysts from P&P Industries are available. These catalysts offer high resistance to heavy-metal poisoning, making them ideally suited for waste-gas treatment in the secondary metallurgical sector. Moreover, two years of continuous operation in a metallurgical plant's off-gas treatment unit, without significant catalyst deactivation (data not shown), underscores the capability of P&P's PPH catalysts in challenging environments.

The presented study confirms the PPH catalysts to be a highly effective and industrially robust solution for the oxidation of sulphurous compounds (VividOx), CO and VOCs (AeroClear) under demanding conditions. Compared to conventional bulk catalysts, it offers lower pressure drop, higher activity, and exceptional sulphur and poisoning resistance. Thanks to its modular design, thermal stability, and resistance to poisoning, the respective catalysts are highly advisable for demanding industrial environments such as Claus tail gas treatment, fibre production, metallurgical off-gas cleaning, and VOC or CO abatement. The portfolio is completed by P&P's most recent release, the PrimePurity PPH catalyst, which has been developed for highly selective oxidation of post SCR ammonia slip to nitrogen.

Overall, the PPH catalyst technology developed by P&P Industries is a versatile, scalable, and energy-efficient solution that couples emission control with economic value creation – validated by customer trust and strong performance across more than 30 operating plants worldwide. Finally, the ability to reclaim platinum at end of life is a further benefit of this innovative technology. ■

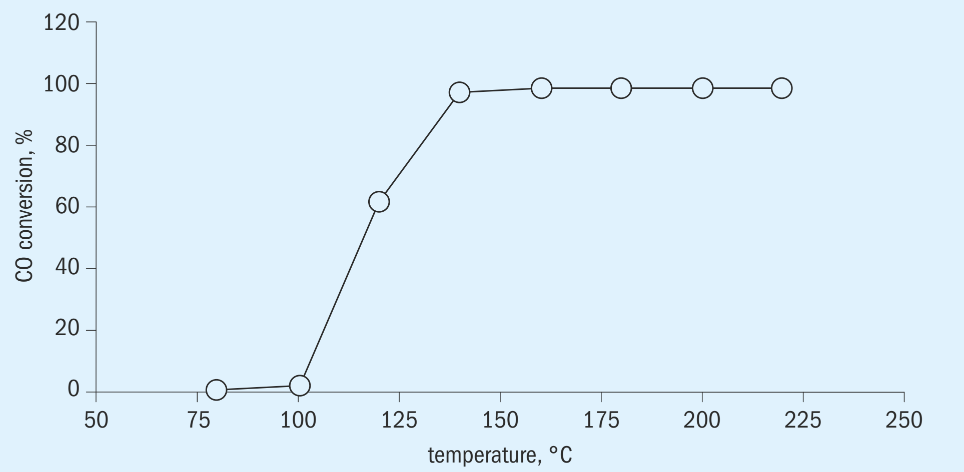
Fig. 2: **Conversion of H_2S to SO_2 and subsequently to SO_3 over P&P's VividOx PPH catalyst – indicative figures**



Source: P&P Industries

Fig. 3: PPH catalyst hurdle equipped with P&P's VividOx catalyst.

Fig. 4: **Conversion of CO over P&P's AeroClear PPH catalyst – indicative figures**



Source: P&P Industries

Neutralisation of heat stable salts – Part 1

Joel Cantrell of Bryan Research & Engineering and **Clay Jones** of INEOS GAS/SPEC re-evaluate the historical practice of intentionally adding strong base such as caustic (NaOH) to amine with the purpose of improving performance and reducing corrosion by "neutralising" heat stable amine salts (HSAS) which have accumulated in the amine.

Neutralisation with caustic in amine systems has long been a debated topic in the gas sweetening industry. Neutralisation is the practice of intentionally adding a strong base (NaOH, Na_2CO_3, KOH, etc) to amine for the purpose of improving performance and reducing corrosion by "neutralising" heat stable amine salts (HSAS). While this article is not likely to resolve all differing opinions on this topic, the authors hope that it will serve as a useful reference by summarising the current state of understanding.

The article will approach the topic in four sections which are supported by simulation case studies and plant data as applicable:

- Chemistry review to explain theoretical considerations and list relevant chemical reactions which will be referenced throughout the rest of the paper.
- Heat stable salt (HSS) effects on amine chemistry and corrosion.
- NaOH effects on amine chemistry and corrosion.
- Effects of adding too much NaOH.

The article has been split into two parts, Part 1 features the first two sections, with the remaining two sections in Part 2, which will be published in the next issue of *Sulphur*.

For brevity's sake, this article focuses on a representative subset of the chemicals which are currently in use in industry. The only acid gas addressed extensively is H_2S, the only amine considered is MDEA, and the only strong base discussed is NaOH. While there are other acid gases, amines, and strong bases that are important in industry, it is hoped that all of the relevant points can be made more effectively by focusing on the underlying chemical principles rather than juggling a larger list of similar reactants.

The main conclusions of this paper are:

- HSS are common contaminants in amine units. They increase corrosion rate, chemically bind or neutralise amine, and often they accumulate over time. Dealing with HSS is a typical challenge in operating an amine unit.
- There are several established methods for handling HSS. Neutralisation is one option. It has the goal of neutralising HSAS (converting HSAS into Inorganic HSS) and extending the time before the more effective (and expensive) methods are used. Neutralising does not get rid of HSS anions, but tries to mitigate some of their negative effects.
- Published studies and reports from operating plants are not unanimous about whether or not neutralising reduces corrosion rate. However, there are several effects which are generally accepted to happen:
  - ○ Neutralising can convert bound amine to free amine, which restores incremental acid gas pickup capacity.
  - ○ Neutralising can increase lean loading. In some cases, this can hurt the solvent's treating performance.
  - ○ Injecting too much or too fast creates a risk of precipitation, pluggage, and alkaline stress corrosion cracking (SCC).
  - ○ Neutralising is not a permanent solution for on-going HSS contamination. It is intended to be a coping mechanism for extending the time between reclaim/purge events. Neutralisation is commonly used as one part of a comprehensive HSS management strategy.
- A significant number of operating sites neutralise their amine, and contend that they get benefits which out-weigh the risks.

Chemistry review

The conclusions of this paper rest on several concepts from chemistry, which are reviewed here for convenience.

Electrolyte chemistry concepts

There are several important electrolyte, or ionic, chemical reactions which happen in the aqueous amine solutions used in gas treating. These reactions are responsible for the primary function of the amine: absorb acid gas in the contactor then release the acid gas in the regenerator.

For example, equation 1 and equation 2 below demonstrate how H_2S is chemically trapped in an MDEA solution. In equation 1, aqueous H_2S lives up to the name "acid gas" by giving an H^+ ion to the solution. This renders the remaining HS^- ion as completely non-volatile and chemically traps the H_2S in solution. In a complementary reaction, MDEA acts as a base by accepting H^+ ions to create a protonated MDEA molecule, $MDEAH^+$.

$$H_2S_{(aq)} \leftrightarrow HS^- + H^+ \qquad (1)$$

$$MDEA + H^+ \leftrightarrow MDEAH^+ \qquad (2)$$

These reactions underscore two important concepts:

Firstly, equation 1 is the underlying mechanism for chemically capturing acid gas in amine. Ionic charged species such as HS^- are not volatile; they are chemically trapped in solution. Conversely, non-charged molecules are volatile to the extent allowed by vapour pressure or Henry's constant. This is a key concept for how acid gases get captured in amine, but in the context of this article, it also drives the influence of neutralisation on the volatility of HSS species in the regenerator's reboiler. This effect is also responsible for one of the undesired consequences of over-neutralisation, which is elevated lean loadings.

Secondly, reactions affect each other through the common ion effect. In water, equation 1 does not proceed very far to the right. However, the presence of MDEA greatly increases the amount of H_2S which can be held in the aqueous phase by a factor on the order of 1000x. This is accomplished through Le Chatelier's principle: If an equilibrium is disturbed, the system will shift to counteract that change and establish a new equilibrium. In the case of equation 1, as H^+ ions are produced by H_2S, those ions are captured by MDEA through equation 2. This drives equation 1 further to the right, making it harder and harder for the volatile $H_2S_{(aq)}$ molecules to exist in solution, since they're preferentially converted to non-volatile HS^- ions after giving up their H^+ ions to MDEA. Le Chatelier's principle will be important in several aspects of the discussions below.

Ionic vs covalent bonds

The following discussion draws heavily on Chapter 3 of Reference 1.

The term chemical bond encompasses two distinct modes through which atoms are held together: covalent bonding and ionic bonding.

The term covalent bond refers to the bonding mechanism in which the outer orbitals of the bonded atoms overlap, resulting in increased electron density between the atoms. There are several sub-types of covalent bonds, including the metal-ligand bonds discussed later in this paper. The term ligand refers to molecules which bond to a central metal atom. All atoms are not created equally when it comes to covalent bonding: some atoms are much more available for covalent bonding due to their electronic configuration whereas others are less able to do so. For example, the Fe^{2+} cation can readily form coordinate covalent bonds with various ligands when it is in an aqueous solution, because it is a transition metal and therefore has d-orbitals in its outer shell. In contrast, the Na^+ cation's outer electronic configuration is much less available for covalent bonds.

The term ionic bond refers to bonds where atoms of opposite charge are attracted to each other by electrostatic forces. The concept of an ionic bond is an idealisation which does not perfectly reflect real world solutions. In actuality, all ionic bonds also include some amount of covalent bonding, though the relative importance of those covalent bonds is much smaller.

Cation behaviour in solution

Two cations are of special interest for the purposes of this article: iron and sodium. These species behave quite differently in amine solutions. The Fe^{2+} cation enters the solution through corrosion, and Na^+ might be intentionally added during neutralisation, or it may unintentionally enter the amine through contaminated makeup water, leaking isolation valves, amine reclamation etc.

When Fe^{2+} enters the solution, it enters as a complex surrounded by water molecules. Because of its electronic configuration, which includes the d-orbitals of a transition metal, each central Fe^{2+} cation is surrounded by six water molecules. The water molecules serve as ligands, as shown below in equation 6 and equation 8. The six ligands organise into an octahedral complex around the cation. Each ligand shares a coordinate covalent bond with the central iron atom. Both electrons of the bond are donated by the ligand. The metal-ligand bonds are true chemical bonds with measurable bond enthalpy. The solubility of a metal is strongly influenced by the stability of the metal-ligand bonds. As will be discussed, ligands can be substituted: the water molecules can be replaced by other molecules such as HSS anions.

In contrast, the electronic configuration of Na^+ cations is relatively inert with respect to covalent bonds. In fact, the outer shell of Na^+ cation has the same configuration as the noble gas neon. Given its electronic configuration, Na^+ is not very likely to have orbital overlap or participate in covalent bonds. However, it has a concentrated electrostatic charge in a relatively small volume, so it exerts considerable influence on polar and charged molecules in its vicinity. Approximately 16 to 17 water molecules are attracted to each Na^+ cation to such an extent that they can be considered as bound to the Na^+ with an ionic / electrostatic force.

That being said, coordinate covalent bonds with Na^+ cations still form at a detectable concentration, though they are less favoured than bonds with transition metals such as Fe^{2+}. For example, reference 3 documents the critical stability constant for complexes of K^+ cations with oxalate and complexes of Na^+ cations with acetate. By analogy, complexes of Na^+ and oxalate should be expected to exist as well.

Corrosion reactions

Iron corrosion proceeds through the anodic, or oxidation, reaction listed in equation 3. Typically, in amine systems, the corresponding cathodic, or reduction, reaction involves protonic acids, which provide H^+ ions that react as shown in equation 4. Adding these two reactions together, we get equation 5 which shows a simple corrosion reaction for iron. The H^+ ions in equation 5 can come from the surrounding solution or from protonic acids like H_2S or HS^-.

$$Fe(s) \rightarrow Fe^{2+} + 2e^- \tag{3}$$

$$2H^+ + 2e^- \rightarrow H_{2(g)} \tag{4}$$

$$Fe_{(s)} + 2H^+ \rightarrow Fe^{2+} + H_{2(g)} \tag{5}$$

Iron cations from equation 5 can go into solution surrounded water ligands as shown in equation 6. In an amine system with H_2S present, it is also likely that the iron could be converted into a solid corrosion product as in equation 7, with HS^- serving as the source of H^+ for corrosion. (Recall that chemically captured H_2S primarily exists as HS^- in amine solutions.) Iron sulphide created in equation 7 also has some solubility, which can be expressed as equation 8[2].

Equation 6 shows the general principle that everything else being equal, more acidic solutions will be directionally more corrosive to iron. Equation 7 shows how amine solutions with higher acid gas loading become more corrosive, and also how captured H_2S leads to the formation of solid iron sulphide. Iron sulphide can be deposited as a layer coating the inner surface of pipes and equipment; it can also (through equation 8) form as a particulate floating in the amine. The adhered layer of solid iron sulphide is known to significantly slow down the overall corrosion rate by slowing down mass transfer between the bulk amine solution and fresh, uncorroded iron underneath.

Equation 8 is a reversible reaction. This fact is one reason for the common observation that even when the lean amine is clear when it enters the absorber, the rich amine leaving the absorber will often have a significant amount of iron sulphide particles leading to dark or green appearance. In the absorber, as the amine picks up H_2S, the equilibrium of equation 8 will naturally shift to the left due to increasing concentration of $HS^{-}_{(aq)}$ ions, causing more of the dissolved iron cations to precipitate as FeS solids.

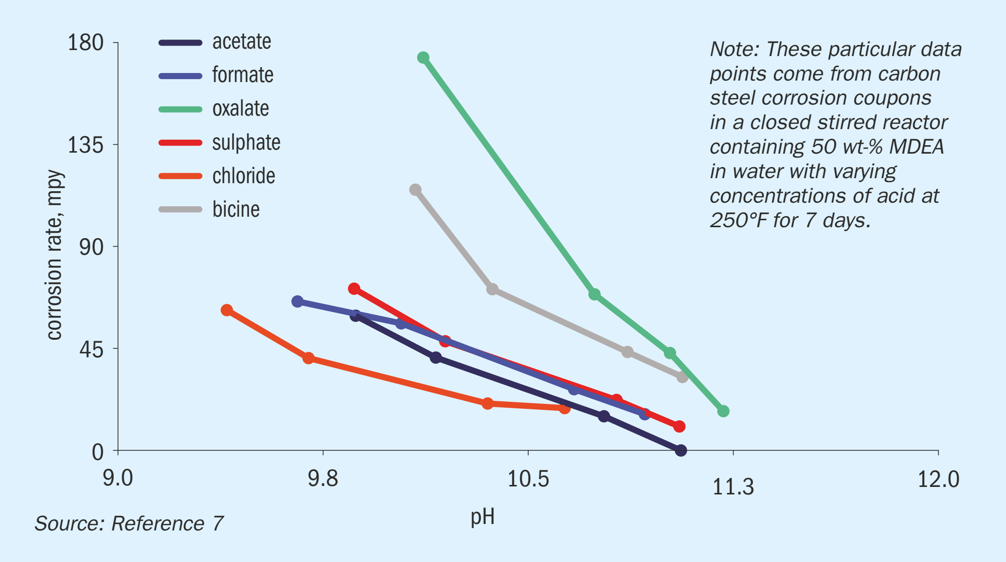
Ligand substitution and chelation

As discussed above, in amine solutions, dissolved iron cations exist as the central metal atom surrounded by ligands, which are covalently bonded to it. For many metal atoms, these ligands will be water as shown in equation 6 and equation 8. However, other species can displace water to serve as a ligand. Equation 9 shows an example of a ligand substitution reaction where formate ($HCOO^-$) enters the complex to become a ligand. While equation 9 shows one water molecule being displaced, it is also possible for more than one displacement to happen for the same central iron cation.

Researchers have catalogued equilibrium constants for reactions such as equation 9, which can be found in published tables of critical stability constants, for example Reference 3. Substitution reactions such as these are one way that HSS anions increase the net corrosion rate: they stabilise iron cations in solution, i.e., they shift equation 6 and equation 8 further to the right.

An additional effect, called chelation, happens when one ligand molecule is able to form more than one bond with a central metal cation. The oxalate anion, which is sometimes present as a contaminant in amine solutions, is an example of a chelating anion. Each oxalate anion ($C_2O_4^{2-}$) has two carboxylic acid groups, each of which carries a -1 charge. Oxalate can displace two water molecule ligands as shown in equation 10. Ligands in chelate structures make more stable complexes. This stability is at least partially due to statistical/entropic considerations: If a random encounter leads to a bond with one of oxalate's sites, then the oxalate's second bonding site will stay in close proximity and have a much better chance of creating a second bond. The reverse reaction, i.e., displacement of one oxalate ion by two water molecules, is similarly less likely because it requires the concurrent displacement of two bonds. The chelation effect explains why, relative to other HSS anions, oxalate has a significantly higher critical stability constant with iron[3] and has been observed to lead to significantly faster corrosion rate in amine solutions, as shown in Fig. 1.

Fig. 1: **Corrosion rate increases as an amine solution is progressively acidified by HSS**



Note: These particular data points come from carbon steel corrosion coupons in a closed stirred reactor containing 50 wt-% MDEA in water with varying concentrations of acid at 250°F for 7 days.

Source: Reference 7

Soluble metal vs corrosion rate

Even though soluble metal concentrations are frequently reported for amine solvents, there is some nuance to understanding what this measurement tells us. There is not a rigorous direct relationship between the concentration of metal held in solution and the corrosion rate experienced in an amine unit. The corrosion rate in an amine unit depends on many parameters which are well documented in literature, for example in Reference 4. In general, the corrosion rate will vary quite significantly from one place to another within the same amine unit. Local factors typically govern the severity and location of the worst corrosion in the unit. For example, the following factors are common culprits in corrosion failures: high rich loading, high velocity/turbulence from flashing 2-phase flow, high wall shear due to mechanical design that creates eddies and/or impinging flow[5]. These local factors must be identified through a unit review and cannot be identified through laboratory analysis of the amine.

The effect of the various local corrosion factors are additive in an operating unit. A unit which has a step change increase in rich loading will have an incremental increase in corrosion rate in the rich amine circuit. Similarly, a unit which has a step change increase in soluble iron concentration should be expected to have incrementally faster corrosion rate. The significance of any specific increase in corrosion rate will include considerations of the remaining corrosion allowance in the specific pieces of equipment, the quality of the inspection program in the plant, etc.

The cycle of taking Fe^{2+} cations from the internal surface of equipment/pipe, then precipitating that iron as FeS fouling is described as an "iron pump" in Reference 8. Under this paradigm, we can think of a solvent that holds more iron as a higher capacity iron pump. Therefore, we should expect a directional relationship between iron solubility and corrosion rate: higher soluble iron concentration is directionally worse than lower soluble iron concentration. Nonetheless, it is not easy to determine when the difference is significant enough to justify taking action. Good unit monitoring practice is to watch trends of soluble metals over time and

$$Fe_{(s)} + 2H^{+} + 6H_2O \rightarrow [Fe(H_2O)_6]^{2+} + H_{2(g)} \qquad (6)$$

$$2HS^{-}_{(aq)} + Fe_{(s)} + H_2O \rightarrow FeS_{(s)} + H_{2(g)} + HS^{-}_{(aq)} + OH^{-}_{(aq)} \qquad (7)$$

$$FeS_{(s)} + 7H_2O \leftrightarrow [Fe(H_2O)_6]^{2+} + HS^{-}_{(aq)} + OH^{-}_{(aq)} \qquad (8)$$

$$[Fe(H_2O)_6]^{2+} + HCOO^{-} \leftrightarrow [Fe(H_2O)_5(HCOO)]^{+} + H_2O \qquad (9)$$

$$[Fe(H_2O)_6]^{2+} + C_2O_4^{2-} \leftrightarrow [Fe(H_2O)_4(C_2O_4)] + 2H_2O \qquad (10)$$

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

to interpret step changes or shifts as potentially serious signs of increased risk.

Important chemical reactions

The list of chemical reactions below shows the primary reactions in a typical amine solution. Acetic acid, H_3C_2OOH, is included as a typical HSS. These reactions are listed here as an introduction and for easy reference in the rest of the article.

One important feature of this reaction set is that the acid H_2S and stronger acids such as acetic acid H_3C_2OOH, do not react directly with the amine MDEA. Instead, these acids donate H^+ cations to the solution, and the basic amine MDEA accepts H^+ cations from the solution. It is important to realise that the H^+ cations in solution are all equivalent to each other regardless of which molecule they came from. This relationship between different reactions is called the common ion effect; it is the mechanism through which the concentration of one ionic species affects the concentration of another across a network of reactions.

For example, consider the impact of increasing the amount of acetic acid H_3C_2OOH in a solution with H_2S and MDEA. Acetic acid is a stronger acid than H_2S. Increasing the concentration of acetic acid in solution will increase the concentration of H^+ ions, which in turn will both increase the extent of MDEA's protonation (equation 14 moves further to the right) and it will also decrease the extent of H_2S dissociation (equation 12 moves further to the left). Both of these effects of HSS (i.e., more protonation of amine, less dissociation of acid gas) will be discussed further soon.

Another key aspect of this set of reactions is that NaOH can be assumed to completely dissociate into Na^+ and $OH^–$ in the aqueous solution. These dissociated ions are not tightly bound to each other, so they will move independently through the solution. The reader is encouraged to look through the list of reactions and identify the ones which involve Na^+ and $OH^–$. In the case of $OH^–$, its only reaction is the reversible reaction with H^+ to make water. ($OH^–$ also appears in equation 7 and equation 8, but these are less significant side reactions due to the low concentration of soluble iron, which is typically 10s of ppmw Fe or less.)

Reactions between Na^+ and HSS anions, such as equation 16 are not extensively documented, but they do seem to happen. These complexes are important for considering corrosion phenomena related to neutralisation. Any HSS anions which are complexed with Na^+ ions will be less available for complexing with iron in reactions such as Equation 9 and equation 10. Therefore equation 16 is a mechanism for neutralisation to slow down corrosion.

Evidence for reactions such as equation 16 can be found in the literature. Reference 3 gives the critical stability constant for a complex of potassium cation with oxalate anion; presumably complexes of sodium and oxalate also exist, though they are not listed. Reference 9, which focuses on bicine corrosion, documents that critical stability constants for complexes between alkali metals and amino acids are available from the public data resource NIST SRD 46 – which the authors of the present paper were not able to confirm due to time and IT constraints (the freely available NIST SRD 46 database is accessed through an executable compiled to run on Windows XP or earlier). The authors of Reference 9 note that the NIST database does not contain a critical stability constant for complexes of sodium and bicine, but it does contain constants for complexes of sodium with related or analogous amino acids. They reasonably conclude that, by analogy, some amount of coordinate covalent bonding would be expected between sodium and bicine as well.

$$H_2O \leftrightarrow H^+ + OH^- \qquad (11)$$

$$H_2S_{(aq)} \leftrightarrow H^+ + HS^- \qquad (12)$$

$$H_3C_2OOH \leftrightarrow H^+ + H_3C2OO^- \qquad (13)$$

$$MDEA + H^+ \leftrightarrow MDEAH^+ \qquad (14)$$

$$NaOH \leftrightarrow Na^+ + OH^- \qquad (15)$$

$$Na^+ + H_3C_2OO^- \leftrightarrow Na(H_3C_2OO) \qquad (16)$$

HSS effects on amine chemistry and corrosion

More acidity, more iron complex stability

It is well-documented in industry that amine solutions become more corrosive as HSS anions accumulate. This general principle can be seen in Fig. 1 which shows how corrosion rate increases as an amine solution is progressively acidified by HSS. This lab study did not reflect all aspects of typical industrial conditions - especially the presence of H_2S. Since there was no H_2S present to create a protective iron sulphide film in the experiments, an important factor that influences corrosion rate in real world amine units was missing. Nonetheless, there is a clear relationship for each acid showing that corrosion rate increases as pH falls. In the limiting case of a completely absent or destroyed FeS passivation layer, this corrosion behaviour could be expected. This study also shows that oxalate and bicine are significantly more corrosive than other anions at the same pH, which is attributed to the ability of oxalate and bicine to chelate iron.

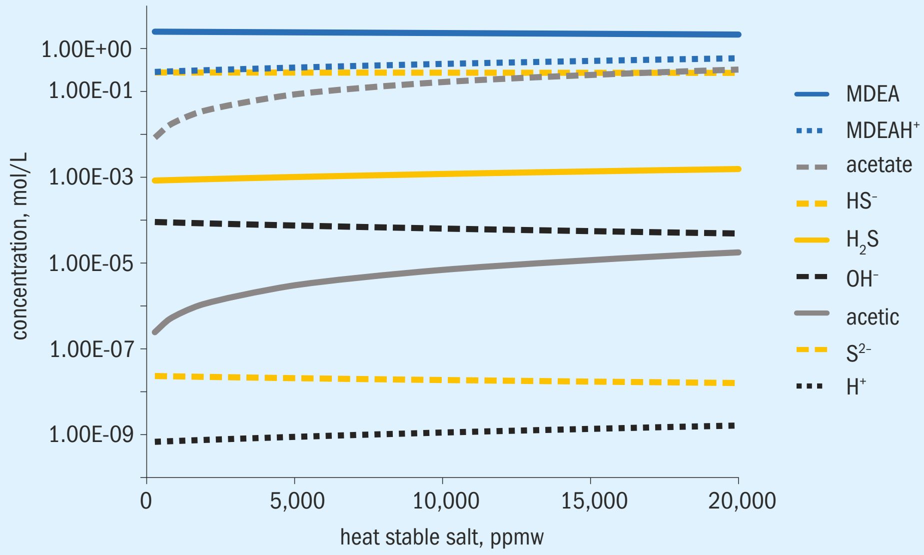
Other studies[2,6] present data showing an analogous relationship between increasing HSS concentration and increasing corrosion rate in the presence of H_2S and CO_2. Since the accumulation of HSS will reduce the solution's pH (more H^+ available, less $OH^–$ available), corrosion rate from equation 6 and equation 8 should naturally increase. Additionally, HSS will increase corrosion rate by stabilising iron in solution through reactions similar to equation 9 and equation 10. This effect will act to stabilise any iron cations in solution, regardless of how they got there, but it is thought to be especially damaging to process equipment in amine service because – through the common ion effect and equation 8 – increased HSS concentrations damage the protective iron sulphide layer which has a strong influence on overall corrosion rate.

Fig. 2 shows the effect of HSS on the speciation of a rich MDEA solution with increasing acetate content, based on ProMax simulation. The acetate (and acetic acid) increase, causing a rise in H^+ and a decrease in OH^-. Increasing H^+ increases $MDEAH^+$ at the expense of MDEA. The $HS^–$ remains roughly constant, while H_2S rises and $S^{2–}$ falls. These results demonstrate how increasing amounts of HSS lead to more bound amine (more $MDEAH^+$) and less solubility of H_2S (molecular uncharged – and therefore volatile –H_2S is a larger fraction of total H_2S).

Volatile acid in reboiler

There is another mechanism for HSS-driven corrosion, which specifically affects the bottom of the regenerator, the reboiler, and the reboiler vapor return line. This mechanism involves increased volatility of some acids as the overall concentration of HSS increases. Equation 12 and equation 13 show how acids will find an equilibrium between the volatile

Fig. 2: **Speciation of 0.1 mol/mol loaded MDEA solution with increasing heat stable salts (acetate)**



Source: ProMax simulation, courtesy Bryan Research & Engineering.

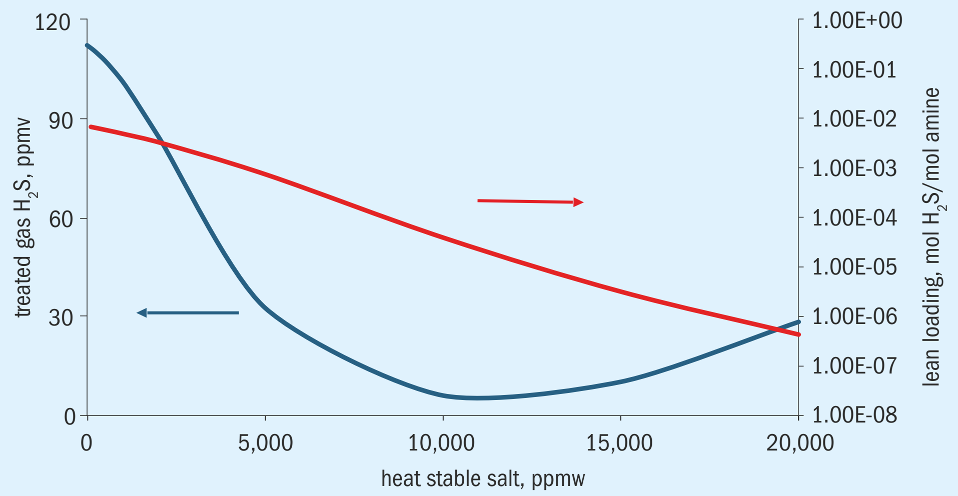
molecular form and the non-volatile ionic form. The fraction of molecules that exists in volatile vs non-volatile forms is dictated by the temperature-dependent pKa value for each acid. Of course, the reason that we call these acidic contaminants Heat Stable Salts is that under normal operating conditions they are almost completely trapped in the non-volatile ionic form and cannot be steam stripped from the amine to a significant extent. However, some of the weaker acids (such as acetate with pKa = 4.76 and formate with pKa = 3.75) can sometimes achieve small but significant volatility in the regenerator's reboiler. Volatile acids pose a particular corrosion risk in the reboiler because the acid vapor can be absorbed into droplets of water which condense on the inner surface of the reboiler shell, reboiler vapor return line, etc. Since these water droplets contain much less amine than the bulk circulating solvent, the pH of the droplets is much lower than the bulk solvent, which can lead to increased corrosion rate. This effect is explored further later. This effect will be explored further in Part 2 of this article.

Beneficial side effect: Lower lean loading

Increasing concentration of HSS contaminants results in increased acidity (less basicity) of the amine solvent. As discussed above, increased acidity naturally shifts the ionic equilibrium of captured acid gas towards its volatile molecular form, with the net effect of making it easier to strip acid gas out of the solvent and achieve a lower lean loading. This effect is a natural consequence of equation 12. In some units (especially TGUs), this effect can improve unit performance, but in other units the effect will not provide a significant benefit.

Fig. 3 shows the simulated impact of increased HSS on the overall behaviour of a typical TGU. For a constant reboiler duty, as HSS increase, the lean loading goes down. This lower lean loading improves treating performance to a point. After sufficient MDEA is tied up in HSAS, the treating performance is degraded and the treated H_2S content increases.

Fig. 3: **Effect of HSS on TGTU performance, constant reboiler duty**



Source: ProMax simulation, courtesy Bryan Research & Engineering

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This article will be continued in the January-February 2026 issue of *Sulphur magazine*.

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Sulphur pit turnaround and rehabilitation

A full sulphur pit turnaround and rehabilitation is typically a once in a lifetime experience for refinery personnel. Specialists in sulphur pit turnarounds, **Gavin Palmer** of Brindley Engineering, **Tom Kline** and **Bob Hall** of Structural Technologies have compiled a database based on multiple sulphur pit turnarounds to identify typical deficiencies in mechanical systems, along with improvements to enhance operability, restore functionality and meet all codes/standards and best practices.

How many refinery facilities can say they have the luxury of prior experience when entering a sulphur pit for turnaround? Often, these concrete vaults in the ground are overlooked as truly being a piece of refinery process equipment, often being run until the last feasible point of failure and limped into turnaround. Hence, it can be upwards of 15 to 20 years between full pit turnaround and rehabilitation, with personnel having prior experience of pit entry having been promoted, reassigned to other roles/units, or even having left the company. The current team may not even know who was involved during prior work.

Brindley Engineering, in partnership with Structural Technologies, has been involved in upwards of 30 sulphur pit turnarounds in the past seven to eight years alone. During this time a database of common deficiencies has been compiled to assist in execution of future pit turnarounds, whether it be due to poor initial design or installation, changes in codes/standards/best practices, operational changes etc.

Sulphur pits strive to maintain an elevated temperature range for their molten sulphur contents via steam coils that provide heat and, hence, fluidity to the molten sulphur. This must be accomplished without significant temperature fluctuations which can hamper process flow within the sulphur train. Perimeter backfill soils surrounding the buried pit provide consistent temperature profiles if groundwater, condensate or steam coil malfunctions are controlled and maintained in accordance with OEM guidelines.

Typically, the "last straw" before bringing a pit down for turnaround and rehabilitation tends to be the interior condition of the pit; be it concrete damage, ground water intrusion, steam coil failure or roof panel condition. In this instance, all mechanical systems (e.g. jacketed sulphur rundown lines, sulphur seals, steam and condensate piping, instrumentation, eductor inlet lines, air vents, pumps and associated sulphur transfer piping etc.) are typically removed back to the first flanged connection outside of the pit to facilitate roof removal and access. Many sulphur pits also have manway access hatches/explosion hatches which are included in the pit roof system. Hence, this is a time when improvements to these systems can be evaluated and often implemented with minimal incremental cost to the project.

Whilst the majority of sulphur pits are unique, in this article, typical deficiencies in mechanical systems are identified, along with improvements to enhance operability, restore functionality and meet all codes/standards and best practices. Knowing the potential for these deficiencies in time to engineer a solution can aid in the timely execution of the overall rehabilitation work within evertightening turnaround windows, returning the pit to reliable service on time.

PHOTO: BE / STRUCTURAL TECHNOLOGIES

Fig. 1: Sulphur pit roof and wall failure due to lack of maintenance bringing down sulphur containment in a sulphur recovery unit at a Southwest USA petroleum refinery

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Concrete liner and effect on pit volume/capacity

The primary reason for pit rehabilitation is the need to repair deterioration in the concrete structure, often by way of a concrete liner (a 4-inch durability liner or a thicker, up to 20-inch, structural liner). Ground water intrusion, steam leaks, rainwater entry etc. can all introduce water into the pit, which, in combination with the molten sulphur, results in a complex corrosion mechanism that spalls the interior concrete surfaces over time, particularly the walls and roof panels. Not generally thought of as a revenue generating asset, the failure of civil/structural components associated with the support or containment of process operations can quickly limit processing capacity, perhaps even reducing overall unit throughput – costing precious revenue until repairs are made and the process is brought back online (see Fig. 1).

Given the nature of sulphur flow, rundown lines from the back end of the reaction furnace waste heat boiler and its downstream sulphur condensers must slope towards the pit and be installed with no pocketing of the piping runs. Hence, the sulphur pit is often located immediately adjacent to, and sometimes tightly within the bounds of, the overall sulphur unit footprint. Access is limited, and further hindered by all the mechanical systems serving the pit – piping, pumps, instruments, electrical feeds, pipe supports and racks etc.

These services must be pulled back to the edge of the pit to access the pit for structural repairs to the walls and new roof panels (either pre-cast or cast-in-place) to be installed (see Fig. 2).

Fig. 2: Man-way portals and sleeved process lines in sulphur pit roof slab prior to concrete placement

PHOTO: BE / STRUCTURAL TECHNOLOGIES

Residence time for degassing

Sulphur rundown to the pit can contain up to 400 ppm of dissolved and entrained H_2S gas, which must be evolved into the vapour space and removed (see air sweep section below). However, the rate at which this H_2S can be "degassed" from the molten sulphur is mass transfer driven, and empirical data suggests that this can take in the region of 2 to 4 hours. With the thickness of the new concrete liner being taken into account, an analysis should be carried out to ensure that existing residence times are not adversely affected. In some instances, it can be determined that the pit did not offer adequate residence time as originally designed and improvements can be made. These can include relocating inlet lines to increase their distance from the pumps / sump area (easier when external sulphur seals combine to a single inlet line), modifying the civil design to include partition walls and create/extend "degassing" sections within the pit or installation of a simple baffle wall to lengthen internal flow paths. The goal should be to maintain or increase the residence time to acceptable values, particularly for cases where the molten sulphur is loaded to trucks/railcars for immediate delivery to off-site customers.

Storage capacity reduction

Similarly, a reduction in pit volume must be evaluated from a logistical standpoint to ensure that truck/rail loading and/or transfer operations are not adversely affected.

Location of services (e.g. roof nozzles) due to thickness of concrete liner

Often, services such as steam inlets, condensate outlets, pump penetrations etc. are located around the edge of the pit and simple replacement-in-kind is not feasible due to the thickness of the new concrete liner. The design must be adjusted to incorporate the new dimensions and eliminate any potential clashes between the liner and the mechanical components of the pit.

Sulphur rundown piping to pit and sulphur seals

Option to replace conventional liquid seal legs

Many installations still utilise in-ground or in-pit liquid seals to ensure that H_2S laden process gas at unit pressure does not breakthrough into the low pressure vapour space (typically a slight draft under atmospheric pressure) in the sulphur pit. These seals are essentially a liquid seal-leg, or p-trap type device constructed as a pipe within a pipe; given the length required (typically 16-18 ft or 0.78 psi/ft) to hold back unit pressure (see Figs 3 and 4). They are often housed in cylindrical vaults in the ground

Fig. 3: Conventional sulphur seals not installed in the pit

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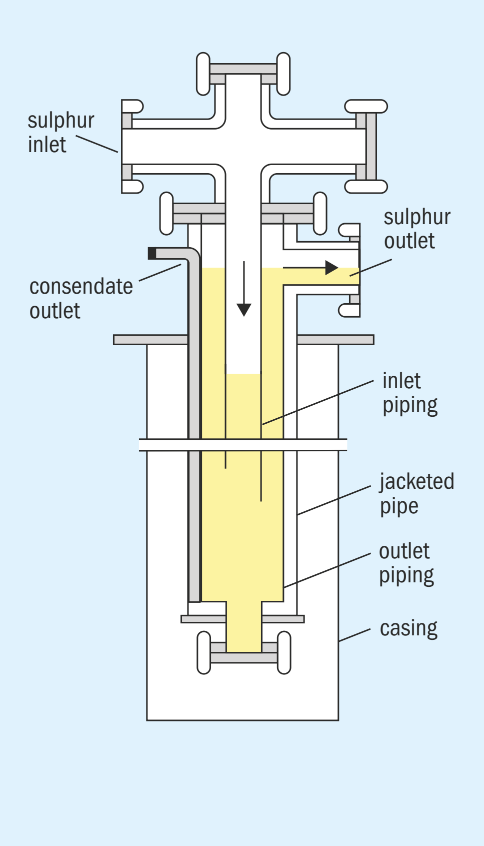
Fig. 4: **Diagram of a conventional sulphur seal leg**



outside the pit, or directly inside the pit itself. Whilst they are a known and well-proven apparatus, they do have their drawbacks. A consistent unit pressure will maintain a liquid level in the seal and over time localised corrosion of the inner pipe can occur at the liquid-vapour interface, eventually breaching the pipe wall and allowing process gas to "burp" directly into the pit at pressure. This creates a safety concern with regards to pit overpressure, as well as incidental release of H_2S-rich vapour to the environment through pit air inlets or look-box covers. Ground water intrusion can also corrode the outer pipe in some installations, resulting in process gases leaking directly to atmosphere at grade.

Liquid seal legs are cumbersome to remove from service for maintenance given their size and location, requiring a crane and vertical clearance considerations to remove and reinstall. Many facilities have upgraded these seals to a more compact mechanical float design (examples include CSI Ametek's Sx Seal® or the SOS SulTrap™). These traps are installed above grade with a more compact overall design, requiring less clearance for installation and removal, and with adequate isolation can be maintained or repaired in place.

Fig. 5: Sulphur pit sidewall leaking steam coil penetrations resulting in concrete degradation and reduced molten sulphur heating efficiency.

A pit revamp is the perfect opportunity to make this switch, especially given that existing in-pit seals may need to be relocated/redesigned anyway to accommodate any potential clashes with the concrete pit liner. These designs can also incorporate built-in sight glasses to verify liquid flow, eliminating the need for look boxes (see below). The design must consider the slight difference in level required between inlet and outlet piping for these devices, especially in situations where there is a limited elevation change between the sulphur rundown source (e.g. condenser outlet nozzle) and the entry into the pit.

Elimination of look boxes

Arguably the most hazardous portion of the sulphur pit, if not the entire unit, are older style look boxes; whether using a hinged lid (clipped or wired in the closed position) or a bolted cover, they are typically the source of most of the hazardous sulphur and H_2S leaks seen at the pit. In some instances, pressure excursions in the pit, or even flow surges local to the seal (due to corrosion and potential breaching of the pipe wall inside a seal leg for example) have caused box lids to be blown open and molten sulphur to shoot tens of feet through the air, while also releasing H_2S to the atmosphere. A pit outage is an ideal time to upgrade to a more secure look box (with built in sight glasses) or even to eliminate the look boxes completely and provide an inline "pour behind" type sight glass for flow verification. These devices avoid typical issues with fogging and discoloration of the sight glass by taking a small slipstream of the sulphur flow and pouring it a short distance behind the glass, providing a much finer level of flow verification by operations personnel.

Steam coil design

Likely secondary only to the physical condition of the concrete pit itself, the steam coil system on a sulphur pit is often in incredibly poor condition once the pit is available to be rehabilitated. Coils may be leaking steam and condensate into the pit, exacerbating damage mechanisms to the pit walls, while some may have been shut off and abandoned completely. Condensate trapping systems may be stalled due to poor condition, maintenance and/or initial design, with condensate (or worse, live steam) being directed to "safe" locations at grade to reduce backpressure on the coils. Leaks from steam coil assemblies can also have their own detrimental effects on the condition of the concrete walls, as shown in Fig. 5.

A dead giveaway to poor heating performance is putting steam into a coil and seeing some of that same steam venting from a cracked open strainer valve. Whilst the intention is typically good (one would think that some flow is better than no flow) steam must condense to provide the full benefit of its heating capability; any sensible heat is just a fraction of the available latent heat.

In this section, we'll break down the ideal steam coil system design, and explain why attention to the details of steam/condensate movement are critical in this particular application:

Steam pressure

The sulphur temperature is not directly controlled by modulating steam flow through the coils; instead, the pressure is restricted to 60-65 psig to limit the heating potential of the steam. At temperatures of around 312°F, there is a marked viscosity increase in pure degassed liquid sulphur, making it near impossible to handle in

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sulphur pit applications – certainly for centrifugal type pumps. Hence, limiting saturated steam temperatures to 307°F (60 psig) eliminates any possibility of reaching this condition. Note that the pump vendor will have specific steam supply pressure requirements for the jacket of the sulphur pump which is typically 35 psig saturated steam; this pump steam pressure requirement is separate from the sulphur pit steam supply pressure. There is, however, a drawback – even 60 psig offers a limited driving force to maintain condensate movement out of the coils, particularly given that the low point of the system is below grade.

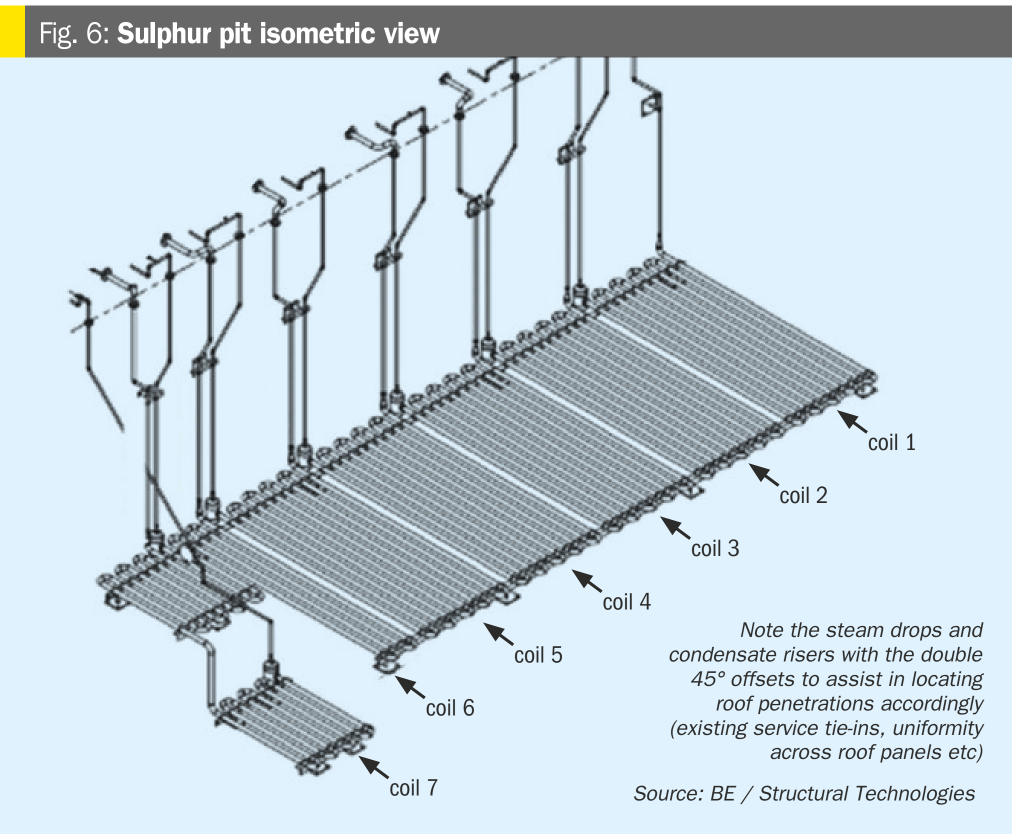
Optimal physical design of coils

Empirically, a 2-inch diameter coil offers the best balance of surface area for heat transfer, steam velocity and 2-phase flow of steam and accumulated condensate – as well as being physically strong enough to withstand damage across a potentially 20-year service life. A smaller diameter coil results in a high pressure drop and stalling of condensate in the system, while larger diameter coils have a low surface area relative to their volume. Coils should be limited in length, typically 150 to 200 ft maximum per coil to avoid cold spots in the pit (a long coil will condense all steam prior to the end of the coil, and condensate has a negligible heating value relative to steam) – this is a similar concept to other critical steam applications such as process steam tracing for heat loss mitigation. Coil runs are typically limited to 8 to 12-inch on-centre spacing, often driven by the pipe fittings used to make the 180° bend but also close enough to avoid cold spots and provide uniform heating across the entire floor. Coils should be designed to run as close to the walls as is feasible, typically 4 to 8-inch based on overall pit geometry. Note here that the installation of a 4-inch durability liner or up to 20-inch structural concrete liner often drives a complete rework of the coil layout to begin with. Similar shape, coverage, geometry coil panels are often designed to cover the bulk of the pit for simplicity in engineering and fabrication. However, a small number of specialty coils may be required, particularly around pump suctions and other pit internals close to the floor (see Fig. 6).

Steam drops

The steam drop (i.e. the vertical piping run from the top to the bottom of the pit) itself is not required to transfer heat to the molten sulphur, in fact it is preferred that it not. A 1-inch diameter line provides a slightly higher velocity and less residence time in the vertical drop to the coil to assist in this, whilst not adding much in appreciable pressure drop. It is also easier to route a 1-inch diameter line down the wall of the pit from entry point to coil, particularly if this is not a straight shot vertically down. In this case, 45° fittings should be used to offset the piping. The steam drop is often clipped to wall of the pit for support (Fig. 6).

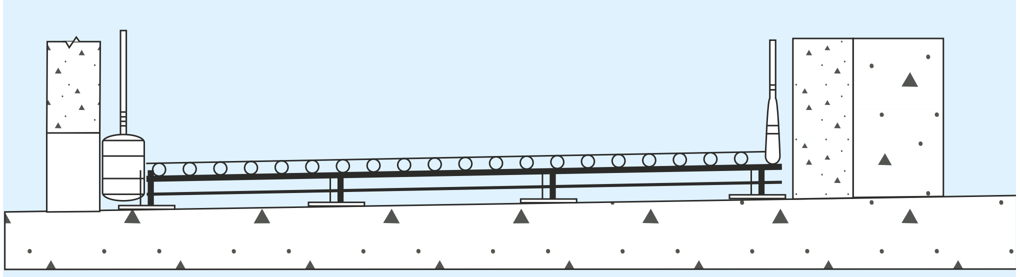
Fig. 6: **Sulphur pit isometric view**



Note the steam drops and condensate risers with the double 45° offsets to assist in locating roof penetrations accordingly (existing service tie-ins, uniformity across roof panels etc)

Source: BE / Structural Technologies

Fig. 7: **An example of a steam coil, flowing from right to left**



Source: BE / Structural Technologies

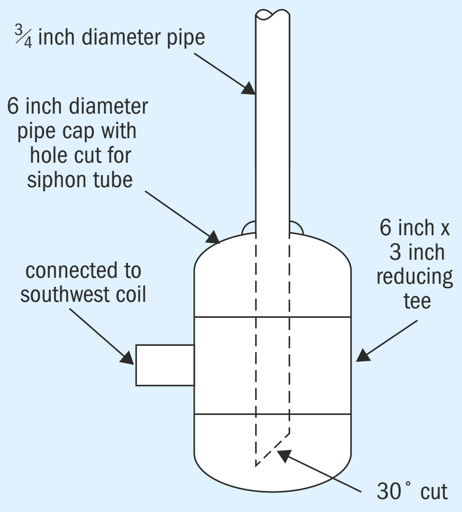
Note: a 1-inch diameter steam drop into the pit, 2-inch diameter coils and a lift fitting with a ¾-inch diamter condensate riser

Lift fittings and siphon tubes (condensate risers)

Perhaps the most critical and unfortunately the most overlooked part of the steam coil system, a well-engineered lift fitting is key to efficient and consistent removal of condensate. Steam traps typically serve as the physical boundary between steam and condensate in heating applications such as this, however, they are always placed at the low point of the system, where gravity allows condensate to accumulate. This is not feasible in a below-grade concrete pit filled with molten sulphur. Hence, a lift fitting with no moving parts is used as a de-facto steam trap – the steam trap at grade, outside of the pit, is a back-up device should steam breakthrough occur in the lift fitting below.

There are a few designs that achieve this requirement, the most effective being a small vertical cylindrical chamber at the end of the steam coil, 4 to 6-inch in diameter. Condensate draining from the coil piping enters the lift fitting in the centre of the side wall and exits up a ¾-inch diameter siphon tube that extends down into the lift fitting (see Figs 7 and 8). Condensate will typically accumulate in the lift fitting above the siphon tube's lower opening, ensuring

Fig. 8: **A cross-section diagram of a lift fitting**



Note: the ¾-inch diameter condensate riser extends down into the body of the fitting to within 1½-inch of the bottom.
Note: the 6-inch x 3-inch reducing tee, this particular lift fitting was connected to a 3-inch steam coil

Source: BE / Structural Technologies

that only condensate will be pushed up to the trap at grade. In fact, for steam breakthrough to occur, almost all the condensate would need to be evacuated, which is unlikely when correctly sized. A 4 to 6-inch diameter fitting provides adequate volume to prevent steam breakthrough due to any variation in rates of condensate formation. This also provides a relatively large area for residual steam pressure in the coil and upper portion of the lift fitting to act on the liquid surface, assisting in pushing condensate up the siphon tube to the steam trap.

Correct selection and optimised installation of steam traps

Even though the actual trap at the surface is a back-up to the lift fitting as discussed above, its selection is critical to steam coil performance and must not be overlooked. A well performing lift fitting will ensure that the steam trap only sees condensate most of the time and will remain open. It will only close if steam breaks through the lift fitting and travels up the siphon tube to the trap. Given that steam pressure is limited to ~60 psig by design (see above), a low pressure drop trap is critical here, as is a trap that maintains condensate movement regardless of temperature. An inverted bucket or floating ball trap (see Fig. 9) is ideal for this application and should be specified with a vent hole or other non-condensable vent capability for consistent operation. Note that thermostatic traps must not be used in this application, as they require a higher pressure drop for condensate to flow and require that condensate be subcooled by 15-20°F before opening. This action will fight the function of the lift fitting described above and back up subcooled condensate into the coils. One additional feature that can be employed in the piping installation around the trap is small siphon loop up, over and down prior to the trap (shown in Fig. 10). This is recommended in sub-surface condensate removal applications by many steam trap vendors to assist in reestablishing condensate flow after a steam breakthrough event. Finally, beware the steam trap vendor who comes into your facility and makes wholesale changes to trap technologies across the entire plant or unit. This is the number one reason for the incorrect type of trap being installed in sulphur pit steam coil applications.

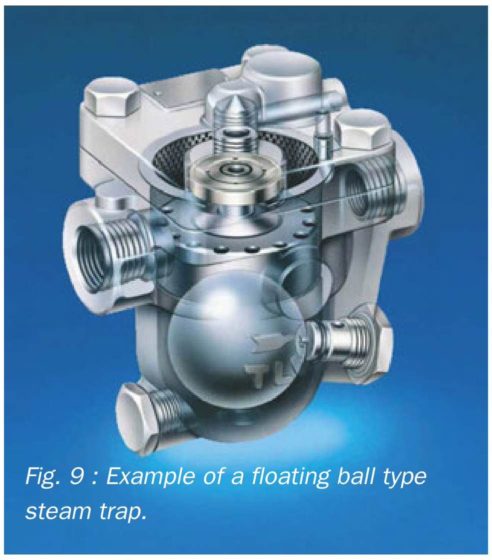


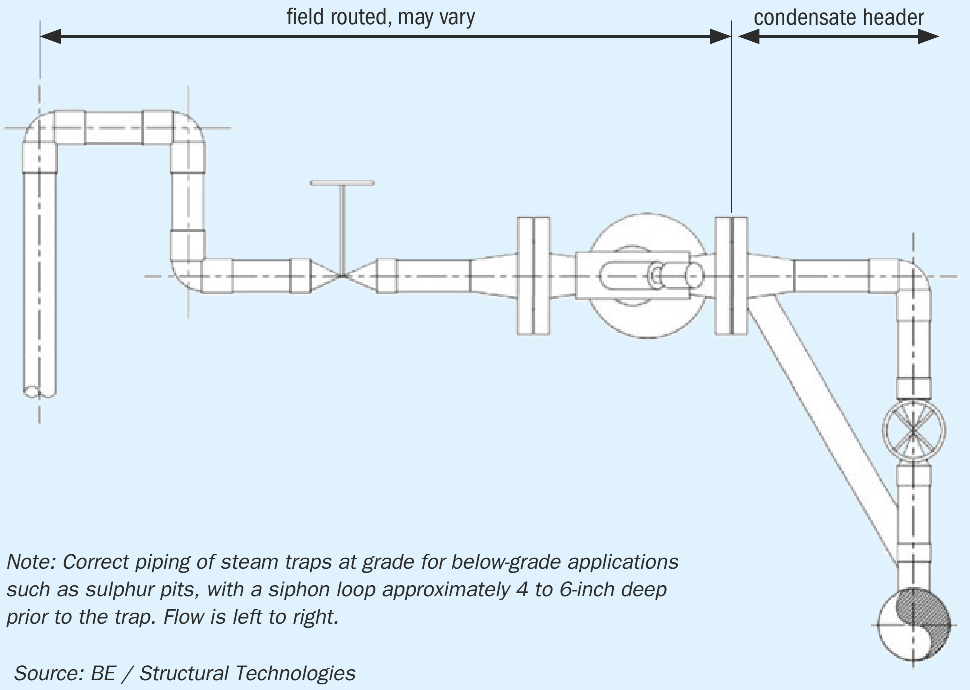
Fig. 9 : Example of a floating ball type steam trap.

Metallurgy selection

Older installations utilised carbon steel for many of the internal mechanical components in the pit, particularly below the expected minimum level of sulphur in the pit. Corrosion of carbon steel in an anaerobic wet H_2S environment allows the formation of Iron sulphide, a pyrophoric material that can become an ignition source for fires or explosions within the pit vapour space – particularly during shutdown/decommissioning for turnaround/maintenance.

Iron sulphide can form in anaerobic pockets under deposits of solidified sulphur at cold spots within the pit; should the deposit later be released from its position somehow, this iron sulphide is exposed to air and will ignite spontaneously. There is also the ever-present risk of wet sulphur corrosion to carbon steel components in the vapour space, due to moisture in the sweep air. It is typically recommended to install only stainless steel (SS) components inside the pit, including all pipe nozzles, coil piping, clips and supports etc. It is often considered acceptable to transition to carbon steel (CS) below the normal low sulphur level within the pit, however, the dissimilar weld at the CS/SS transition is a known

Fig. 10: **Typical condensate return piping**



Note: Correct piping of steam traps at grade for below-grade applications such as sulphur pits, with a siphon loop approximately 4 to 6-inch deep prior to the trap. Flow is left to right.

Source: BE / Structural Technologies

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point of accelerated corrosion and leaks here can occur. Given the length of time between internal pit inspections and maintenance, it is generally recommended to push for all-stainless construction. Piping can be transitioned to carbon steel at the first available flange outside of the pit.

Air sweep – eductor(s) and air inlet(s)

Verification of eductor capacity, or maximum unit throughput at code limitations (35% of H_2S LEL) – NFPA 655: Prevention of Sulphur Fires and Explosions, clearly states that, "5.2.3 Operations shall be discontinued whenever instruments show a combustible gas concentration of 35 percent or more of the lower explosive limit in the gas space of liquid containers" and that, "5.2.4 Operations shall not be resumed until the instruments indicate a concentration of 15 percent or less of the lower explosive limit". Now, "discontinuing operations" in a refinery sulphur pit is not easy to define or even achieve, however, both are shall statements – yet very few installations have the ability to measure or even calculate H_2S levels in the pit in real time. In many instances, design calculations for eductor sizing and expected H_2S content of the incoming streams are also not available for reference, or may be outdated compared to current operating throughputs. At a minimum, it is recommended to install (a) flow measurement device(s) in either the air inlet(s) or the piping to the eductor and use this flow to calculate a predicted H_2S content within the sulphur pit based on known H_2S content of the sulphur inlet streams combined. A more robust approach is direct H_2S measurement in either the pit vapour space or the inlet piping to the eductor. Packaged H_2S measurement systems designed specifically for this application are available.

Simulation of H_2S content in rundown streams (HYSYS Sulsim) – where existing heat and material balance (HMB) data does not contain detailed H_2S content for the streams entering the pit, the required concentrations can be determined by simulation, either of the entire unit or just the condensers and their outlet streams to the pit. This model can then provide input to eductor sizing calculations, either to verify existing capacity (or determine a maximum allowable throughput with existing eductors), or to size new. The H_2S/H_2S_x content of the individual sulphur condensers and total liquid sulphur feed to the pit and pit sulphur outlet can also be accurately measured by Fourier Transform Infrared (FTIR) spectroscopy; companies specialising in SRU analytical testing can provide this testing which can be very important for establishing the design basis for pit sweep systems and validating any simulation models.

Adequate heating of air inlets to mitigate blockage potential (steam jacketing) – air inlets to the pit should be sized to provide adequate sweep air volumes as described above; hydraulic calculations are key to ensure that the eductor can provide its rated flow. Air inlet stacks should be constructed with steam jacketed piping to ensure that air is heated prior to entry into the vapour space of the pit.

Without this heating mechanism, cold spots in the vapour space can lead to solidified sulphur deposits, particularly around the air inlets themselves, potentially leading to blocked inlets, reduced airflow and elevated H_2S levels. During a pit outage, existing stacks should be checked for steam jacket leaks, as any steam entering the air inlet through a leak in the jacket will reduce the available draft to the eductor and can also entrain and release liquid sulphur from the top of the stack.

Adequate heating of eductor inlet line to prevent entrained sulphur deposition (steam jacketing or other engineered system, e.g. ControTrace) – usually well understood and not often found as a need during the pit outage, the sweep air line from the pit to the inlet of the eductor must be well heated to ensure that blockage does not occur. Most applications utilise jacketed piping all the way to the steam jacketed eductor, however, if the piping run is longer than typical, an engineered system (such as ControTrace or similar) can be used and the heating intensity (by tracer density/coverage) lessened along the length of the piping.

Redundancy of eductor service, convective sweep via multiple air inlets – A pit outage is an excellent opportunity to prepare for future redundancy in eductor service. Loss of an eductor leaves a pit vulnerable to unsafe levels of H_2S in the vapour space per NFPA code; even the use of a dedicated convective stack that can be opened in the event of eductor loss, will almost certainly fail to maintain a safe atmosphere in the vapour space at design rates. Addition of a redundant (full spare) steam eductor or shared sparing of an eductor with another nearby pit can provide much better protection in the event of future eductor failure, or loss of design capacity. Even though eductors are reliable and contain no moving parts, they do represent a single point of failure.

Deflagration and overpressure calculations – the use of deflagration vents as a means of protecting the sulphur pit from overpressure in the event of a deflagration event is a grey area to say the least. Many pits offer no protection, relying on all the other engineering controls already mentioned here to prevent the buildup of an explosive atmosphere in the vapour space in the first place. Where deflagration venting is already in place, it can be hard to justify its removal in terms of an engineering Management of Change (MOC). Often, no (or at best, poor) calculations exist and it is generally recommended to create/update these calculations even when replacing panels in kind, or with larger panels if currently undersized. Following the code-required sizing calculations by the letter results in deflagration panels that would cover a significant surface area of the roof panels, affecting engineering design in terms of constructability, and is often not feasible.

Like any code, however, it is subject to interpretation; NFPA 68 is based upon an assumed fully enclosed concrete structure, whereas a typical sulphur pit uses roof panels that are held in place by their own weight. If we assume that the failure mechanism for a sulphur pit would be the lifting of the roof panels (failing perhaps as they fell back into place), the dynamic load factor (DLF) that reduces the allowable pressure due to a deflagration to account for inelasticity of the enclosure can be relaxed. This results in a smaller required panel area. The approach taken here is perhaps the subject of a future paper covering deflagration events in their own right. It is important to note that the location of deflagration panels is key to their sizing; they must typically be located along the central axis of the pit to minimise their size, as relief of a deflagration is based on the movement of a pressure wave due to a flame front. The worst-case distance from the point of ignition to the relief panel is a contributing factor to the size of the vent(s).

Instrumentation

Level instrumentation upgrades – many sulphur pit installations still use a bubbler type instrument for level measurement, a

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somewhat dated technology – though still reliable due to its simplicity. The device simply uses a pressure transmitter to determine how much pressure is required to bubble air or nitrogen through a certain depth of liquid. With replacement of the pit's roof slab/panels, there is a chance for more modern technology to be installed, typically a radar type device. Whilst this is an excellent technology, certain installation considerations are required. Namely, the nozzle assembly penetrating the roof should be steam jacketed and insulated above the roof, the instrument should be located such that no internal equipment will interfere with accurate readings and the installation of an optional air/nitrogen purge ring can be considered to further prevent the potential for material build-up on the device's internally exposed surfaces.

Temperature transmitters – a minimum of two temperature transmitters is recommended in sulphur pit service. One should be deep enough that it will always read the temperature of the molten sulphur (i.e. below the minimum operating level) in order to verify that the steam coil heating system is functioning correctly. The other should be in the vapour space (i.e. above the maximum liquid level) where a high temperature can indicate the presence of fire in the pit. This device can also be used to automate a snuffing steam activation valve (see below). For larger pits, or those with separate chambers for degassing and storage, multiple temperature instruments in both the liquid and vapour space may be desirable.

Snuffing steam

Number and size of snuffing steam connections – NFPA 655 section 5.5.1 (2) states that sulphur pits using steam as the firefighting medium must be able to supply 2.5 lb/min of steam per 100 ft3 of pit volume. This is typically the same 60-65 psig steam used elsewhere in the sulphur pit area. One or more snuffing steam lines must be sized accordingly using industry standard criteria for steam headers and drops to ensure this minimum flow can be met upon activation of the system.

Location of snuffing steam connections – NFPA 655 section 5.5.1 (3) also suggests a means of rapidly sealing the enclosure to exclude air. Hence, best practice in more recent designs has been to locate snuffing steam connections local to the inlet air vents on the sulphur pit. Some pits even pipe the steam directly to the base of the air inlet stack versus a dedicated nozzle on the pit roof panels. This immediately fills the air inlets with steam and prevents further ingress of air to further feed a fire event. Replacement of the roof slab/panels during a sulphur pit outage is a good time to update the location of the snuffing steam connections if they do not currently comply with this best practice.

Rupture discs at snuffing steam inlet flanges – To prevent sulphur from plugging the empty portion of the snuffing steam piping connections to the pit (i.e. downstream of the activation valve), rupture discs can be placed in the first flange set outside of the pit. A weep hole in the piping immediately above the rupture disc will allow any condensate (from steam leaking past the activation valve) to freely drain out of the piping. The nozzle assembly penetrating through the lid should be steam jacketed to prevent sulphur build-up on the inside surface of the rupture disc. If using multiple snuffing steam entry points from the same supply header, the rupture disc pressures should be sufficiently low and hydraulic calculations performed to ensure that all discs will burst when the system is activated.

Jacketed piping and roof nozzle assemblies to prevent plugging – while it may seem strange to use steam jacketed piping for steam service, this is considered an excellent way to prevent steam and/or sulphur condensation and maintain a clear snuffing steam line downstream of the activation valve. Often overlooked, the nozzle assembly that penetrates the roof panel and provides the first flange for connecting piping outside of the pit should also be jacketed.

Automation of snuffing steam activation – in the interest of improved response time and to limit personnel exposure in the event of a fire, an automated snuffing steam activation valve can be used, with an alarm and control signal to the valve from the temperature transmitter in the vapour space of the pit.

Correct location of snuffing steam valving – it is considered best practice, though not a code requirement, to position the activation valve for the snuffing steam (especially if manually operated) 50 ft or more away from the edge of the sulphur pit. This allows actuation without personnel exposure to an ongoing fire event. During a number of sulphur pit revamp projects, we have noted this valve to be near or even on top of the pit, not in safe reach should there be a fire in the pit vapour space. We believe the closer locations are based upon the premise that an empty line downstream of the valve that can plug with sulphur, rendering the line useless when needed. However, the use of rupture discs at the snuffing steam entry points and steam jacketing the steam line, as mentioned above, can mitigate this concern. Air purges have also been used to keep the lines clear.

Conclusion

Below-grade reinforced concrete sulphur storage pits provide containment and bulk conveyance of molten sulphur products in the sulphur recovery process flow scheme. With appropriate detailing, these civil assets can provide long-term service in incredibly harsh process environments, allowing for dependable process throughput. However, like all man-made construction, maintenance is required, and programs should be in place that can be implemented quickly when required. Sulphur pit civil maintenance programs should focus on repair and restoration of these assets not unlike those in place for electro-mechanical systems and equipment. As stated earlier, civil assets don't necessarily generate revenue, however when they fail, they can certainly cost owner/operators revenue in the form of lost production. In fact, this is somewhat true of the entire SRU itself, it is often hard to gain approval for expenditure (either capital or maintenance related) on a unit that does not generate significant revenue directly. When a pit is down for repair during a turnaround, an excellent opportunity exists to upgrade the mechanical services around the sulphur pit, as they require modification anyway due to the installation of the new concrete liner. The incremental capital cost is relatively low to make these process and mechanical improvements. Facilities are encouraged to involve engineering early-on in the process, and to resist the temptation to assume that this is a remove and replace-in-kind exercise. ■

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