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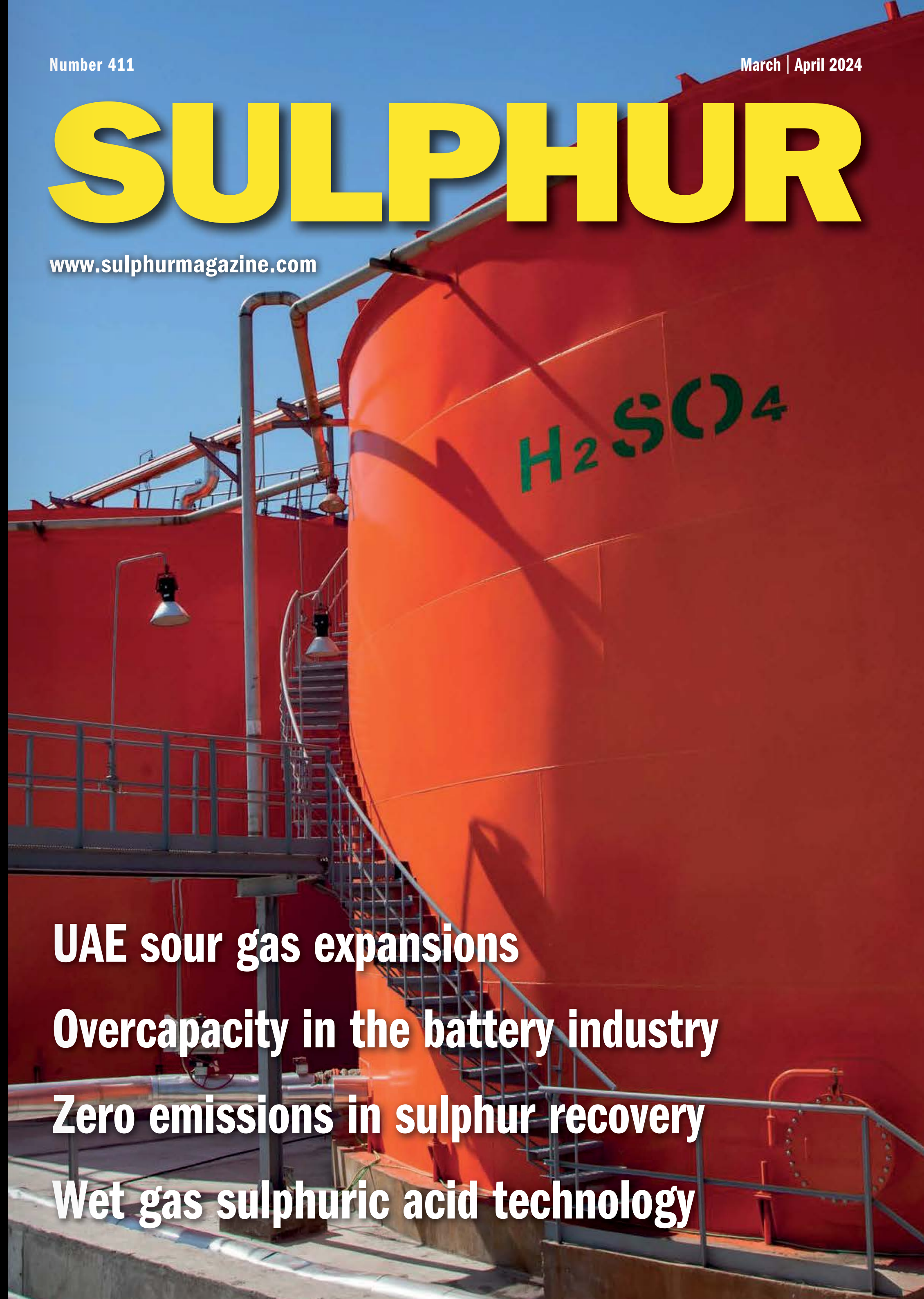

SULPHUR
ISSUE 411
MARCH-APRIL 2024

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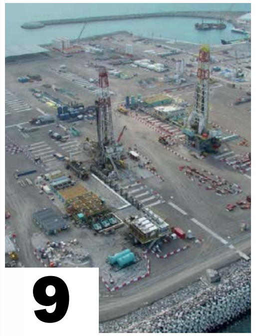
Cover: *Sulphuric acid storage tanks in Kzyl-Orda, Kazakhstan.*
Photo: Alexey_Rezvykh/Shutterstock



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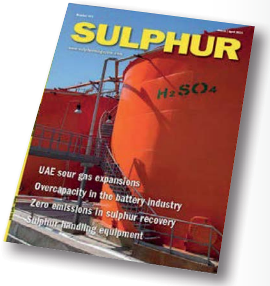
Revolution in speciality phosphates



The phosphate industry, the dominant consumer of sulphuric acid worldwide, has grown to its present size on the back of fertilizer consumption. And while this has seen considerable growth over the past decades, especially in countries like China, India and Brazil, it has generally been fairly steady and – subject to the annual vagaries of weather and the commodity cycle – relatively predictable. However, the world economy is now in the throes of a major transformation towards less carbon intensive generation and use of energy, and that is disrupting many markets, including that for phosphates.

The speciality phosphate sector has previously focused on additives for food and animal feed, as well as water soluble fertilizers such as technical grade mono-ammonium phosphate (tMAP), but the rapid growth in demand for lithium iron phosphate (LFP) batteries is changing the demand picture for speciality phosphate derivatives, particularly high grade purified phosphoric acid (PPA), as well as tMAP. CRU has recently considerably revised upwards its estimates for LFP uptake over the next few years, with projections that the current usage will triple by 2028 to the equivalent of 1.4 million t/a P_2O_5, and more than double again out to 2035 to reach 3.1 million t/a P_2O_5. While this is still relatively small compared to overall phosphate consumption, it nevertheless represents 3% of all phosphate demand by 2028. It is also a 50% increase in PPA demand over the same period, or an annualised growth rate of 7%. Growth rates for tMAP are higher still, averaging 8% year on year.

> **"Current usage will triple by 2028..."**

China has so far been the driver of this, with its focus on LFP for electric vehicle batteries. Much of this has hitherto been satisfied by thermal process phosphoric acid (TPA), but there is now increasing focus on purified wet process phosphoric acid. Overall, Chinese PPA capacity may rise by 1.7 million t/a P_2O_5 out to 2028, bringing the total global capacity to over 7 million t/a P_2O_5. But there is now sign of some LFP development outside of China, with plants for making LFP cathodes being developed in several phosphate producing countries, often with Chinese battery making companies involved in the investment. This is the case in Morocco, where 130,000 t/a of cathode active material (CAM) capacity is under development, and Chile, where another 50,000 t/a is being developed by BYD. Other projects are in the United States, Germany, Taiwan, Finland, Canada, Australia, Korea and Belgium, with ex-China projects possibly contributing 20-25% of global LFP production by 2028.

In the longer term, the focus on LFP and lithium magnesium iron phosphate (LMFP) is likely to plateau as a percentage of battery sales for the electric vehicle market, at around 40%. Other promising technologies are also in the running, including lithium nickel manganese oxide (LNMO), lithium- and manganese-rich (LMR) cathodes, and variations on lithium nickel manganese cobalt oxides. But the world of battery technology is moving so quickly at the moment that it is difficult to make predictions beyond the end of the decade. What does seem to be sure is that at least for the 2020s, lithium iron phosphates are set to make a big impact on the speciality phosphates sector.

Richard Hands, Editor

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Price Trends

SULPHUR

Sulphur prices reached a low point in mid-February, with buyers looking to the tender from Muntajat as well as the return of Chinese buyers following the Lunar New Year holiday for the direction that the market would turn. CMOC's 5 February tender for 40,000 tonnes of sulphur for early-April arrival was indicated awarded in the upper $90s/t c.fr on supply from the FSU, though details were not confirmed.

Availability appeared to be tighter from the US Gulf, but demand was lacklustre and availability seemed ample from most origins worldwide, with buyer requirements limited. Downstream fertilizer production has yet to increase substantially in key markets outside China, where fertilizer production has been cut due to export restrictions. Meanwhile, sulphur availability from most origins is ample. Still, affordability is exceptionally good, and downstream production in some areas may grow over the coming months, with further price recovery likely within Q1 and beyond. Downstream fertilizer production remains weak, though affordability is attractive and some believe prices will increase further, particularly as many expect China's phosphate exports to increase from March.

Indonesian buyers have recently purchased crushed lump sulphur from Saudi Arabia, with price indications around $80/t c.fr, well below the $95-100/t c.fr level of granular sulphur cargoes. This crushed lump supply is likely to reduce buyers' requirements for new granular sulphur cargoes, limiting price support from Indonesia demand. Increased interest in the battery metals sector has prompted a new wave of nickel leaching projects, with Indonesia being the centre of attention for new additions. Indonesia's sulphur imports for 2023 reached 2.7 million t/a, up 31% from the previous record high of 2.06 million t/a in 2022, when imports climbed 75% year on year. While some market participants are concerned the recent falls in nickel prices may reduce Indonesia's sulphur demand, CRU believes that sulphur consumption there will still increase further this year, though demand may be partly offset by increased domestic smelter acid production.

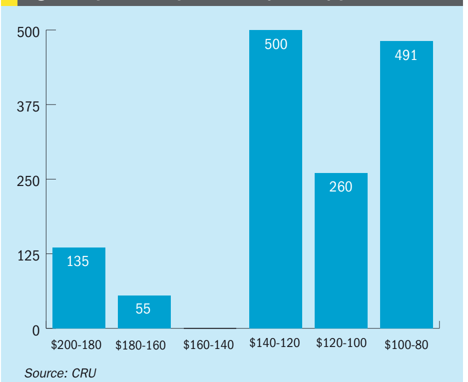
There is considerable speculation in downstream phosphate markets surrounding the potential lifting of Chinese export restrictions and the possible imposition of sanctions by the US against Russian fertilizers. Clarity is still being sought in both cases, but DAP and MAP prices rebounded in the US in the meantime on the back of tight supply, which is also continuing to support prices elsewhere.

Availability of liquid sulphur is reported to be good in the US. The supply of liquid sulphur in the US tightened considerably following the onset of the Covid-19 pandemic as refineries cut output, and the Texas storms of February 2021 also led to large cuts in sulphur output. Since then, domestic production has picked up due to higher refinery run rates and more sour crude inputs. This, along with some demand destruction, has left the domestic molten sulphur market in a surplus. In January, US Gulf sales were concluded in the $60s/t f.o.b. as export availability was long, but the market has since tightened, partly due to refinery maintenance being conducted in the western Gulf, as well as some technical issues at export terminals. Meanwhile, US exports of sulphur climbed 10% year on year to 1.91 million t/a for 2023.

Following the low point in mid-February, global sulphur prices climbed as China returned from Lunar New Year holidays, with a range of benchmarks assessed higher this week. Chinese sulphur prices declined in 2023 Q4 following the climbs of Q3 amid ample availability and limited spot demand. Prices rebounded slightly in late January 2024 and increased further after Chinese New Year holidays. Sulphur prices are now assessed at RMB 910-920/t free carrier (FCA) ($126-128/t) and $97-107/t c.fr, up RMB20/t ($3/t) and $8/t on average respectively from their pre-holiday levels.

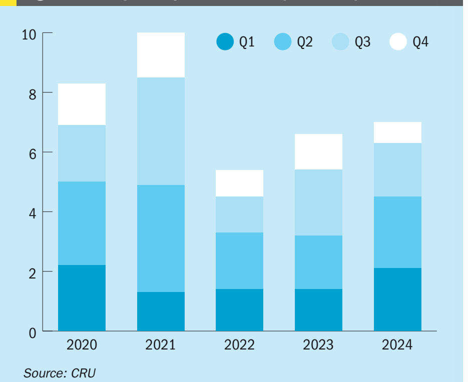
The price rises were in spite of rising inventories at Chinese ports. Sulphur port inventories in China jumped 92,000 tonnes in February to around 2.86 million tonnes, the highest level since October 2020. The total remains well above the 2022 average of 1.44 million tonnes and the 2023 average of 2.07 million tonnes, as stocks climbed by over 1 million tonnes between mid-June and the end of October in 2023. The volume at Yangtze River ports increased 61,000 tonnes to 1.05 million tonnes. Dafeng port inventory was steady around 430,000 tonnes. These stocks are understood to be mostly held by traders rather than end-users. The majority of stocks were built up at prices of $100-140/t c.fr, CRU estimates, while current inland port prices indicate a netback of around $104-105/t c.fr. Consumption of stocks remains slow, as traders are reluctant to take losses.

Fig. 1: **Sulphur China port inventory build by price, '000 t**



Source: CRU

Fig. 2: **China quarterly DAP+MAP exports, Mt product**



Source: CRU

SULPHURIC ACID

Sulphuric acid prices were broadly stable across the globe in February, as market participants awaited China's return to the market following the Lunar New Year holiday. Chilean demand was lacking and fresh Atlantic market deals were awaited. However, there was a rise in Atlantic markets towards the end of the month due to limited spot export availability from Europe. Most major European producers seem relatively well-committed and unwilling to accept prices below the $40s/t f.o.b. on new business. Tightening molten sulphur availability in Europe is adding some additional acid demand from European buyers, while demand from Morocco has been soaking up most available export volumes on offer. Spot prices for acid exports from northwest Europe were assessed at $35-45/t f.o.b. for several consecutive weeks as most market participants agreed with the range, though sentiment remained mixed.

Some sources pegged c.fr prices for the US Gulf and Brazil at higher levels as they argue that trans-Atlantic freights were higher, though recent freight broker indications do not support this. Spot prices for sulphur exports from the US Gulf were assessed up at $70-75/t f.o.b. from $65-70/t, based on latest indications. There were reports of sales possibly into the $80s/t f.o.b., though these were understood to be for smaller volumes. Recent Brazil prices into the upper $90s/t c.fr should enable netbacks within the published f.o.b. range. Firm spot sales on an f.o.b. basis have been limited in recent weeks.

Demand from key import market Chile was also lacking. Frequent closures at Mejillones port in recent weeks due to ocean swells have also slowed acid trade. In addition, recent arrivals of vessels that were previously delayed due to Panama Canal issues have left buyers well covered, with some indicating they would require no additional acid until April at least. Mexico's Fertinal scrapped its sales tender due to a lack of appropriate bids, according to sources. This may also be a result of the lack of Chilean demand.

Saudi Arabia's Ma'aden closed another purchase tender, this time for April arrival. The session was again indicated awarded in the $60s/t c.fr, roughly in line with current published prices for Asia/Pacific markets given current freight rates. Other Asia/Pacific markets were quiet. Prices in Asia/Pacific markets were stable as spot demand remained scarce Far East export prices have come under pressure from high freight rates and weakening import demand from some key import destinations, such as India and Indonesia.

The only change in published assessments was a further decline in the India c.fr to $55-60/t based on last reported business. Indian demand is decreasing due to new domestic supply, while sulphur is a much more attractive alternative at current prices. Buyers CIL and IFFCO have slower demand due to new sulphur-burner capacity starting or having already started. In addition, Adani group is planning to start new smelter production with 1.5 million t/a of sulphuric acid capacity. Latest reports suggest the smelter will be running by the end of March.

Indonesia's acid imports are also likely to decrease this year due to increased domestic production expected from smelters and sulphur burners, after imports for 2023 increased 253% year on year to 1.09 million t/a. Indonesia's Lygend was out with a tender for 30,000 t for March delivery. Given the cargo size requirement, this will likely need to draw supply out of China, which could require higher prices than previous Indonesia business.

Producers in China have been increasing their offers, although the China spot f.o.b. was assessed unchanged in late February at $5-15/t f.o.b. Buyers and traders show little appetite for double digit f.o.b. prices, with current freights and c.fr prices creating pressure for lower f.o.b. rates amid limited demand, particularly with sales from Japan and Korea concluded at negative f.o.b. prices in some cases. China producers have been resisting pressure to lower offers further, and sources suggested that recent offers have climbed to the $20s-30s/t f.o.b. Resistance to lower export prices is partly the result of relatively higher prices available on domestic sales.

Price Indications

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

Cash equivalent	October	November	December	January	February
Sulphur, bulk ($/t)					
Adnoc monthly contract	111	100	90	77	69
China c.fr spot	115	105	99	90	97
Liquid sulphur ($/t)					
Tampa f.o.b. contract	102	102	102	69	69
NW Europe c.fr	139	139	139	139	139
Sulphuric acid ($/t)					
US Gulf spot	115	115	100	85	100

Source: various

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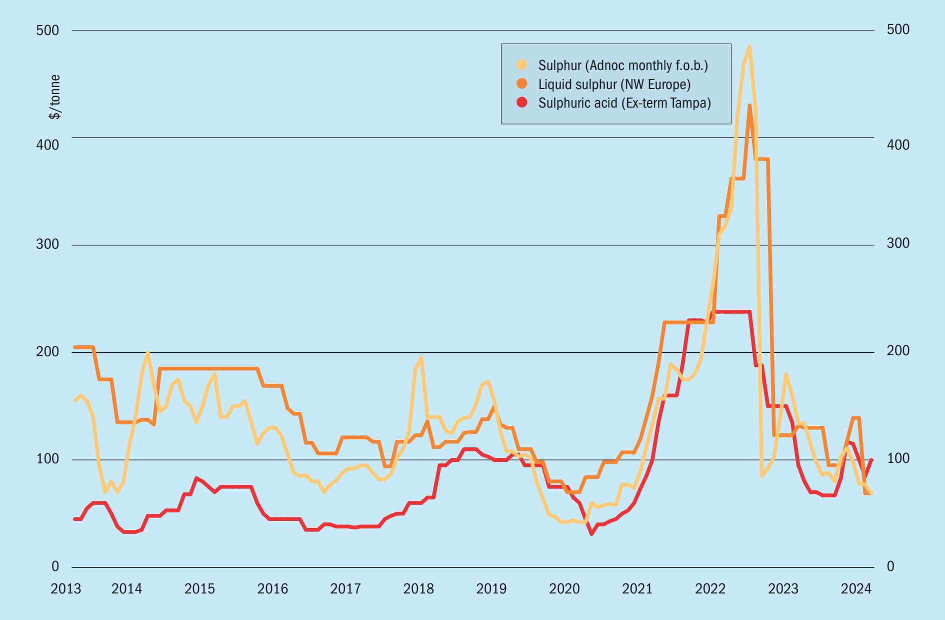
Market Outlook

Historical price trends $/tonne



Source: CRU

SULPHUR

- CRU expects sulphur prices to be supressed in early 2024 by high port inventory and limited phosphate export business. However, affordability continues to support raw materials purchases and leaves room for price increases, especially if downstream production picks up as expected and sulphur stock drawdown slows.
- Two key factors are expected to influence China sulphur prices in 2024: port inventory and phosphate export restrictions. High inventories in Chinese ports will continue to limit the upwards potential for prices in the short term, and keep sulphur prices low relative to phosphates.
- In the meantime, phosphate fertilizer producers in China, the largest importer of sulphur, have suffered from escalated export barriers since November 2023. They have cut downstream production as a consequence and hold limited sulphur inventory However, export restrictions are expected to be eased after China's spring application season.
- Furthermore, the affordability of sulphur relative to phosphates remains good even at lower forecast DAP prices. As such, sulphur demand should increase when phosphate export activity picks up, as phosphate producers can purchase the raw material without price pressure.

SULPHURIC ACID

- Global spot prices are likely to decline further over the coming weeks and months, but severe decreases are not expected. Downstream production rates remain relatively weak overall and domestic production is increasing in some key import markets. Still, affordability (relative to downstream markets) is broadly acceptable, even though it is the worst it has been for some time and looks particularly bad when compared with upstream sulphur.
- Pressure from increasing acid availability across the globe will continue to weigh on European f.o.b. prices for acid, as will low-sulphur prices outside Europe.
- News that Enami's Paipote smelter would close in April may add some support to acid demand for Chile in the coming months. The company announced in late January that the smelter, which produces around 290,000 t/a acid in the Atacama region, would close in late April. Company officials previously announced that the smelter was scheduled to close temporarily in January 2025, although it was expected to be brought forward to 2024.
- Production at Chinese copper smelters has remained high, but some sources expect smelter maintenances in April-June may tighten availability. The ramp-up of several new smelter projects, such as Houma II, Nanguo II, Baiyin II, and Guorun Copper II, as well as resumption at the old Daye smelter could significantly drive smelter output growth in 2024.
- In India, the Adani group is planning to start production at a new smelter with 1.5 million t/a sulphuric acid capacity. Latest reports suggest the smelter will be running by the end of March.

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Sulphur Industry News

KAZAKHSTAN

Contracts awarded for Kashagan expansion

Qatar construction services company UCC Holding has signed a memorandum of understanding with the Kazakh Ministry of Energy for a gas treatment plant at the Kashagan field with a capacity of 6 billion cubic meters as part of the Phase 2B expansion. The memorandum was signed by Minister of Energy Almassadam Satkaliyev and Mohamed Moutaz Al Khayyat, chairman of UCC Holding.

Progress on the gas processing plant has been complicated by issues with the previous contractor, GPC Investment, which was awarded the contract in 2020, but which had run into financing and project management issues that stalled the project in 2022. The Kazakh government subsequently bought GPC Investment for an undisclosed sum, paving the way for the new appointment, in conjunction with state pipeline operator and gas producer Qazaqgaz.

The gas processing plant will receive 1 bcm per year of gas from the Kashagan field. The Eni-led consortium that runs Kasahagan, the North Caspian Operating Company (NCOC), began construction of a pipeline to the site of the new facility in September last year. The gas processing plant will allow NCOC to increase oil output from Kashagan by 25,000 bbl/d. NCOC also includes ExxonMobil, Shell and TotalEnergies, alongside China National Petroleum Corporation, Inpex and Kazakh state player KazMunayGaz. Production at Kashagan is partially constrained by the gradually increasing share of associated gas in the flow of hydrocarbons to the surface, with the operator having to reinject produced gas into the reservoir. Qazaqgaz says that the new completion date for the processing plant is 2025.

In the meantime, NCOC and the Kazakh government appear to be closing in on a resolution to the ongoing dispute over sulphur storage at the project site. The government had tried to impose a $5 billion fine for allegedly storing sulphur in excess of permitted quantities for several months. The suit was rejected by a court last year, but the government had appealed the decision. Press reports suggest that an out of court settlement is under discussion involving dropping the fine in return for NCOC investing $100 million in social projects over two years.

BRAZIL

Brazil joins OPEC+

On January 1st Brazil became the newest member of the OPEC+ group of countries. However, it will not become a formal member of the Organisation of Petroleum Exporting Companies, nor will it be bound by OPEC oil production quotas. Instead it will remain effectively an associate member, like Russia and several other states like Mexico that help form the wider OPEC+ organisation. The reasoning is supposedly that Petrobas, while state owned, is a publicly traded company,

Brazil is a significant oil producer, with an output of 3.7 million bbl/d in 2022, and this is projected to rise to a peak of 4.8 million bbl/d by 2028, as the country exploits deep offshore oil fields. Petrobras has $102 billion of investment spending planned to 2028.

Speaking to OPEC ministers, Brazilian Minister of Mines and Energy Alexandre Silveira de Oliveira said that this was "a historic moment for Brazil and the energy industry and we look forward to joining this distinguished group… Brazil benefits significantly from the stability of oil and energy markets".

NORWAY

Feasibility study on refinery conversion

Equinor ASA has let a contract to Aker Solutions ASA to execute a feasibility study for the proposed transformation of subsidiary Equinor Refining's 226,000 bbl/d refinery at Mongstad, on Norway's western coast, into a low-carbon industrial cluster equipped for production of blue hydrogen and sustainable aviation fuel (SAF).

The study aims to identify solutions to significantly reduce CO_2 emissions from the existing refinery and transform the site into a new low-carbon industry cluster whilst demonstrating safe, technical, and economically feasible solutions. The scope includes a new greenfield facility which will be developed to produce blue hydrogen from natural and refinery fuel gas, along with a carbon capture and export solution. It also covers a new facility to produce sustainable aviation fuel (SAF) from municipal solid waste with more than 70 % reduced emissions.

Aker Solutions' consultancy will deliver a feasibility study for both new and existing facilities, integrating brownfield, greenfield and third-party technologies to examine options for future operations. Consultants and engineers from Aker Solutions' Oslo, Bergen and Mumbai operations are involved, delivering expertise in onshore and downstream project execution, gasification, CO_2 storage, brownfield, and integration.

"We are excited to support Equinor on this truly transformational study, maximizing industrial synergies to produce low-carbon solutions and sustainable fuels at a time when decarbonization is very high on the agenda," said Roddy Macpherson, senior vice president, consultancy at Aker Solutions.

"For decades, we have worked with customers and partners to minimize commercial uncertainty and enable informed decision-making for first-of-a-kind projects across the globe. Building on our strong engineering and construction expertise, and our understanding of the evolving energy system and landscape, we aim to drive change at pace for our customers. The Mongstad study will help to further accelerate Norway's energy transition, transforming the country's only remaining oil and gas refinery to create energy sources of the future."

SWEDEN

Renewable fuels plant

Topsoe has signed a licensing and engineering agreement with Preem, Sweden's largest fuel company, to produce sustainable aviation fuel (SAF) and renewable diesel, using Topsoe's HydroFlex™ technology. Preem is revamping a major isocracker unit at its refinery in Lysekil. The unit will have a capacity of 1.2 million m^3/year (22,000 bbl/d) of sustainable aviation fuel and renewable diesel, with production expected to begin in 2027. Preem has a long-term target of producing 5.0 million m^3/year (92,000 bbl/d) of renewable fuels, as well as achieving a climate neutral value chain by 2035. Once the revamped Lysekil refinery starts operating in 2027, Preem will become one of Northern Europe's biggest producers of SAF. Demand for SAF is rapidly growing. According to the International Energy Agency's Net Zero Scenario, over 10% of fuel consumption in aviation by 2030 needs to be SAF to stay on course for net zero CO_2 emissions by 2050. In 2022, the International Air Transport Association estimated global SAF production to make up only around 0.1% to 0.15% of total jet fuel demand.

Elena Scaltritti, Chief Commercial Officer at Topsoe, said: "Society needs a significant upscaling of renewable fuels for aviation. We're excited to take another step on the path to reduce carbon emissions in the transportation sector and aviation in particular. Together with Preem, we already have a proven track-record of delivering impactful results within renewable fuels production, and we're looking forward to continuing working with Preem on this important task."

The Richard's Bay port facilities.

PHOTO: RICHARDS BAY INDUSTRIAL DEVELOPMENT ZONE

SOUTH AFRICA

Reload Logistics acquires sulphur terminal

Reload Logistics has acquired a 50,000 m^2 bulk sulphur terminal at Richards Bay, South Africa. The facility has 20,000 m^2 of indoor storage of 20,000, a 10,000 m^2 loading area, and has operations for simultaneous offloading, bagging, and loading for both rail and trucks of containerised or break-bulk cargo. Reload says that the acquisition, the latest in a series for the logistics company, is a strategic asset, empowering the company to deliver reliable and efficient services for the handling, storage, and distribution of sulphur and other dry bulk commodities to clients.

Since taking over the facility in November 2023, Reload Logistics says that it has made significant upgrades to the complex, equipment, and related systems, enhancing the discharge rate of sulphur vessels, and increasing the holding capacity of the undercover warehousing. These enhancements have allowed it to achieve a record for tonnage unloaded from a vessel in a 24-hour period.

"We are thrilled to share this news with our clients and the public. This acquisition and upgrade underscore our commitment to providing the best logistics solutions for our clients and the industry. We take pride in our team and the remarkable results they have achieved thus far," said Michael-John Saunders, Managing Director of Reload Logistics.

UNITED STATES

Martin Midstream sees higher earnings in 4Q 2023

Martin Midstream announced better than expected results for the final quarter of 2023. Speaking at the company's 4Q earnings call, CEO Bob Bondurant said that the company had achieved an adjusted earnings before interest, taxes, depreciation, and amortisation (EDITBA) of $29.2 million compared to a revised guidance of $26.9 million, an improvement of 9%. For the year, the company's adjusted EBITDA was $117.7 million, with the Transportation segment the best earner. The second strongest cash flow generator in the fourth quarter was Martin's Terminalling and Storage segment, which had adjusted EBITDA of $9 million. The Sulfur Services segment had adjusted EBITDA of $7.4 million compared to guidance of $6 million, with stronger fourth quarter sales compared to forecast for both liquid fertilizer and degradable sulphur products. There was strong sulphur production from the company's refinery suppliers, with total sulphur volume received 17% greater than forecast. Next year adjusted EDITBA for million, higher than for 2023 because of the new electronic grade sulphuric acid (ELSA) project at Plainview, Texas. Construction of an oleum tower was begin in 2023, and $10.4 million is budgeted for the expansion in 2024. The plant will supply sulphuric acid to the DSM Semichem semiconductor joint venture, which includes Martin, Samsung, C&T America and Dongjin.

SAUDI ARABIA

Prayon to supply technology for Ma'aden 3

Prayon says that it has been as a technology provider for the merchant grade phosphoric acid plant that will form part of the Ma'aden Phosphate 3 Project. Prayon Technologies will provide the process for the new factory, which will be fitted with Prayon's proprietary equipment, via its Process Filtration and Liquid Equipment division Profile.

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Sulphuric Acid News

KAZAKHSTAN

Acid shortage impacting uranium production

In January, Kazakh uranium producer Kazatomprom warned of potential adjustments to its 2024 uranium production due to challenges with sulphuric acid availability and construction delays at new uranium mining operations. In a statement the company said that its projected uranium output for 2024 will be between 21,000 t/a and 22,500 t/d U_3O_8, around 20% lower than the amount it had been expecting to be able to mine. Kazatomprom's uranium output was 21,100 t/a U308 in 2023, down 1% on 2022 figures, with output flat during 4Q 2023. While it said it had sufficient inventory in stock to cover contracted deliveries in 2024, there could be problems for 2025 deliveries.

Kazatomprom is the world's largest producer of uranium, with over 40% of global output, and frequently uses in-situ mining for uranium in carbonate rocks, which consume relatively large volumes of sulphuric acid. In a statement Kazatomprom said that due to increased domestic consumption and the demand for sulphuric acid for fertilizer production over the past few years, a shortage of acid has developed in the domestic and regional markets, with a combination of factors such as supply chain disruptions and geopolitical uncertainty. Kazatomprom also says it is actively pursuing alternative sources of sulphuric acid, with the deficit expected to alleviate as a result of the potential increase in supply from local non-ferrous metals mining and smelting operations. The company also has plans to increase its own acid output, with a new 800,000 t/a plant under development, but this will not be completed until 2026.

Uranium markets have been under-supplied, and the price of uranium doubled during 2023 to a 16-year high of around $106/lb. Japan has been bringing its nuclear power stations, many of them idled in the wake of the Fukushima nuclear accident, back online, and there is also strong demand from US utility companies, as well as a great deal of new reactor construction in Asia, especially China. High oil and gas prices over the past couple of years and an increased push for lower carbon electricity generation are leading to a boom in nuclear generation at a time when a run of lower prices had led to uranium mine closures. Meanwhile, supply from Niger, the 7th largest uranium producer, have been interrupted by a military coup last year.

Some supply relief may come from Australia, where additional production is expected this year from Boss Energy's Honeymoon project in South Australia. Elsewhere, Paladin Energy plans to restart its mothballed Langer Heinrich mine in Namibia in the first half of this year. There are also projects by Deep Yellow, Bannerman Energy and Elevate Uranium in Namibia, and Peninsula Energy in Wyoming, USA.

PHOTO: KAZATOMPROM

Kazatomprom's offices in Astana.

CANADA

First Phosphate produces first phosphoric acid

First Phosphate Corp. has started up a pilot plant to convert high purity phosphate concentrate produced from its La a Paul phosphate deposit in Quebec into battery-grade purified phosphoric acid (PPA) for the lithium iron phosphate (LFP) battery industry. The merchant grade phosphoric acid (MGA) pilot plant, designed by Prayon Technologies SA, successfully achieved start-up in September 2023, transforming First Phosphate's phosphate concentrate. Subsequently, Prayon completed the second stage of the process to transform the MGA into PPA in conformity with the Prayon food grade/battery-grade specification.

"Our full transformation process from Quebec igneous phosphate rock to PPA for LFP batteries is now complete," said First Phosphate CEO, John Passalacqua. "We can now engage our partners to begin the pilot process of producing LFP cathode active material and LFP battery cells from a fully North American source of battery-grade PPA."

First Phosphate is engaged in a feasibility study for the large scale production of merchant-grade acid and lithium iron phosphate at Saguenay, further south, on a tributary of the St Lawrence river.

JORDAN

New phosphoric acid tank for JIFCO

The Jordan India Fertilisers Company (JIFCO) intends to build a phosphoric acid storage tank at the southern Jordanian port of Aqaba, on the Red Sea, according to local press reports. JIFCO operates a 1,500 t/d phosphoric acid plant and 4,500 t/d sulphuric acid plant at its site at Eshidiya in the southeast of the country. The company exports phosphoric acid and imports sulphur to operate the phosphate processing complex.

BULGARIA

Aurubis awards contract for flash smelter rebuild

Aurubis Bulgaria AD has awarded Metso a contract for a copper flash smelting furnace rebuild project for its smelter in the Zlatitsa-Pirdop valley. Metso says that the value of the contract exceeds EUR 10 million. An Outotec® flash smelting furnace and related technologies were implemented at the Bulgarian primary copper smelter already in 1987. Since then, various upgrades and improvements have been done at regular intervals in close cooperation between the two companies. The previous flash smelting furnace rebuild was executed in 2016. The scope of this new order includes the delivery of new Outotec® cooling elements and the related advisory services to support the rebuild project.

RUSSIA

PhosAgro increased acid production in 2023

Russian phosphate company PhosAgro has announced production figures for financial year 2023. It says that its total mineral fertilizer production increased by 2.1% year-on-year to 11 million t/a, with the production of other agrochemicals amounting to about 300,0000 t/a. This growth was driven primarily by an 8.4% increase in DAP/MAP production to more than 4.5 million t/a, as well as a 4.4% increase in ammonium nitrate production to 723,000 t/a and a 1.6% increase in urea production to 1.7 million t/a. The DAP/MAP figures included a 12.9% increase in MAP production, due to the start-up of a new plant at Volkhov, part of the company's long-term development programme.

In tandem with output of finished fertilizer, production of key feedstocks rose 2.1% year-on-year in FY 2023, mainly due to a 4.6% increase in production of phosphoric acid and a 2.5% increase in the production of sulphuric acid to more than 8.1 million t/a. PhosAgro says that this increase was the result of improved operation efficiency at the sulphuric acid production unit in Cherepovets, and the launch of a new sulphuric acid plant at Balakovo at the end of 2023.

INDIA

Coromandel to build new sulphuric, phosphoric acid plants

Coromandel International's board has approved the construction of new phosphoric acid and sulphuric acid plants at the company's site at Kakinada, Andhra Pradesh with a total investment of 10.3 billion rupees ($120 million). Existing capacity at the plant is 1,550 t/d of phosphoric a and 4,200 t/d of sulphuric acid, but has reached 100% capacity utilisation. The capacity addition will be 750 t/d of phosphoric acid and 1,800 t/d of sulphuric acid, with completion set for 2026. In a stock market filing, Coromandel said that the projects, to be funded through internal accruals/loans, will reduce dependence on imports and make Kakinada an integrated facility. The company further said that the investment is in line with its long-term objectives to secure key materials for its fertiliser production.

SAUDI ARABIA

Lithium plant will use alkaline leach

EV Metals Group has selected Metso as its technical partner for a lithium chemicals plant to be built at Yanbu Industrial City in Saudi Arabia. Metso will provide technical, operational, maintenance, and systems support to operational performance and asset management. Metso will supply its alkaline leach technology to produce the high-purity chemicals required by electric vehicle and battery cell manufacturers. It will collaborate with EVM through all phases of the project, from project sanction to steady state operations.

"The technical partnership with Metso is a significant development to accelerate the progress of our lithium chemicals plant. EVM will take a collaborative approach to securing all requirements necessary to ensure successful start-up and operation of the LCP, fully aligning with the goals of Vision 2030. Metso is the ideal partner to provide processing technology and equipment for the entire lithium production chain, from mine to battery materials," said EVM's CEO Luke Fitzgerald.

AUSTRALIA

Metal price crash puts projects at risk

The slide in the price of nickel has put several nickel extraction projects at risk, with BHP in Australia taking a massive hit in 2H 2023 profits and considering the closure of its Nickel West operation. Nickel prices peaked after the Russian invasion of Ukraine at around $32,000/t, although they slumped through the rest of the year before rallying to $29,000/t at the end of 2022. During 2023, however, increasing supply from Indonesia has increasingly made itself felt, while the Chinese economy has slowed, and the nickel price is now below $19,000/t, and set to stay low for a couple of years at least.

BHP reported a net profit of $927 million for 2H 2023, with the underlying profit of $6.6 billion for the full year being masked by a one-off impairment of $3.5 billion related to their nickel operations. The company is reviewing its operations at Nickel West, which include a mine and a smelter, in spite of healthy demand for electric vehicles, and the Australian government has been considering production tax credits, royalty relief and loans to keep the operation going in the short term.

Prices of rare earths have also been similarly affected, and also potentially at risk is Lynas Rare Earths' $780 million Kalgoorlie plant, which would use sulphuric acid to produce around 9,000 t/a of rare earth materials and 330,000 t/a of gypsum. Lynas says construction costs have increased at the site and recently unsuccessfully attempted merger negotiations with MP Materials Corp, a US-based rare earth minerals company.

IRAQ

Bids to be invited for phosphate project

Khalid Battal Al-Najim, Iraq's Minister of Industry and Minerals, has said that the country will reopen its call for bids from domestic and foreign businesses to construct a $3 billion phosphate plant in the western part of the country. Iraq received bids from five companies last year that it considered too low, and is now seeking to widen the offer to more bidders, Al-Najim said at a press conference. The announcement of the request for bids will take place within two months. The capacity of the facility was not disclosed.

Iraq has the world's second-largest phosphate reserves, according to Iraqi Geological Survey Commission. The deposits, located in the western desert, account for 9% of the global total. Prior to the US invasion in 2003, Iraq operated a large scale phosphate mine at Akashat which produced 2.4 million t/a at its peak in the 1990s, but damage and lack of investment meant that production slumped from 200,000 t/a to just 500 t/a from 2003-6. There was also a State Enterprise for Phosphate plant at Al-Qaim with the capacity to produce phosphoric acid and TSP, although production of both has been idle since 2002. Previous plans were to reopen the Akashat mines along with 1.0 million t/a of downstream

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phosphoric acid and DAP production. Sulphur to produce sulphuric acid for phosphate processing would come from the revitalisation of the Mishraq sulphur mine near Mosul, as well as revamped refinery projects, but the destruction of Mishraq during the fight against ISIL put those plans on the back burner.

GHANA

New refinery includes acid alkylation unit

China's Sentuo Group has commissioned the first phase of a new grassroots refinery at Tema, approximately 30 km east of the capital Accra in Ghana. The Sentuo Oil Refinery Ltd. (SORL) will process 40,000 bbl/d of crude oil as part of a public-private partnership to reduce the nation's dependence on petroleum product imports from abroad, according to president Nana Addo Dankwa Akufo-Addo. Ghana currently relies on foreign sources to meet 97% of its overall demand for finished petroleum products, Akufo-Addo said. The first phase is believed to include diesel hydrogenation, and 60,000 t/a of sulphur recovery as sulphuric acid to feed acid alkylation at the plant. A second phase, which will increase capacity to 120,000 bbl/d, is reportedly under development and due for completion by 2026.

CHILE

Codelco and SQM to partner on Atacama

Codelco and SQM have signed a memorandum of understanding to establish a new operating company for the Salar de Atacama brine operation. Under the terms of the MoU, Codelco will own 50% plus 1 share of the company. State-owned Codelco is the world's largest copper producing company, accounting for ~8% of global mined copper supply. Early in 2023, the Chilean government gave Codelco the mandate to negotiate on behalf of the state all future contracts and potential partnerships with third parties for the operation of Atacama.

SQM's current agreement for the Atacama Salar is set to expire at the end of 2030 and it is uncertain if it would have been granted an extension. The new agreement will allow capacity to be expanded beyond the envisaged 250,000 t/a lithium carbonate equivalent (LCE) by an additional 60-70,000 t/a towards the end of the decade, a time when the current slump in the lithium market is expected to have been corrected by new demand. It will represent almost 20% of global lithium supply.

The MoU says that the new company will produce and commercialise products derived from the brine extracted from the mining concessions in the Atacama Salar. The main products currently produced at the mine site include lithium chloride (or a concentrated brine with ~6% lithium concentration), potassium chloride and potassium sulphate.

PHOTO: SQM

Brine pools for lithium extraction, Chile.

MAURITANIA

India seeking phosphate supply deal

India is negotiating a long-term phosphate rock supply contract with the government of Mauritania, according to state Chemicals and Fertilizers Minister Mansukh Mandaviya. India already has existing supply deals with Morocco, Morocco, Senegal, Israel, Oman, Canada, Saudi Arabia and Jordan, but is seeking to ensure supply security and price after phosphate markets have been volatile over the past few years due to the covid-19 outbreak, the war in Ukraine and more recently the attacks on shipping in the Red Sea. Speaking to local press, Mandaviya also said that a three year supply deal with Egypt is also possible to improve the domestic availability of phosphate fertilizers like DAP. India relies upon foreign imports for 90% of its phosphate needs and imports nearly 5 million t/a of phosphate rock, 2.5 million t/a of phosphoric acid and 3 million t/a of DAP.

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Sasol and Topsoe have appointed **Jan Toschka** as CEO of the joint venture established by the two companies to develop, build, own and operate sustainable aviation fuel (SAF) ventures and to market the products. Previously Toschka was president of Global Aviation for Shell, responsible for Shell's global network of operations, joint ventures and sales of fuels, lubricants and sustainable solutions to the aviation industry. During his tenure at Shell, he has led teams across sales, mergers and acquisitions, trading, and retail businesses globally, spanning various industries including Marine and Retail. Toschka will assume his new role as CEO on 1 March 2024 and the joint venture will be launched during the same month. The new company will be headquartered in The Netherlands.

Roeland Baan, CEO at Topsoe, said: "I'm excited, that Jan Toschka has accepted the position as CEO for the joint venture. Jan holds unique competencies from having already been working with the aviation industry, and he has a highly entrepreneurial mindset, which is what we need to get the joint venture off to a great start. There's no time to waste in boosting production of SAF to decarbonise the aviation industry, and with Jan joining, I am confident that the joint venture will deliver a remarkable contribution to the world's global ambition of reaching Net Zero."

Jan Toschka said: "The joint venture is formed by two industry leaders, and their ambition to take on one of society's biggest challenges, to help reduce carbon footprint of the aviation industry. This industry is close to my heart, and I am very excited to lead the new company."

bp has appointed **Murray Auchincloss** as chief executive officer, following the resignation of previous CEO Bernard Looney in September 2023. Auchincloss, who has been interim CEO since September 2023, will continue as a member of the bp board. Helge Lund, chair of bp said: "Since September, bp's board has undertaken a thorough and highly competitive process to identify bp's next CEO, considering a number of high-calibre candidates in detail. The board is in complete agreement that Murray was the outstanding candidate and is the right leader for bp.

"Many already know Murray well, and few know bp better than he does. His assured leadership, focus on performance and delivery, and deep understanding of the opportunities and challenges in the energy transition will serve bp well as we continue our disciplined transformation to an integrated energy company."

Before becoming interim chief executive officer in September 2023, Auchincloss had been bp's chief financial officer since July 2020, at which time he also joined bp's board. He had previously served as CFO, deputy CFO and head of business development for bp's Upstream segment. From 2010-2013 he was head of bp's group chief executive's office, working directly with Bob Dudley.

Auchinloss' replacement as CFO will be **Kate Thomson**. Thomson joined BP nearly 20 years ago and had previously led the finances of BP's oil and gas production and operations division.

First Phosphate Corp says that **Jérôme Cliche** will cease to act as vice president, Business Development, although he will, via his own corporation, LMC Communications Inc., continue as a consultant to First Phosphate until October 5, 2024. Under the terms of the revised consulting agreement, the options held by Mr. Cliche have been forfeited.

"First Phosphate wishes to thank Mr. Cliche for his dedication and service in his role as vice president Business Development," says Company CEO, John Passalacqua. "I look forward to continuing to work with Jérôme in his consulting capacity to the Company."

"I would like to thank the management of First Phosphate, and in particular Mr. John Passalacqua, for the confidence they have shown in me since my appointment," added Cliche. "I believe that First Phosphate is and will remain a promising project, both for the company and its shareholders, and for the development of the LFP battery industry, which extends far beyond Quebec's borders."

Calendar 2024

APRIL

2-4
TSI Sulphur World Symposium 2023, CHALESTON, South Carolina, USA
Contact: Sarah Amirie, The Sulphur Institute
Tel: +1 202 296 2971
Email: SAmirie@sulphurinstitute.org

22-25
Sulphuric Acid Round Table, ORLANDO, Florida
Contact: Cathy Hayward, Sulfuric Acid Today.
Tel: +1 (985) 807-3868
Email: kathy@h2so4today.com

29-MAY 3
REFCOMM 2024, GALVESTON, Texas, USA
Contact: CRU Events
Tel: +44 (0)20 7903 2444
Email: conferences@crugroup.com

MAY

20-23
Middle East Sulphur Conference 2024, ABU DHABI, UAE
Contact: CRU Events
Tel: +44 (0)20 7903 2444
Email: conferences@crugroup.com

JUNE

7-8
46th Annual International Phosphate Fertilizer & Sulfuric Acid Technology Conference, CLEARWATER, Florida, USA
Contact: Michelle Navar, AIChE Central Florida Section
Email: vicechair@aiche-cf.org
Web: www.aiche-cf.org

SEPTEMBER

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

11-12
Oil Sands Conference & Trade Show, CALGARY, Alberta, Canada
Contact: Bruce Carew, EventWorx
Tel: +1 403 971 3227
Email: marketing@eventworx.ca

NOVEMBER

4-6
CRU Sulphur & Sulphuric Acid Conference 2023, BARCELONA, Spain
Contact: CRU Events
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Web: www.events.crugroup.com/sulphur/

PHOTO: PETROFAC

An artificial island at the Upper Zakum offshore field similar to those which will form part of the Hail/Ghasha project.

Abu Dhabi's sour gas expansions

Already the world's largest exporter of sulphur, Abu Dhabi continues to expand its sour gas production and sulphur output.

Abu Dhabi is the capital of the Untied Arab Emirates and its second largest city. In contrast to the Emirates' commercial and tourism hub Dubai, Abu Dhabi's growth has been solidly predicated on oil and gas reserves in the deserts to the southwest and the shallow seas northwest of the city. The Emirate of Abu Dhabi has most of the territory of the UAE, encompassing around 75% of its area. The city has grown rapidly over the past few decades, from just 300,000 in 1990, and approximately doubled in population from 900,000 to 1.6 million people from 2010 to the present. Another 1.1 million people live in the other cities and towns and villages of the Emirate. The total population of the UAE rose to 9.4 million people in 2021, with around 90% of these being expatriate workers from elsewhere in the world.

This rapid growth of both Abu Dhabi and the rest of the UAE has put considerable pressure on power demand. In Abu Dhabi this has increased sixfold from 2000 to 2020, with a peak load rising from 3.3 GW at the turn of the millennium to 18.3 GW in 2020, and this is projected to rise by another 50% by 2030 to 26.3 GW, with increasing use for consumer electronics, and because air conditioning is needed year round to cope with the extremely high temperatures of the region. The UAE has consequently become the third largest generator of electricity in the region, after Saudi Arabia and Iran. In order to meet this demand, the UAE has relied predominantly upon natural gas-based power generation. While there is some nuclear power and increasing solar power generation, these collectively accounted for only 10% of the UAE's electricity output in 2021, and 86% came from natural gas.

Although 7 bcm of gas are exported every year as liquefied natural gas from the long standing Das Island LNG terminal, the UAE has become a large net gas importer to feed this electricity generation. In 2022, UAE gas production was 58 bcm, while consumption was 70 bcm. This meant that in 2022 the UAE imported 19 bcm of gas. Around 0.9 bcm arrived as LNG shipments, but the remainder came from the Dolphin pipeline, which runs from Qatar east to the UAE.

Gas reserves

The UAE is assessed to have the seventh largest reserves of natural gas in the world, at 7.0 trillion cubic metres. However, some of these are associated with oil production, which makes their output dependant upon OPEC quotas, while much of the reserves are in fact highly sour and often in remote desert locations. As a result, while many of these fields were discovered in the 1960s, production was deemed too expensive and difficult, and large scale exploitation of these reserves did not begin in earnest until the 2000s when the UAE's need for gas began to grow ever more pressing. Figure 1 shows the location of these reserves.

Oil and gas production in Abu Dhabi is organised by the state owned Abu Dhabi National Oil Company (ADNOC). However,

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actual production is often handled via a number of joint ventures with foreign partners. Chief among these for oil production is ADNOC Onshore, formerly the Abu Dhabi Company for Onshore Oil Operations (ADCO), which is 60% owned by ADNOC and the remainder by Total (10%), BP (10%), CNPC (8%), Inpex (5%), ZhenHua Oil (4%), and GS Energy (3%). ADNOC Onshore produces around 50% of the UAE's oil, from 11 oil and gas fields across four main areas: Bab, North East Bab (NEB), Bu Hasa, and South East (SE). They also operate two export terminals in Jebel Dhanna and Fujairah, as well as a large pipeline network.

Offshore oil exploitation is in the hands of ADNOC Offshore (a merger of the Abu Dhabi Marine Are Operating Company and the Zakum Development Company or Zadco). Again ADNOC holds 60% of the shareholding, with the rest co-owned with Exxon/Inpex (for Upper Zakum), Inpex (for Umm Al Dalk and Satah), Total, Eni, ONGC and Inpex for Lower Zakum, and Eni for Umm Shaif and Nasr, and CEPSA and OMV for Sarb and Umm Lulu.

Natural gas assets are mainly in the hands of ADNOC Gas Processing (formerly known as Gasco). ADNOC Gas Processing is 68% owned by ADNOC, with the remainder in the hands of Shell (15%), Total (15%) and Partex (2%).

Finally, the non-associated sour gas fields are being developed by ADNOC Sour Gas (formerly Al Hosn Gas), which is a 60-40 joint venture between ADNOC and Occidental Petroleum.

Sour gas projects

To date, the largest sour gas field development has been at Shah, about 210km southwest of the city of Abu Dhabi. Project development dates back to 2007, with ConocoPhillips originally involved as project partner, replaced by Occidental when the former dropped out of the project in 2010 as part of a retrenchment following the financial crash or 2008-09. It is now operated by the ADNOC Sour Gas joint venture.

The project presented considerable technical challenges for the companies involved. The gas lies up to 5km down, with, as noted, 23% hydrogen sulphide and 10% carbon dioxide content. At that depth the temperature is 150C and the pressure as high as 5,500psi. The remoteness of the site also meant that work had to begin from scratch; building roads to allow access for a site population of 35,000 during the construction phase, who must operate 210km from the nearest city in temperatures of 50C.

The initial development was designed to process 1.0 bcf/d of sour gas. Sulphur output was around 3 million t/a. Original plans for a heated sulphur pipeline to carry the sulphur to the coast at Ruwais were eventually replaced by a granulation plant 15 km from the sour gas wells (to provide safety in case of a sour gas blowout) and a rail link to the export terminal at Ruwais. First gas production began in January 2015. An expansion project, conducted by Saipem, was begun in 2021 and completed in September 2023 which has taken processing capacity to 1.45 bcf/d of gas and lifted sulphur output to 4.2 million t/a sulphur at capacity.

Fig. 1: **Abu Dhabi's gas processing facilities**

Habshan

Habshan is an oil field to the southwest of Abu Dhabi city, which has been producing since 1983. It is also a hub for processing associated gas from nearby oil and gas fields, including a link from the Das Island LNG plant completed in 2013 as part of the Integrated Gas Development. Habshan also shares some facilities with the nearby Bab oil field, where there is a natural gas liquids extraction train which also separates acid gas out from the gas flow and passes it to Habshan for treatment.

The Habshan gas complex, operated by ADNOC Gas Processing, comprises 14 processing trains in five plants and has a total processing capacity of 6.1 bcf/d of gas. It includes the huge Habshan 5 complex, which was completed in 2013 by Tecnimont, and the associated Habshan Sulphur Plant which handles all of the sulphur from the Habshan complex, including liquid sulphur feeds from Habshan phases 1-4, and which can produce 3.6 million t/a of granulated sulphur. In late September 2023, ADNOC awarded a $615 million EPC contract to Petrofac for a carbon capture, utilisation and storage project at Habshan as part of its strategic initiative to reach net zero carbon emissions overall by 2045.

Expansion projects

As well as these existing sour oil and gas projects, there are several large expansion projects under way. Foremost among these is the Hail/Ghasha development in the Ghasha concession, offshore northwest of the city of Abu Dhabi (see Figure 1), which includes the Hail, Ghasha, Hair Dalma, Bu Haseer, Satah, Nasr, SARB, Shuweihat, and Mubarraz offshore fields. The concession is majority (55%) owned by ADNOC, with other stakes being held by Eni (25%), Wintershall (10%), OMV and Lukoil (5% each).

The Hail and Ghasha development project will use artificial islands and drill the Hail and Gahsah fields, and act as a hub for exploitation of the other fields. In October 2023 ADNOC approved a final investment decision for the project, which aims to produce 1.5 bcf/d of natural gas, with a completion date set for the end of 2029. An $8.2 billion EPC contract was awarded to NPC and Eni for the artificial islands and processing plant, pipelines and drilling centres. Another, $8.7 billion EPC contract went to Tecnimont for the project's onshore scope, two gas processing units, three sulphur recovery sections, associated utilities and offsites, as well as export pipelines. Tecnimont says that its scope will the development of digital solutions aimed at reducing emissions and optimising energy consumption at the project's onshore installations.

ADNOC says that this project will operate on a zero carbon basis, capturing 1.5 million t/a of carbon dioxide and using electricity from renewable and nuclear sources. The project will also produce low-carbon hydrogen to replace fuel gas used in operations. The gas in the Ghasha concession varies in H_2S capacity, but averages around 14-15% H_2S, slightly sweeter than at Shah. Nevertheless, sulphur output at Hail/Ghasha could reach 3.5 million t/a at capacity towards the end of the decade.


The Ruwais refinery, Abu Dhabi.
PHOTO: SAMSUNG

Shah expansion

A third expansion of the Shah project is also under development. This will take total processing capacity at the site to 1.85 bcf/d, with sales gas output rising from 740 million cfd to 940 million cfd. This will also life sulphur production by 1.1 million t/a. Tenders for the front end engineering and design of the project are anticipated soon.

Bab

There is also a sour gas development planned at the Bab field, approximately 150km southwest of Abu Dhabi city, just east of Habshan. The project was originally planned to be on a similar scale to the Shah project, with a throughput of up to 1 bcf/d of sour gas, but recent assessments have lifted this to 1.9 bcf/d. However, the gas at Bab is even sourer than at Shah, with an average H_2S content of 33%. This is one of the reasons that the project has been delayed for several years, and it is also why the project as currently envisaged will involve reinjection of acid gas into the wells and little or no sulphur recovery. The project is reportedly still in the pre-FEED stage, with no firm timescale.

Associated gas

In addition to gas expansions, ADNOC is working to increase its oil production capacity to 5 million bbl/d by 2027, although this may require some renegotiation of its OPEC quota, which currently stands at just over 3.2 million bbl/d, against existing capacity of around 4.6 million bbl/d. CNPC has been recently awarded the EPC contract for expansion of capacity at the Bab oil field by 91,000 bbl/d and another expansion at Bu Hasa which will lift capacity by 100,000 bbl/d.

The expansion will produce additional volumes of associated gas from fields including ADNOC Onshore and Lower Zakum, possibly leading to an additional 1 bcf/f of associated gas being processed. A FEED contract was recently awarded for the expansion of existing facilities to handle the increase, which will also produce additional sulphur volumes.

Refining

In addition to its oil and gas extraction, ADNOC also operates ADNOC Refining (Takreer). Since 2019 this has operated as a joint venture with Eni and OMV. There are three refineries, the oldest at Umm Al Nar, which opened in 1976, and which has 150,000 bbl/d of capacity, and two at Ruwais, one with a capacity of 400,000 bbl/d (Ruwais Refinery East, which came on-stream in 1982) and one with a capacity of 417,000 bbl/d (Ruwais Refinery West, which began operation in 2014). However, ADNOC Refining has recently awarded a front-end engineering and designing (FEED) contract to a joint venture of Tecnicas Reunidas and Abu Dhabi's National Petroleum Construction Co (NPCC) for the Ruwais Refinery 3 project, which will recover hydrogen, ethane-rich gas, and sales grade propane, butane and pentane from off-gases discharged by units at the Ruwais refinery.

Sulphur output

Currently Abu Dhabi's sulphur production comes mainly from the Habshan and Shah gas processing plants. There is a total of 7.8 million t/a of sulphur capacity between the two sites. Another 400,000 t/a comes from the Das Island plant, with the Ruwais refinery generating another 200,000 t/a. A railway was constructed to bring granulated sulphur from Shah and Habshan to the port terminal at Ruwais, which has a capacity of 9 million t/a of sulphur. The new sour and associated gas projects are likely to add more than 5 million t/a of sulphur production capacity over the next five years, and sulphur production from Abu Dhabi is projected to rise to 11.5 million t/a by 2028, representing most of new incremental sulphur capacity in the Middle East and a substantial slice of new sulphur capacity worldwide over that period.

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Overcapacity in the battery industry

China's drive to build new battery production capacity for electric vehicles and stationary storage is leading to a familiar problem for the Chinese economy; overcapacity.

PHOTO: BYD

Chinese EV manufacturers like BYD are major consumers of batteries

China has been an enthusiastic proponent of electric vehicles and has been rapidly developing the capacity to produce them. It is home to the two largest battery cell manufacturers, CATL and BYL, which between them have 50% of the market for electric vehicle battery supply, and 73% of the Chinese market between them. And that supply is growing quickly. In 2022, global lithium ion battery cell capacity reached 706 GWh, but this increased by 44% in 2023 to reach 1,107 GWh. China accounted for 76% if this capacity in 2023, and 75% of incremental capacity growth that year. Europe and North America made up the bulk of the remainder. However, China's gigafactory capacity utilisation lagged behind at only around 45% in 2022, and similar or lower in 2023, far lower than the 75-85% utilisation that would be make or break for profitability in the rest of the world. The result has been a price war between manufacturers.

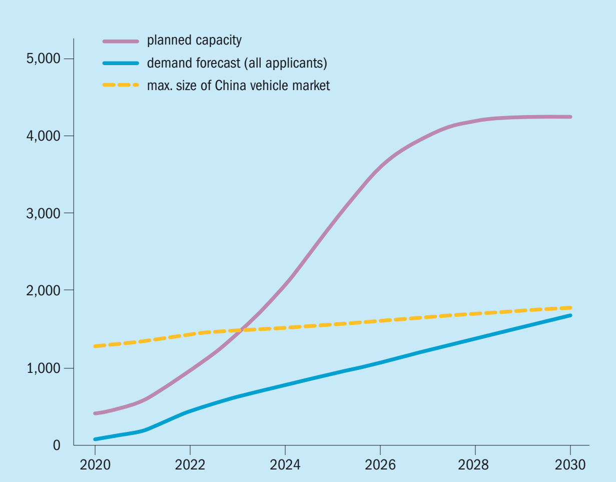
Industry observers have been warning that China was rapidly moving towards overcapacity for some months, but in January 2024 there was belatedly some recognition of this by the Chinese government. Xin Guobin, the country's vice-minister of industry and information technology, said that Beijing would crack down on "disorderly" competition in the electric vehicle market, and said that the government will take "forceful measures to prevent superfluous projects."

China is no stranger to overcapacity. It has overbuilt in a number of areas, from property to industrial sectors like steel and fertilizers. In the battery sector the Chinese government strongly encouraged the development of a domestic industry, designating electric vehicles a "strategic emerging industry" in 2009 and providing generous subsidies including tax breaks, land, energy and bank credits, as well as protectionist measures to shield the domestic industry from outside competition. The result has been breakneck growth over the past decade, to the extent that by the late 2010s the Chinese government felt able to allow foreign competition into the market. Tesla opened a gigafactory in Shanghai in 2018, and BYD's sales fell by 20% the following year. But the company was able to bounce back, introducing a new battery model and quadrupling sales from 2020 to 2022.

No sign of slowing

Despite the low utilisation rates, China's gigafactory capacity pipeline continues to grow, in theory to an ambitious 4,200 GWh by 2030, and new announcements continue to be made. This figure is twice the capacity that would be required if the entire existing Chinese vehicle fleet were to be converted to battery-electric vehicles. China accounts for 98% and 93% of all announced manufacturing capacity expansion plans until 2030 for cathode and anode production respectively. Yet many of the companies involved continue to press ahead with expansions, thanks to access to cheap capital, and investments have been de-risked by government support. There also seems to be a mindset of weighing the opportunity cost of not making investments. In some cases, the overall cost of producing and storing batteries has been less than the cost of idling the plant. This has led to a gradual accumulation of inventory.

Fig 1: **Lithium-ion battery cell gigafactory capacity in China, GWh**



Source: CRU

Export sales

In theory, it might be possible to sell excess product into export markets. Producing a battery pack in China is around 40% cheaper than it is in Europe. However, the impact of this is likely to be limited. Batteries are expensive to ship and are often designed for specific vehicles, making their use by other manufacturers more limited. There are also strong anti-dumping regulations in the major battery-consuming regions. In the US, the Biden administration has introduced measures to restrict the supply of batteries from China. Both the Bipartisan Infrastructure Law, which allocates credits for batteries and the critical minerals required to make them, and the Inflation Reduction Act (IRA), which includes a subsidy of up to $7,500 for each new energy vehicle, explicitly exclude any 'Foreign Entity Of Concern', which it has recently confirmed will apply to Chinese companies with more than a 25% stake in the company. From 2025, the restrictions will widen to include any critical minerals in the battery that are extracted, processed or recycled by a company from the restricted list of states.

Consequently, Chinese battery companies are focusing on the EU market. China represented around 8% of electric vehicle sales in the EU in 2023, and this could reach 15% in 2025. BYD is selling five models in eight European countries, including Germany, France, Italy, Spain and the UK. However, last year, the European Commission launched an investigation into low-cost Chinese EV imports, which could lead to import tariffs.

The more likely scenario is one of consolidation among battery manufacturers in China. At some point, the lack of orders, the build-up of stock and the accumulation of capital expenditure in new facilities will lead some manufacturers to failure.

Outside of China, however, countries aiming to reduce their dependency on Chinese production will continue to invest in and ramp up cathode and precursor projects. South Korea increased its cathode and precursor production by 35% year on year in 2023, and heavily reduced its imports from China as a result. Chinese companies will also look to comply with, or circumvent, adverse policies and trade tariffs, and form joint ventures in free trade agreement countries to make their material eligible for tax credits. Often these companies are partnering with established Western and South Korean battery and EV OEMs.

Lithium iron phosphate

It is a similar story with lithium iron phosphate (LFP) batteries. China has rapidly expanded LFP battery production, particularly for stationary energy storage systems. This has led to rapidly rising inventories of LFP cathode materials and cells, which manufacturers are attempting to offload at discounted prices. Oversupply is compounded by China's cost advantage. CRU's Battery Cost Model suggests that average production costs of Chinese-made LFP cells fell dramatically in 2023 due to cost savings within the cathode, especially the price of lithium carbonate. Lithium accounts for up to 35% of the cost makeup of LFP. The largest battery manufacturers are vertically integrated with stakes in lithium mines, while refineries in China are some of the lowest-cost operations globally. Thus, downstream companies are paying less for lithium chemicals compared to their Western counterparts. Chinese companies also have considerable experience in optimising production, leading to better factory yields, and have lower labour and electricity prices. So most western LFP battery manufacturers will continue to rely on Chinese materials and other components for several years while their nascent LFP industry develops. LFP cells produced by China will remain the cheapest on the global market, falling to as low as 50 $/kWh by 2028. Chinese companies are also spearheading sodium-ion technology, which will eventually deliver a further cost reduction.

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Stationary energy storage has massive growth potential in parallel to the build-out of renewable energy infrastructure, especially solar photovoltaic (PV) electricity generation. If nations start to follow their net-zero targets more closely, the demand from energy storage would easily surpass that of electric vehicles. An estimated 200 GWh of LFP cells intended for energy storage were produced in 2023. Actual demand was only 135 GWh, but this was still more than double the 2022 figure, in line with unprecedented growth in the PV sector.

At the same time, LFP is seeing increasing uptake in electric vehicle use as well. A total of 14.2 million electric vehicles and plug-in hybrids were delivered during 2023, an increase of 35% on 2022. Of this, 10 million were pure electric vehicles and 4.2 million plug-in hybrids. EV sales are forecast to reach 65 million per year by 2045, accounting for more than two-thirds of total light-duty vehicle sales, globally. LFP's share of this was 15% in 2020, but had reached 27% in 2022, and is forecast to reach 37% by 2028. China has particularly seen an uptake, as journeys tend to be shorter and LFP's lower energy density is outweighed by lower cost and greater battery life relative to nickel-rich batteries. Around 90% of demand for LFP batteries is currently accounted for by China.

However, the result of expanding vehicle use and the growth in stationary applications will be a substantial increase in global LFP demand, which is forecast to grow more than ten-fold over the next 20 years, spreading well beyond China to regions such as Europe, North America, and the rest of the Asia-Pacific.

Impact on mining

In 2023, the price of lithium ion battery packs fell from \$151/kWh to \$139/kWh, due to overproduction in China, with an associated fall in the price of lithium salts. CRU expects lithium carbonate prices to remain between \$10-15,000/t, with hydroxide trading at a \$500 – \$1,000 discount. This in turn has the potential to slow the pace of lithium extraction project development. The world's largest lithium producers have already issued revised guidance for 2024, and the start of new capacity expansions are being delayed. If the trend of lower pricing persists as expected, more companies will be forced to reconsider their plans. At current prices, higher cost lithium producers in Zimbabwe, in addition to Chinese lepidolite operations, are already likely to be producing at a loss. If prices continue to fall sharply, there could be some significant closures, which may be enough to plunge the market back into deficit, adding support to higher prices. Conversely, significantly lower raw material prices will support demand growth in the longer term.

Nickel projects are better protected against weak battery market fundamentals, given that battery demand only comprised 17% of primary consumption in 2023. Mines may still face cutbacks with oversupply mounting – the first indications of curtailments have already been announced from Australia. There are even concerns that Chinese investment into low-cost Indonesian projects will be reduced. Although prices of cobalt sulphate are hovering around record lows, investing in production cutbacks are unlikely to materialise. Smaller Ni-Co sulphide miners may be forced to rethink their plans, but cobalt producers in Indonesia and the DRC are unlikely to be deterred as long as they continue to enjoy healthy profits on nickel and copper.

Policy will continue to be a key factor in determining raw material prices, with the Inflation Reduction Act creating parallel markets for high-cost chemicals like lithium salts and nickel sulphate as companies fight over the limited supply of compliant materials. This will allow producers to charge more for their product for an extended period, even during times of relative oversupply in the wider market for materials, as will be seen in the nickel markets.

Phosphoric acid

The automotive sector currently represents about 5% of purified phosphoric acid (PPA) demand, for LFP production, but that number is expected to jump to 24% by 2030. The global purified phosphoric acid industry will likely need to double in size over the next 20 years to cater to the projected growth in LFP usage. Only a small fraction of total phosphoric acid supply is currently suitable for lithium ion battery applications. For LFP, food grade purified phosphoric acid is needed, with demand for this battery input so far being driven by food and industrial usage.

Currently, virtually all the world's LFP cathode capacity is based in China. The iron phosphate that is used to produce those cathodes is also sourced domestically, as China is self-sufficient in phosphate and is already a significant importer of iron ore for its steel industry. However, recently there have been a number of announcements of new LFP battery cell plants in North America and Europe for construction over the next 5-10 years, with total planned cell capacity surpassing 150-200 GWh in these regions. How this impacts purified phosphoric acid demand worldwide depends upon how much capacity outside China ends up being developed, but at a global level – regardless of whether China continues to dominate LFP cathode and iron phosphate production, or other regions become more self-sufficient – long-term forecasts show overall demand for purified phosphoric acid far outstripping current global capacity in the long term, primarily due to this growth in the LFP sector. CRU projects that in the base case, LFP demand growth would require global purified phosphoric acid capacity to nearly double in size by 2045 relative to current levels (+95%), while in the upside scenario capacity growth could be as high as 120%.

The magnitude of this LFP demand growth globally, and the uncertainty regarding the extent to which it will be distributed geographically, presents a number of strategic questions for existing and potential stakeholders in the industry – whether they be phosphate producers, other raw material suppliers, cathode and battery manufacturers, investors, or policymakers.

Continuing technology evolution

Meanwhile, the battery market continues to make significant technological progress and 2024 will be a year in which some of this new technology is rolled out on a commercial scale. CRU anticipates sodium-ion and lithium manganese iron phosphate (LMFP) cells will power vehicles on the road. While these technologies will initially be constrained to the Chinese market, it will be a sign of bigger things to come for the global battery industry. JAC's Yiwei vehicles, powered by HiNa sodium ion batteries, have already rolled off the production line in January, while BYD recently broke ground on its first 30 GWh sodium ion cell plant in Xuzhou, China. Use of sodium-ion cells in stationary energy storage (the forecasted primary market for the technology) is also expected to grow rapidly. Similarly, LMFP cells will be used towards year-end as major battery manufacturers, including CATL and Gotion, work to resolve some of the technical challenges with the chemistry. ■

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Sulphur in Europe

Falling volumes of sulphur from refining and sour gas could turn Europe into a sulphur importer.

Petroineos' Grangemouth refinery, Scotland, soon to convert to green feeds.

Europe's supply of sulphur is falling, potentially turning the continent into a net importer and changing the dynamics of the market away from liquid sulphur. Traditionally, European sulphur output has come from three sources; refining, sour gas processing, and Poland's sulphur mine. However, output from all of these sources has been in long term decline.

Refining

The European refining industry has seen a prolonged contraction. Since 2009, out of 100 operational refineries in Europe, 26 have closed, and another five have switched towards biofuels processing. The drivers behind this have mainly been falling domestic demand and cheaper imported products. European demand for refined products has fallen from a peak of around 15.2 million bbl/d in 2000-2005 to 12.7 million bbl/d in 2019, and then dropped by another 1.0 million bbl/d due to covid. Although there has been a bounce back after covid restrictions were lifted, the war in Ukraine has also had a major impact by restricting imports of Russian crude and – at the end of 2022 – banning it altogether, although there is now a growing industry in sanctions evasion by, for example, transferring oil between vessels to mix Russian crude with crude from other sources to disguise its origin. European refinery output in late 2023 was down by 600,000 bbl/d compared to the same period for 2022. Most of the decline in demand from 2005-2015 was not from reduced use of transport fuels, but rather the phaseout of electricity generation from oil and oil products, but now European refiners face a continuing fall in fuel demand from reducing consumption as more electric and hybrid vehicles are sold. Out to 2030, fuel consumption is expected to drop by about one third compared to 2018 figures, removing around 2 million bbl/d of demand for refined products.

Refinery margins are also back lower, after a year following the invasion of Ukraine when high fuel prices meant that refineries were making money for a while. The reduction in supply of diesel from Russia has also kept margins for that product good. Nevertheless, periods of loss making have dissuaded European refiners from investing in upgrading and modernising refineries, and also led to cutbacks in maintenance which have led to a spate of incidents forcing shutdowns in the past year or so.

There is also increased competition from cheaper refineries in other regions, including the Middle East such as Kuwait's new 615,000 bbl/d Al-Zour refinery, and West Africa, with the 650,000 bbl/d Dangote refinery in Nigeria due to start up in 2024.

The expected weaker demand outlook for oil products, and an increased focus on emissions performance has prompted a wave of announcements by oil refiners to close or convert capacity to non-crude feedstock. Six European refineries have closed since 2020, mostly older, less complex refineries. This may reach eight following the decision by UK-Chinese joint venture Peotrineos to convert its 150,000 bbl/d Grangemouth refinery in Scotland into an import terminal, and the expected closure of Shell's 147,000 bbl/d Wesseling refinery in Germany in 2025. Total loss of capacity between these refineries is around 935,000 bbl/d. Eni is also looking at converting its 84,000 bbl/d Livorno refinery in Italy to focus on base oils and biofuels and ending crude refining.

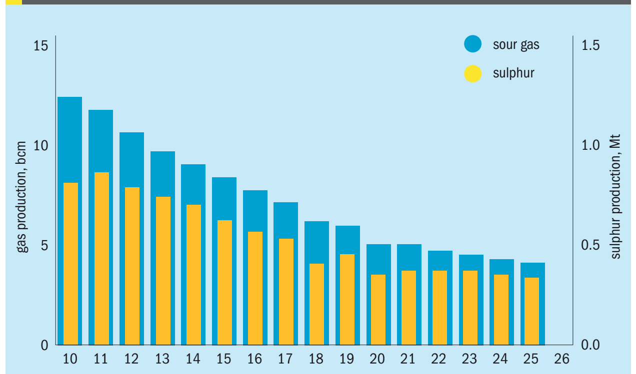
On the sulphur side, the restrictions resulting from the invasion of Ukraine have forced European refiners to replace Russian oil with lighter and sweeter crudes, particularly from the United States. This means a lower output from the refineries' hydrocracking, fluid catalytic cracking and coker units, of potentially up to 7%.

Sour gas

At the same time, sulphur from sour gas processing is also continuing to decline. With the closure of the Lacq plant in France and its conversion to CO_2 capture and storage, sour gas processing in Europe is now limited to the Grossenkneten gas field in Germany. Production here is expected to continue decreasing year on year as reserves are depleted. In 2010, sour gas processing at the Grossenkneten plant was about 12 bcm, but in 2022 that was 5 bcm, and sulphur production has dropped to below 400,000 t/a, as shown in Figure 1.

Based on reported proven reserves, the operation has a few years of production remaining, but there is a risk that it may prove uneconomical before reserves are fully depleted. The tight availability of natural gas in Europe stemming from the war in Ukraine and related trade issues means that the gas field is currently being strongly utilised, and this may shorten its life.

Fig 1: Großenknetten closure forecast in 2026 as reserves decline



Source: CRU, WEG

Demand

On the demand side requirements for sulphur have also been falling. The European chemical industry has faced issues with high feedstock and energy costs since the Ukraine war began, and there have been a number of closures or operators running at reduced rates. This was also true of downstream phosphate processing in Europe to produce fertilizers. Overall European sulphur consumption for 2023 was down nearly 30% compared to 2022, helping to more than offset the fall in production. As with other commodities, there are also issues with cheaper imports, in areas such as caprolactam and titanium dioxide, which have weighed on European chemical production. Falling energy costs should bring some of this capacity back, but it remains to be seen to what extent this occurs.

Remelting

Sulphur consumers in Europe are geared up to handle liquid sulphur cargoes. This limits their option to import and remelt solid sulphur, although small volumes of liquid sulphur are imported from the US. A few years ago, refinery closures and falling sour gas sulphur production led to increased interest in sulphur remelter projects to import solid granulated sulphur from overseas, providing supply flexibility in much the same way that Mosaic's sulphur remelter in Florida has done.

In 2020, Saconix bought the assets of the Brake sulphur terminal as part of its plans for a terminal and melter there, which were announced in 2019 with planned capacity of 200,000 t/a. Aglobis also announced in June 2020 that it planned to build a terminal on the Rhine with 400,000 t/a of remelting capacity. However, as falling sulphur demand helped to offset production cutbacks, and refineries began running at high rates to take advantage of improved margins in 2022 and early 2023, so the need for these projects began to seem less pressing. But now the pendulum seems to be swinging once again, and there is renewed interest in possibly moving these projects forward over the next few years, in anticipation of tighter liquid sulphur markets in Europe, such as have been seen in early 2024.

Acid

There is a trade-off between sulphur and sulphuric acid demand in Europe depending on the relative prices of the two commodities. When sulphur prices are high and acid prices are low it makes sense for consumers to buy acid if they are able to handle it. This is complicated by export demand, however, with importers like Morocco occasionally in competition with domestic buyers. Europe is overall a net sulphuric acid exporter, with a number of base metal smelters providing surplus acid. European sulphuric acid prices dropped considerably from a peak in June 2022 following the Ukraine invasion due to a lack of demand from downstream consumers driven by high energy costs. Prices reached a low point in August 2023, since when they have risen back to around $50/t.

With European acid demand forecast to recover or even increase slightly over the next few years, and sulphur supplies continuing to fall, it is possible that Europe could turn to being a net sulphur importer over the next couple of years. ■

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SulGas Mumbai 2024

More than 155 attendees, representing more than 68 companies gathered in Mumbai, India, from January 31 to February 2, 2024 for the annual SulGas® conference, organised by Three Ten Initiative Technologies LLP. We report on the key highlights of the event.

SulGas Mumbai 2024, now in its sixth year, took place over three days from January 31 to February 2 at Novotel Juhu Mumbai. The event brought together public sector oil companies, private refiners, petrochemical, chemical and fertilizer plants, licensors, engineering companies, solvent and column equipment manufacturers as well as control and instrumentation companies. Notable end users including BPCL, ExxonMobil, HMEL, HPCL, IOCL, MRPL, Nayara, Petronas and RIL were among the participants.

The conference featured 33 speakers in interactive technical sessions, with panel discussions at the end of each session and open Q&A, fostering maximum technical exchange among participants. A dedicated exhibition area with full-day access for all delegates ran alongside the conference.

The opening keynote speaker was Mr. S. Bharathan, Director (Refineries) of HPCL, who set the tone for the conference, discussing how sulphur recovery units are indispensable, how challenges can be addressed through innovations, the importance of collaboration for sustainable practices and the commitment to a greener tomorrow.

The conference agenda comprised ten sessions that covered a broad range of topics including: decarbonisation and carbon capture, enhancing SRU capacity and recovery, advances in SRU instrumentation, simulation and control, SRU waste heat boilers, gas processing, operational challenges with SRUs, emissions reduction and decarbonisation, and tail gas treating.

Some of the main topics of the conference are highlighted below.

Decarbonisation and carbon capture

WSA technology for the Indian market

India is a country that depends on imports of crude oil and gas, as well as sulphur and sulphuric acid, which are essential for various industries. Therefore, energy efficiency and product margins are crucial factors for choosing a sulphur recovery solution. Igor Kostromin of Topsoe showed how the WSA technology could replace the conventional SRU and produce sulphuric acid directly from sulphurous gases, without the need for sulphur burning. To meet the strict environmental standards and to maximise the profitability of sulphur recovery, one of the leading refineries in India has opted for Topsoe WSA technology. The plant produces commercial-grade sulphuric acid, which is sold to the domestic or international market. It also generates superheated steam, which is used for power generation or process heating. By using the WSA plant, the refinery significantly reduces its carbon footprint.

Processing ammonia-rich refinery sour gases

Saptarshi Pual of Engineers India Limited discussed the need to explore alternatives for processing of ammonia-rich sour gas streams in refineries as well as gas processing complexes.

Co-processing of theses streams with the H_2S-rich stream for NH_3 destruction in the main burner of SRU often causes severe operational issues, while processing via the incinerator (i.e. Claus section bypass) is associated with high capex, and sometimes may lead to high NOx generation/environmental issues. The destruction of ammonia via these routes in Indian refineries is typically in the region of 41,891 t/a, at a time when ammonia demand in India is increasing every year.

In order to overcome the challenges of processing ammonia-rich refinery sour gases and to convert them into a revenue generating stream, EIL has developed and patented ammonia recovery technology to recover ammonia from NH_3-rich sour gases and convert it into valuable products like anhydrous ammonia or aqueous ammonia. The overall recovery of ammonia is >99% and meets the required product specifications: BIS: 662-1980 for anhydrous ammonia and BIS: 799-1985 for aqueous ammonia, using an approach that helps towards minimising carbon footprint.

Energy optimisation in amine sweetening units

Energy optimisation is a critical concern in the oil and gas industry because it directly impacts operational efficiency, cost effectiveness, and environmental sustainability. One area in which significant energy savings can be achieved is the amine sweetening process used to remove acidic gases such as carbon dioxide (CO_2) and hydrogen sulphide (H_2S) from sour natural gas. Aparnu Saiju of SLB Oilfield Services Company explored the concept of energy optimisation using power recovery turbine (PRT) technology in amine sweetening units, focusing on its potential benefits, implementation strategies, and environmental implications.

The PRT is designed to capture energy that would otherwise be released during pressure reductions and convert it into useful mechanical energy. This recovered energy can be used to reduce the power consumption of various equipment within the unit, such as pumps and compressors, thereby enhancing overall process efficiency. Because the energy produced using PRTs can be used to reduce the power consumption, the PRTs can be instrumental in reducing Scope 2 emissions and help contribute to the industry's sustainability goals. The decreased use of energy generated from fossil fuels reduces the emission of greenhouse gases such as CO_2.

Enhancing SRU capacity and recovery

Employing effective oxygen enrichment

Sulphur recovery units across the globe need to upgrade to meet new demands for the future. The most common requirement is to process higher sulphur loads as refineries across the globe are processing crudes with higher sulphur content and are also implementing residue conversion projects. Other adaptations are frequently required for processing more challenging feed 'cocktails' which may be encountered as there may be a requirement to process lean acid gas streams. Jyoti Bist of Fluor Daniel India Pvt discussed the merits of oxygen enrichment to manage multiple revamp requirements in SRUs, both for capacity enhancements as well as to deal with very lean acid gas streams, as a more efficient and cheaper option to refiners than building a new plant.

Novel case study combining oxygen enrichment and SO_2 recovery

Continuing with the theme of maximising sulphur capacity, Kausik Mazumder of Engineers India Ltd presented case studies carried out on a Claus-based sulphur recovery unit (SRU) to enhance its capacity by up to 76% and improve sulphur recovery from 99.2% to 99.9%. A hybridised process was used, which utilises oxygen enrichment to increase capacity while effectively managing the main combustion chamber temperature and SO_2 emissions through the incorporation of the SO_2 recycle process.

In addition to recovering SO_2 from the incinerator flue gas, the SO_2 recycle process demonstrates the capability to recover and recycle SO_2 from various other flue gases within refineries. Redirecting this reclaimed SO_2 to the SRU can significantly reduce overall sulphur emissions from refineries. The findings of the study underscore the substantial potential of combining oxygen enrichment and SO_2 recycle to not only enhance SRU capacity but also to improve overall unit operation and mitigate SO_2 emissions.

Advances in SRU instrumentation, simulation and control

SRU control strategy

Compositional changes to the acid gas feed to the sulphur recover unit (SRU) cause trouble for plant control and can lead to higher SO_2 emissions or down time for the SRU. There are two main control strategies employed: feedback control and feedback with feedforward control. A third less commonly used control strategy is dual air demand (DAD). Selwyn Pandian of Galvanic Applied Sciences discussed how DAD can be used to improve SRU performance and reduce SO_2 emissions by deploying an H_2S and SO_2 analyser after the first sulphur condenser. The ability to react to and correct for acid gas feed composition and flow upsets quickly reduces the risk of soot formation on the first catalyst bed and protects the tail gas treating unit from the effects of SRU excursions.

Kinetics-based sulphur plant models

SulphurPro® is a mass and heat transfer-based simulation software that employs a reaction kinetics approach to simulate the entire sulphur plant, from the reaction furnace to the stack. It relies on fundamental chemistry and detailed information on kinetic reaction mechanisms and heat transfer, providing a significant advantage over other simulation tools, and incorporates the latest sulphur research from organisations like Alberta Sulphur Research Limited (ASRL).

Dr Anand Govindarajan of Three Ten Initiative Technologies demonstrated four use cases where a kinetics-based model assisted plant operations in maintaining reliability and saving capital and operating expenses.

How to optimise SRU emissions during upset conditions

Modern process instrumentation has the potential to help reduce the emissions from a sulphur recovery unit, but the application challenges with regard to measurement reliability and safety aspects are high (the SRU has the most toxic gas mixtures of the entire refinery). In his presentation Jochen Geiger of Ametek Process Instruments stressed that knowledge, understanding, and awareness training are essential to maintain the instruments, and that without the instrument signals the emission targets are not achievable.

Auto loading scheme for air blowers

Nirmalya Nandi of Bharat Petroleum Corporation described an auto loading scheme that has been introduced for the main combustion chamber air blowers at BPCL Bina refinery. The new auto loading scheme uses the ADA signal and discharge pressure and has successfully overcome the problems that had been experienced with the manual loading scheme, which relied on operator judgement based on acid gas feed flow and reading of the air demand analyser as per design.

The Digital Process Monitor

The pursuit of operational excellence requires continuous process monitoring, together with qualified analysis of the collected data. Digital Process Monitor (DPM), a cloud-based solution co-developed by a series of companies within the Maire Group (Nextchem, Stamicarbon, Tecnimont, KT-Kinetics Technology) provides a process digital twin which consists of an accurate process plant model, which, by incorporating the licensor's knowledge and expertise in sulphur recovery technology, can provide continuous insights into plant

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performance. Process data are captured from the plant to feed a digital replica of plant processes, unlocking operational excellence through increased productivity and energy savings with a consequent reduction in the plant's carbon footprint.

Daniela Boni of NextChem provided an overview of the main features of the Digital Plant Monitor, focusing on the related benefits in terms of overall operational improvements and plant efficiency for the sulphur recovery unit.

Ammonia destruction in SRUs

A detailed reaction mechanism for predicting ammonia destruction in sulphur recovery units has been developed and validated by Indian Institute of Technology Delhi that effectively captures the combustion and pyrolysis chemistry of ammonia in the presence of several active species such as H_2S, CO_2, and hydrocarbons found in the feed stream to SRU. In his presentation, Dr Abhijeet Raj of IIT explained how the mechanism was then used to investigate the suitable process conditions that could lead to the destruction of ammonia in the thermal stage of the SRU. The results suggest that the detailed reaction mechanism proposed in the study can be used to optimise the furnace parameters to achieve the desired levels of ammonia destruction without significantly decreasing sulphur production and aggravating CO emissions from the SRU.

SRU Claus furnace and waste heat boilers

Anurag Kumar of Magnalore Refinery and Petrochemical Ltd shared the root cause analysis for a case study with multiple tube failures in an SRU waste heat boiler. This presentation was followed by another case study by Prasenjit Pal of Engineers India Ltd who reported on failures to Claus furnace refractory, brick lining, choke rings, thermowells, tubesheet and areas around nozzles. A root cause analysis of the failures was carried out addressing design, material selection and quality of workmanship during installation.

Gas processing

Amine foaming issues

Mohd Firdaus Sabturani drew upon PETRONAS' extensive experience of operating amine-based acid gas removal units (AGRUs) in their LNG processing plant where foaming issues are commonly encountered. Severe foaming issues which cause loss of production or plant upset are typically handled via a root cause failure analysis (RCFA) approach whereby each RCFA session shall be carried out by the multi-disciplinary team of engineers including process technologist, operation, maintenance, inspection and reliability engineers.

PETRONAS has identified several common root causes and subsequently recommended the necessary operational and design improvements to address the identified root causes. These operational and design improvements have improved the performance of the amine treating units and reduced foaming issues significantly to achieve a stable AGRU operation.

Application of improved version of Thiopaq O&G

Recently, an improved version of the biological sulphur recovery process Thiopaq O&G (TOG) process has been developed: Thiopaq O&G Ultra (TOG Ultra). Like TOG, the TOG Ultra process is a biotechnological process, and uses naturally occurring bacteria to convert dissolved sulphide into elemental bio-sulphur.

Srinivas Vadlamani shared the results from the multi-year operation of a pilot plant of the TOG Ultra process, and the findings from the design and engineering phases of the implementation of the first full-scale plant. The TOG Ultra process achieves a 50% lower NaOH consumption and bleed stream formation, leading to a 25% decrease in opex compared to the TOG process. In addition to a strong reduction in opex, the TOG Ultra process has improved the acceptance of biological SRUs for larger sulphur loads.

Operational challenges with SRUs

SRU alarm management and operator training

Human errors are still one of the major causes for unit upsets and hazards. The Operator Training Simulator (OTS) provides a perfect platform to address this concern. Pranay Veer Singh of Fluor Daniel India Pvt provided an in-depth insight of the OTS and highlighted the inbuilt scenarios inside the model, the most important being the start-up, shut down and specific upset scenarios.

Alarm management provides further insights to operations personnel as to how to minimise errors resulting from delayed response to reaction to plausible alarms in an SRU. Alarm priority and ranking based upon the criticality of SRU plant operation cycle was also highlighted.

New SRU block at HPCL, Visakh Refinery

Part of the Visakh Refinery Modernization Project (VRMP), a new SRU block has been installed at the HPCL refinery, Visakhapatnam, India. Ellen Ticheler of Worley Comprimo discussed the different stages of the project from the engineering phase up to and including the start-up, and the various challenges encountered during the project.

Tail gas treating

TGTU operations

Akash Mendpara of Sulfur Recovery Engineering presented a concise yet thorough analysis of sulphur recovery in the oil and gas industry, emphasising the critical role of tail gas treating units (TGTUs). Critical cost drivers in a TGTU were discussed supported by real world case studies and simulation model data.

The research identifies natural gas consumption in thermal oxidisers of SRUs as a significant cost driver. Effective management of excess oxygen levels and temperature control in these oxidisers is crucial. This management is essential not only for reducing operational costs but also for minimising CO_2 emissions, aligning with environmental compliance mandates and carbon tax regulations.

SO_2 breakthrough in a tail gas unit

Ganesh Gujar of Bharat Petroleum Corporation discussed ways to prevent and mitigate SO_2 breakthrough in a tail gas unit and presented a range of recommendations including having effective contaminant control in the amine and SWS systems providing feed to the SRU/TGTU, avoiding manual air control operations, making neutraliser injection an automated system triggered by a reliable pH meter, and installing a rapid purge for spent solution in the desuperheater sections of two stage quench towers that use pre-loaded caustic. ■

The seventh edition of the SulGas conference is scheduled to take place in Mumbai from February 5 to 7, 2025.

A smarter way to treat lean sulphurous off-gases

The implementation of WSA technology to recover sulphur as sulphuric acid from lean sulphurous off-gases offers significant environmental benefits. These include waste reduction, resource efficiency and reduced overall CO_2e footprint, while also producing profitable sulphuric acid. By embracing such practices, industries can ensure improved or better consumption and production patterns and foster a more sustainable and responsible future. **J. Feddersen** and **S. S. Johansson** of Topsoe illustrate these benefits using three distinct industrial applications where WSA technology provides a smarter way to treat sulphurous off-gases. It is not only waste stream management in the three cases, but also reduced transportation of chemicals, reduced opex and reduced CO_2e footprint.

Taking a people- and environment-first approach to business can have multiple benefits across sustainability, efficiency, and cost effectiveness. For instance, reducing waste, using resources more efficiently, and implementing practices that help mitigate negative environmental impact allows companies to save on operating costs while improving reputation and image. A more sustainability-focused brand profile is hard to put a price on, but it can increase customer loyalty, attract and retain qualified employees, and help secure access to investment. Embracing sustainability also helps businesses to align with the United Nations' Sustainable Development Goals like the goal on "Responsible consumption and production".

In a multitude of industries, lean sulphurous off-gases, characterised by SO_2 concentrations in the range of 0.1 to 6.0 vol-%, will often go untreated or be treated using scrubbing technologies that generate waste streams. Wet gas Sulphuric Acid (WSA) technology can be utilised to responsibly recover sulphur as sulphuric acid from such lean waste streams. This is illustrated here by three distinct industrial applications where WSA technology provides a smarter solution for waste stream management.

The metallurgical industry, like many industries, generates lean SO_2 gases that are left untreated or treated using scrubbers. Similarly, the pulp and paper industry experiences substantial losses of sodium and sulphur as waste streams throughout the pulp mill, necessitating additional purchases of NaOH and H_2SO_4. Refineries also face the challenge of treating lean off-gases such as the Claus tail gases, often resorting to amine absorption and fuel gas incineration, which leads to increased overall CO_2 emissions. By adopting WSA technology, these industries (and many others) can efficiently recover sulphur as profitable sulphuric acid from lean sulphurous off-gases, mitigating waste generation, reducing the loss of valuable chemicals, and minimising greenhouse gas emissions.

Metallurgical industry

The metallurgical industry is a vital part of the manufacturing sector and the green energy transition, responsible for producing various metals, including nickel, zinc, copper, molybdenum, platinum group metals. It is a highly energy-intensive industry that relies on a range of processes to extract and refine metals from ores. During extraction, several metal processing plants generate SO_2 off-gases from the roasting or smelting of non-ferrous metal ore. From some of the metallurgical processing plants these gases are relatively lean up to 6 mol-% of SO_2, requiring further treatment. Traditionally, these gases have been treated in scrubbers, generating waste products, or they have not been treated at all and simply released through the stack. However, the latter is becoming more infrequent due to environmental restrictions.

WSA technology is a good alternative to scrubbers as the operating cost and waste management are significantly reduced, while the SO_2 off-gases can be converted into profitable sulphuric acid.

Case story – Molybdenum plant in Asia

With increasing demand for molybdenum products, several companies around the world are considering increasing production. A new molybdenum roasting site in Asia required a solution for treating the off-gas with SO_2 concentration around 2 mol-%. After comparing a scrubber using $Mg(OH)_2$ with Topsoe's WSA technology, it became clear that WSA technology was the best match due to several reasons including:

- Scrubbers require continuous chemical consumption and waste management of sludge and water; WSA technology significantly reduces these parameters. This reduction leads to lower operating expenses for WSA technology, making it the cheapest solution after only a few years of operation, despite a higher initial capital expenditure.

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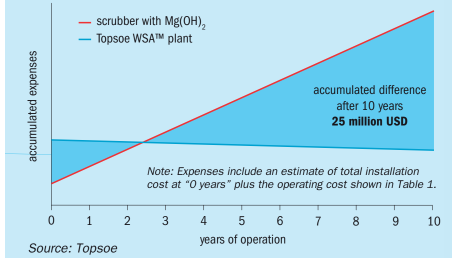
Table 1: Annual operating expenses and income in USD

Expenses	WSA incl. acid concentrator	$Mg(OH)_2$ scrubber
Chemicals (mainly ($Mg(OH)_2$)	-	3,500,000
Energy (power, natural gas)	700,000	600,000
Water	6,000 (cooling water)	200,000
Instrument air	50,000	-
Waste treatment (water, sludge)	-	120,000
Total operating cost per year	756,000	4,420,000
Income of 98 wt-% sulphuric acid	+ 1,000,000	-

Source: Topsoe

Fig 1: SO_2 gas cleaning technologies cost comparison: scrubber using $Mg(OH)_2$ versus WSA technology



Source: Topsoe

- WSA technology produces valuable sulphuric acid, particularly beneficial in a country that needs to import sulphuric acid.

The above benefits are clear when comparing the main expenses for the two technologies in Table 1. WSA technology is proved to be the cheapest option after just a few years of operation (Fig. 1). A WSA unit requires additional equipment, piping and design, hence the investment will typically be higher than a scrubber. Even though the total investment cost is higher, soon the high expense for scrubbing consumables is felt, making WSA more cost efficient in the long run. The profit on 98 wt-% sulphuric acid makes the WSA unit more and more favourable year by year.

The annual operating expenses are compared in Table 1. The list of expenses is a simplified version and does not include expenses for labour, potentially transport cost for chemicals, waste or products, maintenance or operating availability. This is because these factors will be highly dependent on operational excellence and plant location.

The WSA unit includes an integrated sulphuric acid concentrator (in short called an ISAC) to ensure a high purity sulphuric acid of 98 wt-%.

The ISAC uses hot, dry air to drive some of the water content out of the sulphuric acid. Depending on what and where the sulphuric acid will be used, lower concentrated sulphuric acid can be sufficient, and the ISAC is not required. This will reduce the power consumption by approximately 30%.

This example is based on the following parameters:

- off-gas flow up to 35,000 Nm^3/hr;
- SO_2 flucating between 1-2 mol-%;
- off-gas temperature around 45-55°C;
- location in low-cost country;
- maximum allowed SO_2 emission of 450 mg/Nm^3;
- expenses for labour, maintenance, operating availability, cost of transportation have been excluded for simplification;
- the income of 98 wt-% sulphuric acid is based on a price of \$50/t;
- $MgSO_4$ is sent directly to wastewater treatment, hence it generates no income in this case.

Despite the business case not being favourable if only the total installation cost is considered, WSA technology will be the most cost-effective solution over time, while reducing waste management significantly. Hence, the WSA technology was selected for the new molybdenum roaster planned to be commissioned in 2025.

A similar but more extensive assessment was made by Anglo American Platinum to comply with new dust and SO_2 emission standards at Polokwane Metallurgical complex in South Africa. Close to 40 different abatement technologies were evaluated, and the final selection went to WSA technology as it was the best operational match as well as economically. The WSA unit was commissioned in 2021 and is operating very well.

Pulp and paper industry

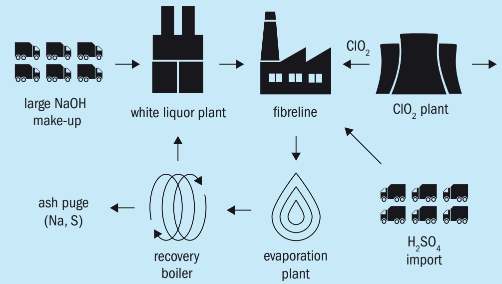
The pulp and paper industry produces paper products from wood, via pulp. Pulp production is a highly energy-intensive process that relies on a range of chemical technologies utilising sodium hydroxide and sulphuric acid. During production, a pulp mill generates concentrated non-condensable gases (CNCG) containing relatively low levels of sulphurous compounds, including mercaptans and H_2S, as well as other hydrocarbons. These gases are traditionally removed in recovery boilers or special CNCG boilers with NaOH scrubbers to collect the waste sulphur and provide the only means of removing sulphur from the recovery cycle. However, this sulphur is recovered as Na_2SO_4, resulting in the loss of sodium in the mill, which then needs to be imported and replenished to the plant. Recovering the sulphur as sulphuric acid for reuse within the site increased circularity of the production process. This can help minimise chemical import to the plant and reduce waste, and reduce waste management, contributing to a lower carbon footprint with less transportation to/from the plant.

Case story – Pulp mill in Brazil

Klabin, a Brazilian pulp and paper producer, is committed to optimising the use of by-products generated in its mills and to significantly reducing greenhouse gas emissions. As part of achieving these goals, the company has implemented the Topsoe WSA solution, which enables the production of sulphuric acid from gases formed in the mill itself. This represents an important step towards a circular economy, which aims to close material and energy loops completely and reduce energy input, emissions, and waste to a minimum.

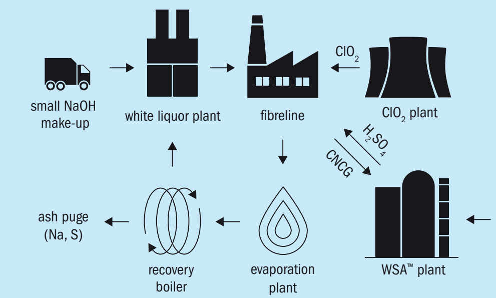
The WSA technology has been tailored to Klabin's specific pulp and paper facility, resulting in a reduced environmental impact and improved economics for the plant. The very high sulphur recovery achieved by the WSA technology leads to a reduced import of both sulphuric acid and sodium hydroxide.

Fig 2: Pulp mill traditional recovery cycle (without WSA)



Source: Topsoe

Fig 3: Pulp mill recovery cycle with WSA technology (Sulfoloop) for recovery of sulphur as sulphuric acid



Source: Topsoe

At the Ortigueira mill, operated by Klabin in southern Brazil, commercial grade sulphuric acid is produced from concentrated non-condensable gases generated on-site, as the first plant in the pulp industry worldwide.

The sulphuric acid production is based on the WSA technology and is designed to produce 150 t/d of high-purity (98 wt-%) sulphuric acid. The plant will supply all the sulphuric acid consumed in the pulp production process in "Puma I" and "Puma II" processing lines at the Ortigueira mill, as well as for the pulp production line at Klabin's Telemaco Borba mill, 25 km away. Other resources are also used more efficiently as the sodium losses in the plant are cut by the introduction of the WSA unit; before producing their own sulphuric acid from waste gases the pulp mill had to remove sulphur from the recovery cycle of the pulp mill by means of taking out $NaSO_4$ which leads to loss of Na in the recovery cycle (see Fig. 2). This sodium is typically replaced by adding NaOH to the mill, which must be transported to site in large quantities. By removing sulphur as sulphuric acid, Klabin could greatly cut down on the import of sodium hydroxide, which further reduced the transportation of chemicals to the site (see Fig. 3).

Previously, sulphuric acid and caustic required in the two mills had to be trucked 500 km from the port, with high labour input and greenhouse gas emissions. The WSA unit has enabled the reduction of trucks covering these 500 km from 6 per day to only 1, with a saving on fuel and CO_2 emissions of 6,000 tonnes per year as per calculations in Table 2. According to Klabin's Projects Director, João Braga, the sulphuric acid plant is an excellent example of how the company is closing its material loops with the aid of technology. Recovering sulphurous gases is particularly important among the by-products generated in Klabin's mills, and the WSA technology represents a significant step towards a circular economy.

Oil refineries

The oil refining industry is a critical part of the energy and transportation sector, responsible for processing crude oil into various products, including gasoline, diesel, and jet fuel. It relies on a range of processes to refine crude oil into high-quality fuels that meet strict regulatory requirements. During the refining process, the H_2S gases are generated from hydrotreaters, via amine units, and SWS gases from sour water strippers. These gases are typically treated in Claus plants to recover the sulphur. The Claus plants generate a tail gas that traditionally did not require further treatment; however, due to updates in most national legislation the lean tail gases will require further treatment to bring down the sulphur emissions. The treatment of such Claus tail gases can be done in many ways; two of the most common ones are H_2S recovery in an amine unit followed by incineration, or incineration followed by SO_2 removal in a caustic scrubber. Both options have drawbacks; a scrubber solution comes with chemical consumption and waste generation, while the amine unit option has higher CO_2 emissions associated with it due to the high energy consumption and low efficiency.

Table 2: CO_2 equivalent savings from reduced truck transport to mill site

Reduction of trucks per day	Operating days/year	Average truck weight (t)	CO_2 emissions per distance* (kg CO_2e (t & km))	Distance travelled by truck (km)	Total annual CO_2e savings (t/a)
5	350	25	0.138	2 x 500	6,038

Source: Topsoe

**Values based on Ecoinvent environmental database v. 3.9*

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Case story – An oil refinery in Eastern Europe

A refinery in Eastern Europe faced the challenge of finding a reliable and effective solution for the treatment of its Claus tail gases to meet sulphur emission compliance regulations. The target was to reach a sulphur dioxide emission of maximum 90 ppmv in the stack, corresponding to a total sulphur removal efficiency of 99.93%.

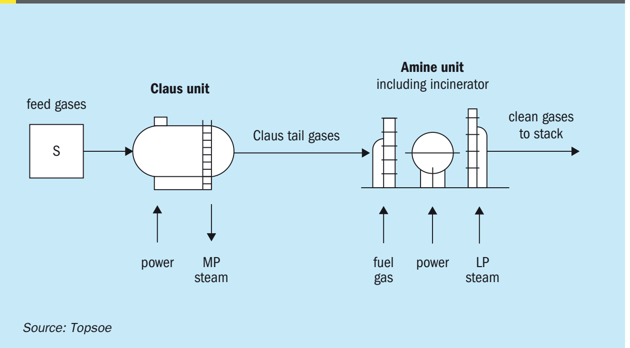
After evaluating different technologies for the treatment of Claus tail gas, the refinery narrowed down their options to two: Topsoe's WSA technology and an amine-based tail gas treating unit.

To highlight the differences between a traditional amine-based Claus tail gas treatment, and Topsoe's WSA technology, a comparison on CO_2 equivalent (CO_2e) savings generated by the two options has been made. The comparison is made on a standard refinery sulphur recovery unit, recovering 270 t/d sulphur.

The main CO_2 equivalent sources for each Claus tail gas treatment option are shown in Fig. 4 and Fig. 5 and can be summarised as:

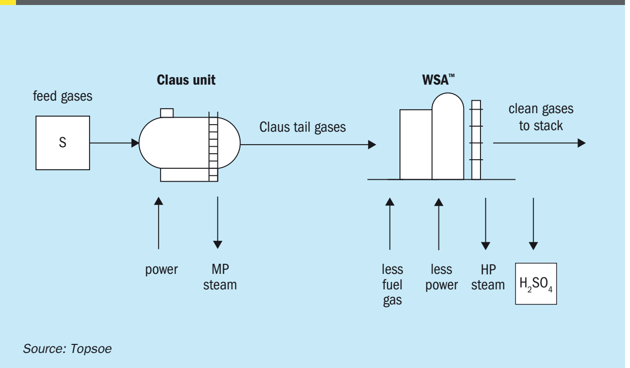
- actual stack CO_2 emissions stemming from the combustion of fuel gas within the tail gas unit;
- CO_2 equivalents from the electricity consumed by the unit (electricity consumed comes from the refinery fuel gas fired boiler with associated CO_2 emissions);
- CO_2 equivalents saved from the production of high-pressure steam (produced HP steam replaces steam produced in the refinery fuel gas fired boiler with associated CO_2 emissions).

Fig 4: **Claus unit utilising traditional amine unit as tail gas treatment**



Source: Topsoe

Fig 5: **Claus unit utilising WSA as tail gas treatment**



Source: Topsoe

The results of the technology comparison are presented in Table 3. The comparison showed that the WSA process contributes significantly to high-pressure steam production, this steam production can replace fossil fuel-based steam production in the refinery's power plant, resulting in a significant reduction in overall CO_2 emissions from the unit. Also, the WSA allows for replacing some fuel gas with acid gas in the tail gas system, resulting in improved operating figures not possible with an amine-based unit. Overall, the comparison demonstrates that the WSA process is a smarter solution for treating the lean sulphurous tail gases coming from sulphur recovery units in the crude oil refining industry.

After comparing both options, the refinery chose Topsoe's WSA technology. The WSA technology proved to be the optimal solution for several reasons:

- It can operate with Claus process off-gas of variable flow and composition, including low sulphur content. This flexibility allows for efficient and effective treatment of lean sulphurous off-gases. Additionally, the WSA process is highly reliable and flexible, providing consistent and stable performance.
- It is a more energy-efficient solution compared to the alternatives. By recovering most of the heat generated in the complete oxidation of sulphur from H_2S to H_2SO_4 it utilises less fuel gas and produces more high-pressure steam, resulting in a reduction of total CO_2 emissions.
- It can produce high-quality concentrated sulphuric acid, which can be used for a variety of industrial applications. This adds value and economic benefits to the refinery operation.
- It has lower investment and operation costs compared to alternative processes. This makes it an attractive and cost-effective solution for tail gas treatment in the refining industry.

Thanks to the higher amount of heat recovery in a WSA unit compared to an amine based TGTU the WSA has a lower fuel gas consumption and a higher HP steam production. In addition, the power consumption is slightly lower in the WSA option.

For this project, Topsoe provided technology, design, equipment, and catalyst to the refinery. The WSA unit has been in operation since 2011. Since the successful commissioning and operation of this plant, the WSA for Claus tail gas treatment has been further developed in cooperation with Comprimo; the new development is called TopClaus™ and it is now possible to recycle the produced sulphuric acid back to the reaction furnace in the main Claus plant. In this way, the sulphur collected in the tail gas treatment can be recovered as elemental sulphur in the Claus unit, ensuring the SRU is only exporting one type of sulphur product (molten or solid sulphur) instead of co-producing sulphuric acid. When sulphuric acid is injected into a Claus furnace the sulphuric acid it decomposes into sulphur dioxide, water, and oxygen, this addition of oxygen to the Claus process gas means that the total process gas flow of the Claus unit can be decreased, leading to a capacity increase in the Claus unit of typically around 10%, further increasing the benefits of utilising Topsoe WSA as the technology for treating Claus tail gases.

Table 3: **SRU tail gas treatment option comparison**

	Claus + amine-based TGTU	Claus + Topsoe WSA
Normalised stack CO_2 emissions	100	82
Normalised equivalent CO_2 emissions from electricity consumption	100	70
Normalised equivalent CO_2 emissions saved from steam production	-100	-146
Relative total SRU+TGTU CO_2 emission	-100	-173

Source: Topsoe

**The values are normalised against the base case SRU + amine based TGTU. Calculations done using emission factors from Ecoinvent environmental database v. 3.9 and IPCC 2016.*

Summary

The WSA process is a flexible technology that effectively can treat sulphurous off-gases in many different industries.

This article highlights three industries where the WSA technology has been successfully implemented to illustrate many of the benefits:

- In the metallurgical industry, the WSA technology can reduce waste and waste management significantly.
- In the pulp and paper industry, the WSA technology increases the circular use of chemicals, avoiding replenishment of chemicals such as sodium and sulphuric acid.
- In a refinery, the WSA technology leads to a saving in CO_2 equivalents of the SRU and tail gas unit as a result of higher HP steam production and less fuel/power consumption.

In addition to being cost-competitive, the use of WSA technology can also enhance a company's image. While it may be challenging to quantify the value of a more sustainable approach, it remains a top priority for many companies as well as for Topsoe.

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Ultra capacity with ultra low emissions

As environmental SO_2 emission regulations become more stringent, tail gas treating options become limited. To potentially achieve lower opex and improved plot plan, utilising a biological desulphurisation process as an alternative to a conventional amine-based TGT unit is becoming of increased interest in the oil and gas industry. At the same time, demands for increased SRU capacity and reliability favour the use of medium and high-level oxygen enrichment.

T.M. Flood, T.K. Chow, M.C. Weber (Fluor) and S. Schreuder, R. De Rink, J.I.H. Timmerman, J-H. Van Dijk (Paqell)

Fluor recently evaluated revamp options for an existing refinery with air operated 3 x 100 t/d SRUs to improve its sulphur removal efficiency to meet more stringent emission specifications.

The primary project objectives were:

- achieve an environmental emission specification below 300 mg SO_2/Nm³ (thermal oxidiser stack SO_2 emissions limit of 100 ppmv, dry at 2% excess O_2);
- increase each train capacity to 150 t/d sulphur;
- optimise capex and opex;
- optimise plot space;
- optimise flexibility in operating window;
- enhance sulphur recovery efficiency and on-stream time;
- enhance client image as an environmentally friendly company;
- reduce carbon footprint by mitigating the need for building new SRU units;
- handle some sour gas streams with unfavourable H_2S/CO_2 ratios.

The existing site uses SUPERCLAUS® tail gas treating (TGT). As with many sites using a solely catalyst-based method for sulphur recovery (SUPERCLAUS®, EUROCLAUS®, or simply three-stage Claus configuration), the existing system can no longer meet the increasingly stringent environmental SO_2 emission regulations.

Two tail gas treating options proven for high sulphur removal efficiency (SRE) were considered:

- hydrogenation followed by amine treatment using a specialty MDEA;
- hydrogenation followed by the biological desulphurisation process Thiopaq O&G (TOG).

The amine TGT process is well known, capable of achieving high SRE and flexible to capacity variations between air-based and oxygen-enrichment operation. However, the client wished to search for alternative systems, considering that amine TGT systems have relatively high capex, plot space requirements and high steam consumption. With the goal to achieve lower opex and smaller plot space, an option utilising a biological desulphurisation process as an alternative to a conventional amine-based TGT unit is becoming of increased interest in the oil and gas industry during this energy transition era.

TOG and TOG ULTRA bio-desulphurisation technologies developed by Paqell, can comfortably achieve an H_2S treated gas specification of <25 ppmv in low pressure units.

Common hydrogenation section

Fig. 1 shows the major equipment items in the common hydrogenation section, which is identical for both amine and TOG systems, and the amine TGT section. For this project tail gas leaving each SRU Claus train is routed to a dedicated tail gas heater. Tail gas enters with an H_2S/SO_2 ratio of between 2 to 4; for optimal Claus sulphur recovery efficiency this ratio is controlled at 2 in the upstream Claus train.

The hydrogenation process catalytically reduces sulphur compounds and elemental sulphur vapour in the Claus tail gas to H_2S, which is subsequently removed in the downstream TOG absorber or amine contactor.

Hydrogenation and hydrolysis reactions for the four primary sulphur constituents are as follows:

$$S + H_2 \rightarrow H_2S \qquad (1)$$

$$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O \qquad (2)$$

$$CS_2 + 2H_2O \rightleftharpoons 2H_2S + CO_2 \qquad (3)$$

$$COS + H_2O \rightleftharpoons H_2S + CO_2 \qquad (4)$$

Process gas is heated in an indirect tail gas heater using HP Steam, prior to introduction into the hydrogenation reactor. Carbon monoxide in the Claus tail gas reacts with water in the hydrogenation reactor to make hydrogen and CO_2. Often, the Claus tail gas has sufficient H_2 and CO for hydrogenation of the sulphur compounds in the tail gas for normal operation with no consumption or a small consumption of externally-supplied hydrogen.

There is a temperature rise across the hydrogenation reactor due to the exothermic reactions. A reactor effluent cooler removes some heat from the reactor effluent by generating LP steam on the shellside. The process gas leaving the reactor effluent cooler is still superheated.

Desuperheater contact condenser

The reactor effluent will be further cooled to a temperature suitable for amine or TOG performance (about 35°C) in a desuperheater contact condenser (DCC) column. The process gas has less capacity to retain water as it is cooled, so the excess water will be removed. This has the benefit of reducing the volumetric flow rate of the cooled process gas.

In a single bed design, the reactor cooler effluent enters the bottom of a packed bed, where it is cooled, and water vapour is condensed by counter-current direct contact with cooled circulating water in a bed of random packing. Water is circulated by the contact condenser pump, which draws liquid from the chimney tray below the top packed section. The circulating water is cooled in the forced draft contact condenser air cooler (not pictured in Fig. 1) and contact condenser trim cooler (by heat exchange against plant cooling water) and returned to the column above the packed bed on flow control.

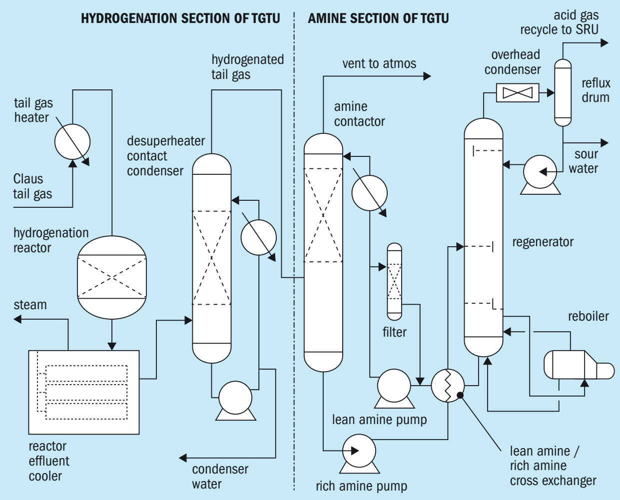
A single bed DCC design requires stainless steel material to reduce corrosion rates, in case of condensing sulphuric acid, which may occur especially during a major SO_2 breakthrough event. Also facilities for either ammonia or caustic injection are required in case of undesired SO_2 breakthrough from the upstream hydrogenation reactor.

If SO_2 breakthrough is not mitigated in the DCC, SO_2 will enter the downstream amine TGT system for that option, where degradation of the circulating amine solvent may occur. There have been incidents where the entire inventory of circulating amine solvent needed to be replaced because the degraded solution can no longer perform sufficiently. Poor H_2S removal in the amine contactor leads to inability to meet the stack SO_2 emission specifications.

In Fluor's proprietary two-bed DCC design, the upper bed serves the same function, namely contact condensing. However, there is also a lower bed, where the superheated reactor effluent enters and is contacted counter-currently against a circulating buffered weak caustic solution. In this manner, some caustic is available at all times to mitigate against SO_2 breakthrough.

Some systems implement ammonia injection based on pH after an SO_2 breakthrough event has occurred to reduce corrosion, but in these ammonia-injection systems, some SO_2 may have already slipped to the downstream amine system. Caustic systems that only inject caustic based on pH similarly have this issue, namely that some SO_2 may have already slipped to the downstream amine system.

Fig 1: **Common hydrogenation and amine TGT schematic**



Source: Fluor

Configuration

For this project, separate trains are included through the hydrogenation section for greater reliability. With the use of Fluor's proprietary two-bed DCC design, the risk of SO_2 breakthrough slipping into the downstream amine system is mitigated. However, per the client's decision, because of the remote possibility of a major SO_2 breakthrough event degrading the entire inventory, or a significant portion of the circulating amine solvent, there are also three separate amine contactors for the amine TGT option.

The TOG system is robust against SO_2 breakthrough incidents. Due to the buffering capacity of the solution, the pH will remain relatively stable, mitigation can be done by temporarily dosing more caustic. Due to this robustness of TOG, only a single absorber is required. When the Claus unit is operated on air, the combined tail gas from the three tail gas treating DCC columns enter the TOG absorber. When the Claus unit is operated with enriched air, the combined tail gas from two tail gas treating DCC columns enter the TOG absorber. The flow rates and compositions of the total feed to the absorber differ for both cases, however the total design sulphur load is identical.

In summary, process gas leaving the common hydrogenation section has nearly all the sulphur species converted to H_2S (with zero SO_2 content), suitable for treatment in either the TOG or amine TGT. This process stream has also been cooled and excess water has been removed (i.e., the process gas leaving the hydrogenation section is water-saturated).

Although the SRU tail gas leaving the final sulphur condenser has nearly equal volumetric flow rate for the SRU air case as for the SRU oxygen enrichment case, there is more water contained in the tail gas for the SRU oxygen enrichment case. This is because water is a by-product of the Claus reaction, and in the SRU oxygen enrichment case, a higher flow rate of acid gases is processed, producing more water. Downstream of the DCC after removal of excess water, the air case process gas has a higher volumetric flow rate.

As part of the revamp for this project, the existing third SUPERCLAUS stage will be converted into the tail gas heater, hydrogenation reactor and reactor effluent cooler. Some modifications are required to accommodate these changes in service, such as sealing the unnecessary liquid Sulphur outlet on the converted reactor effluent cooler and modifications to the reactor bed support internals.

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Note that new and/or modified equipment common for both TGT system options is not included in either system cost estimate.

Thiopaq O&G technology

The Thiopaq O&G process, licensed by Paqell, is an environmentally friendly biological process to remove H_2S from sour gas streams and recover it as elemental sulphur. The most unique aspect of the process is that it utilises a living biocatalyst to oxidise H_2S to elemental sulphur. The process consists of three sections: an absorber column, a bioreactor and a sulphur separation section, see Fig. 2.

The absorber column is a pressure vessel constructed out of stainless steel. In the absorber, sour gas is counter-currently contacted with lean process solution coming from the bioreactor. The mildly alkaline solution (pH 8 to 9.5, project depending) removes practically all H_2S. Due to the alkalinity of the process solution, H_2S is converted into soluble bisulphide (HS-). The treated gas exits the absorber from the top of the column. The sulphide rich solution is collected in the sump of the absorber, from where it is routed to the bioreactor, an atmospheric tank constructed out of glass reinforced plastic (GRP).

In the bioreactor the biocatalyst converts the dissolved sulphide into elemental sulphur using oxygen, thereby regenerating the process solution. Air is sparged into the bioreactor for the supply of oxygen. The biocatalyst consists of naturally occurring haloalkaliphilic sulphur oxidising bacteria (Fig. 3). These organisms are not genetically manipulated or modified. The bacteria gain metabolic energy for growth (i.e. reproduction) from the oxidation of H_2S and use CO_2 as their sole carbon source. The biocatalyst is fast growing and highly resistant and adaptive to varying process conditions. The regenerated solvent is recycled from the bioreactor back to the absorber.

The formed hydrophilic elemental sulphur particles are suspended in the process solution. These are removed from the circulating solution in the sulphur separation section, which typically consists of a settler and/or decanter-centrifuge.

The elemental sulphur has a purity of ~95-98% on dry basis.

The TOG process has the following performance features:

- applicable to sour feed gases with H_2S concentrations ranging from 50 ppmv to 100 vol-%;
- H_2S removal efficiencies of >99.9%;
- suitable for high range of H_2S:CO_2 ratios (down to 1:100);
- simple process configuration and control with stable operation;
- low operating and chemical costs;
- no use of environmentally unfriendly chemicals – no hazardous waste streams;
- attractive capex;
- wide and flexible operating range;
- bacteria produce hydrophilic non-sticky sulphur – prevents plugging;
- environmentally friendly process based on a naturally occurring biocatalyst;
- biocatalyst reproduces by itself; after initial fill, no refills are needed;
- inherently safe operation – no concentrated H_2S stream created.

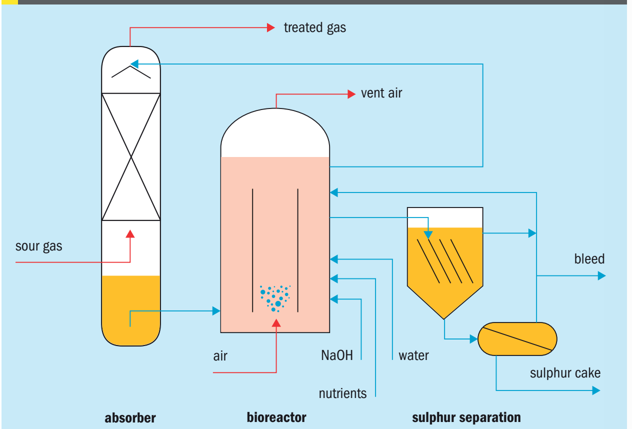

Fig 2: **Simplified process diagram of the Thiopaq O&G (TOG) system**

Source: Paqell

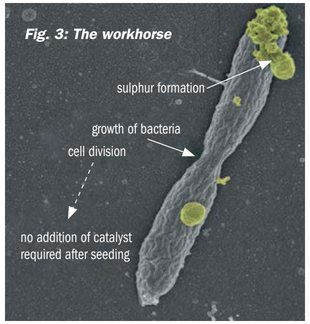

Fig. 3: The workhorse

Engineering and construction for licensed TOG systems can be provided by several sub-licensing engineering companies, including Fluor.

The produced sulphur can be used as raw material for agricultural applications such as fertilizer or fungicide. Produced sulphur is considered as organic. Several brands of bio sulphur-based suspension concentrates are marketed. Other options include melting the produced sulphur to obtain the Claus sulphur purity specification.

The bleed water stream from the TOG section is water with sodium salts, biomass and elemental sulphur. The pH of this stream is the same as the lean process solution (8 to 9.5 for this project). Depending on the location facilities this stream can be sent to the existing site wastewater treatment; otherwise a separate (biological) water treatment unit needs to be installed or the bleed water needs to be sent offsite for disposal.

TOG optimisation options

There are several optimisation options available for the TOG biological treating system.

Opex reduction: At a sulphur load as in this example, the addition of a sulphidic bioreactor called a 'selector' can be considered (TOG ULTRA) that results in a significant reduction in the caustic consumption and bleed water stream formation. In the selector, the sulphide oxidising bacteria are exposed to high concentrations of sulphide. This promotes the growth of sulphur producing microorganisms that tolerate high sulphide concentration and suppresses the growth of sulphate producing micro-organisms for which high sulphide concentrations are toxic.

Feed and product flexibility: Another additional process step that appears attractive to some locations is the conversion of the Thiopaq sulphur product into a product that meets the Claus sulphur purity requirements.

Vent gas stream co-processing can be easily handled in the TOG system despite unfavourable H_2S to CO_2 ratio.

Although not applicable for this project design basis, TOG systems could provide an advantage when refineries convert to processing biofuels, which typically create sour gas streams with a very unfavourable H_2S to CO_2 ratio for SRU treatment. The biofuels sour gas stream can bypass the SRU and be directed to the TOG system for processing.

Amine technology

The amine TGT section consists of the amine contactor (amine absorber), amine regeneration system, and amine filtration section (see Fig. 1). The amine contactor is the key equipment item for meeting the stack emissions; any untreated H_2S in the overhead from the amine contactor will be converted to SO_2 in the thermal oxidiser stack, along with any COS and CS_2 that passes through the hydrogenation section. Sour gas enters near the bottom of the amine contactor and is contacted counter-currently with lean amine solution. H_2S is preferentially absorbed into the lean amine solution, with un-desired co-absorption of some CO_2.

Generic MDEA is the most widely used, inexpensive chemical solvent suitable for selective H_2S removal at low pressure. MDEA has become more widely used than DIPA for refinery and gas plant amine treatment units and for SRU tail gas treating. MDEA provides lower operational costs than DIPA, MEA or DEA, because MDEA requires lower stripping duty per unit of circulation. Lower stripping duty also decreases regenerator overhead condenser duty.

Most specialty solvents are MDEA based, with additives to increase H_2S selectivity (decreased CO_2 co-absorption).

Common proprietary solvents for selective H_2S removal are listed below:

- BASF OASE® Yellow;
- Dow UCARSOL™ HS-101 and HS-103;
- INEOS GAS/SPEC™ TG-10;
- ExxonMobil/BASF FLEXSORB™ SE Plus. This is used for sites with tight H_2S removal specifications where the absorber operating temperature is high;
- ExxonMobil/BASF OASE® SULFEXX™. This is used for sites with tight H_2S removal specifications where the absorber operating temperature is high.

The selectivity of the solvent is important because any CO_2 co-absorbed into the rich amine solution will pass into the regenerator overhead and into the TGT acid gas recycle and be routed to the front of the SRU for further processing. This recycling allows increased conversion of sulphur than can be achieved in the Claus section. However, the TGT acid gas recycle stream increases the volumetric throughput across all the Claus, common, and TGT equipment (entire process gas path). Thus, solvents with higher selectivity for H_2S decrease the TGT acid gas recycle stream, improving the hydraulic profile through the entire process gas path (Claus SRU, common hydrogenation section and amine TGT section equipment).

Specialty solvent has higher fill and makeup costs compared to generic MDEA, but generic MDEA typically requires higher circulation rate, and often cannot achieve the desired contactor overhead H_2S specification. As overall stack SO_2 emission specifications become increasing stringent, higher removal of H_2S in the amine contactor is required, especially when considering that essentially all of any COS and CS_2 present will pass through the contactor untreated.

Oxygen-enrichment technology

Fluor's COPE®II Oxygen Enrichment technology was selected to increase each SRU train capacity to 150 t/d, essentially providing the equivalent redundancy of a spare train. Capacity refers to the nominal sulphur content in the combined acid gases. For the purposes of this article, the produced sulphur (Claus SRE) is fixed at 95% of the sulphur contained in the feed acid gases. Fig. 4 shows a process schematic of the COPE®II process. Oxygen enrichment provides the following major advantages:

- Increases amine acid gas and sour water stripper acid gas processing capability in each train. This could be used for increasing the overall plant processing capability to handle future expansions in upstream refinery units. For this project, pre-investment for future expansions was considered, but not implemented. The overall SRU capacity is fixed at 300 t/d, either by operating three trains at 100 t/d each using only combustion air, or by operating two trains at 150 t/d each using oxygen enrichment. In this manner, the oxygen-enrichment design provides spare capacity while avoiding the need for constructing a fourth SRU train.
- Achieves a higher temperature in the thermal reaction furnace, which enhances destruction of ammonia, hydrocarbons and BTEX in the feed gases. Higher temperature in the thermal reaction furnace also could allow processing of weaker acid gases with higher CO_2 content such as is required for many gas plants and gasification system acid gases. For this project, ammonia is present in the SWS off-gas, which has a typical composition with about 35 to 40 mol-% for each of H_2S and NH_3. The amine acid gas contains about 90 to 93 mol-% H_2S, which is within a typical range for refinery amine acid gas streams.
- In addition, many sites report smoother, more reliable and flexible operation when using oxygen enrichment as well as slightly enhanced Claus sulphur recovery efficiency.

For oxygen enrichment, the total O_2 required for combustion is supplied by a combination of high-purity oxygen (at least 90 vol-% O_2 content) and air from the combustion air blower. Variation in the relative amounts of these sources provides enriched air to the burner, which contains from ~21 vol-% (no enrichment or air-only operation) up to 100 vol-% O_2 blown systems. For H_2S-rich refinery acid gas streams, it is not necessary to use high-level oxygen enrichment that might be considered for treating weak acid gases from gas plants or gasification plants.

In COPE®II operation, high-purity oxygen is introduced to the burner separately, partially substituting for air to provide O_2 for combustion. This can produce a significant decrease in downstream flow rate. The decrease in downstream flow is mostly due to the reduction in nitrogen associated with the combustion air flow that is replaced by the high-purity O_2 stream. Reducing the

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flow rate of nitrogen lowers the pressure drop through the SRU. Consequently, this allows for an increase in the acid gas flow rate processed, with resultant increased produced sulphur capacity.

Combustion with oxygen-enriched air increases the flame temperature in the thermal reaction furnace compared with air-only combustion. If not tempered, the combustion temperature resulting from high oxygen enrichment levels can exceed the limits of the standard refractory lining that protects the carbon steel shell of the main burner (combustion chamber area) and of the thermal reaction furnace.

COPE®II operation allows for higher levels of oxygen enrichment, even for rich acid gases, without exceeding the temperature limits of the standard refractory linings by recycling process gas from the outlet of the 1st sulphur condenser, through the COPE® ejector, to the COPE® burner. The recycle gas flow rate is controlled to moderate the thermal reaction furnace operating temperature. The COPE® ejector uses motive steam; this steam enters the process, also contributing to the attemperation.

For this project, the normal oxygen enrichment level at expanded 150 t/d sulphur capacity per train can be achieving using medium level oxygen enrichment at about 50 mol-% percent oxygen enrichment.

Thermal oxidiser section

The thermal oxidiser section is the same process scheme for both options.

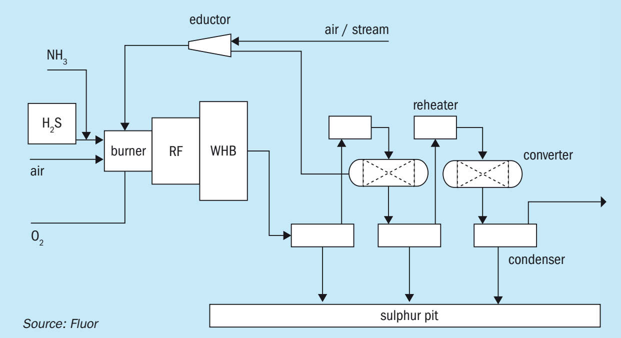
Treated process gas from either the TOG absorber or from the amine contactor overhead is routed to the thermal oxidisers, where essentially all sulphur species are incinerated to SO_2 at 649°C with 2 mol-% excess oxygen prior to release from the stack at safe location.

In the existing facilities, each of the existing SRU trains has a dedicated natural-draft thermal oxidiser. As part of the upgrade, these must be converted to forced-draft thermal oxidisers with low NOx burners. Due to plot limitations, the new thermal oxidisers, associated stacks and associated new air blowers will be located on an adjacent plot area.

Comparison of capex and opex

Fluor prepared an AACE Class 4 estimate (Equipment Factored) based on construction in the US Gulf Coast, 3rd Quarter 2023. Major assumptions include:

Fig 4: COPE® II process schematic



Source: Fluor

- each tail gas treating system is part of an existing larger plant (refinery);
- equipment common for both TGT systems is not included in either cost estimate;
- supply of power and utilities are available from the balance of the plant at the SRU/tail gas treating unit battery limit.

Total installed cost for the Thiopaq O&G TGT case is estimated as $28.5 million. Total installed cost for the amine TGT is estimated as $27.3 million.

The estimated annual opex for the Thiopaq O&G TGT case is estimated as $1.39 million. The estimated annual opex for the amine TGT case is estimated as $1.58 million.

The two options are comparable in terms of both capex and opex.

Discussion and conclusions

Both TOG and amine TGT processes are capable of achieving an environmental emission specification below 300 mg SO_2 / Nm³, emissions lower than the World Bank Standards for SRU facilities. The relative estimated capex is comparable between the two options for this project basis. The relative opex is also comparable between the two options. The opex for TOG could be reduced if the TOG Ultra design is utilised.

Both options allow for flexible operation and can handle the range of operation between the SRU air case and SRU oxygen enrichment case.

Both options provide safe and reliable tail gas treating. TOG provides better robustness against SO_2 breakthrough events.

Although the equipment services count is similar between the options, TOG systems have slightly fewer equipment services to maintain and operate compared with conventional amine technology. The options are comparable in terms of simplicity of operation, with very few equipment items that require frequent maintenance. Comparable operator attention is required for monitoring operation of the two options.

The amine TGT requires greater plot space and more infrastructure for pipe racks and underground drainage facilities.

TOG reduces the load on the Claus, both in terms of sulphur load and gas load (due to absence of amine TGT recycle loop). During oxygen enrichment, somewhat lower supply of high purity oxygen is required in the SRU if a TOG TGT is used, because there is no recycle flow. During future capacity expansions, the advantage TOG provides in terms of debottlenecked SRU processing capacity may be significant.

Moreover, the TOG system can be designed to handle additional other refinery streams with unfavourable H_2S/CO_2 ratios, resulting in reduction of Claus load, reduction in fuel gas consumption from co-firing, and/or lowered oxygen enrichment level.

As another consideration, the client's image can be enhanced by selecting TOG because it is an intrinsically safe and environmentally conscious process. Other intangibles, such as avoiding the carbon emissions associated with the manufacturing of amine solvent, may also influence the client's decision in favour of TOG.

In conclusion, using Thiopaq O&G for tail gas treating provides a cost effective and attractive alternative to more traditional amine TGT. This is especially true for this project, where the client wishes to act as an environmentally friendly company. ■

Cobalt-molybdenum catalyst activation in low temperature TGUs

Part 2

Cobalt-molybdenum (CoMo) catalysts are integral components of tail gas units (TGUs), playing a vital role in reducing harmful sulphur dioxide (SO_2) emissions arising from Claus sulphur recovery units. Effective activation of these catalysts is essential for their optimal performance. The consequence of sulphiding at low temperatures and atmospheric pressure in low temperature TGUs is to compromise effectiveness of catalyst activation. In the final part of this two-part article, **Michael Huffmaster**, Consultant, presents case study results using a discrete reactor model incorporating heat, mass transfer, and activation reaction kinetics to assess the impacts of these variables on in-bed temperature profile and activation effectiveness. Tailoring gas rate, composition, and temperature progression can achieve in-bed exotherms which improve CoMo catalyst activation effectiveness for low temperature tail gas units.

Discrete TGU catalyst bed model – activation simulation

A discrete reactor simulation embracing heat and mass transfer and activation kinetics enables evaluation of process alternatives within constraints. Procedures to improve catalyst activation are assessed with this simulation tool as well as in a case study, evaluating variables and conditions and developing recommended enhanced practices.

The core of the simulation tool is kinetics, representing rate of conversion of metal oxides to respective sulphides, and heat transfer, to determine distribution of heat of reaction between the catalyst and the gas and to generate an in-bed temperature profile. Mass transfer is included, but does not present a controlling influence on sulphiding conditions. The approach taken was fitting kinetics to actual activation based primarily on observed outcomes and measurements, as well as data from the field. Experimental data from a 2019 study of activation at low temperature tail gas conditions are the basis for kinetics derived to represent the degree of activation achieved[9].

This semi-empirical representation embraces the varied, multiple pathways and intermediates, not yet emerged as definitive, but using outcomes that have been measured, especially for low temperature. A formal reaction set lacks sufficient characterisation to apply. Having measurements and parametric variances to assess sensitivities for key variables is very useful.

The model framework is a first order rate model which proved sufficient to represent the data and accommodate the following parameters:

Rate of reaction for metal (oxide) with sulphiding media proportional to metal mass (area); cobalt and molybdenum are combined for "average metal" heat of reaction and H_2S and H_2 consumption:

- knowledge that mixed phase intermediates are likely, e.g., oxy sulphide;
- division of metal into three levels of reactivity/accessibility using crystallites or pillow shaped platelets visualisation – stacked layers
  - fast or vigorous – outside surface and edges
  - restricted – interior (or occluded layers) with diffusional resistance
  - difficult – metals interacted with substrate, higher activation energy;
- reaction kinetic coefficient is proportional to H_2S partial pressures;
- reaction kinetic coefficient is proportional to square root (H_2 partial pressure and adsorption coefficient); hydrogen consumption proportional to H_2S reacted;
- reaction kinetic coefficients fitted with Arrhenius relationship for temperature dependence;
- crystallisation not explicit, approximated as with overall sulphidation.

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Water has minor impact on reaction rate.

Heat effects and heat transfer

- heat from reaction proportional to H_2S consumption/metals reacted;
- heat of adsorption (desorption) for water; considered as chemisorption, catalyst water loading in equilibrium with gas phase Heat transfer and mass transfer based on fluid/material properties, Eckert packed bed correlations, and Colburn analogy;
- effectiveness factors near unity; film fluxes are relatively small and Knudson diffusion resistance is small.

The vision of crystallite sizes used is based on a rationale of what will fit, but not obstruct, pores of alumina, as particles, not a simple mono-layer. The number of "metal oxide atomic units" are on the order of 50 to 200 per nanoparticle with one to three layers stacking; exposed edge and surface ratio to total crystallite, is 100% for single layer and 63% for average 2.6 layers. This size distribution agrees with SEM and TEM and other data representing the arrangement of MoO_3 and CoO on the surface of alumina and in pores.

The simulation model is two dimensional: one in space and one in time. Plug flow is assumed. It is solved in 100 discrete steps along the gas flow path, based on sulphiding gas flow, composition, and conditions. The reactor bed is then moved ahead to the next time increment and the gas flow path solved. The reactor bed is moved through ~100 time steps to the completion the activation. A reactor profile is generated for temperature and gas composition and for catalyst metals, water, and temperature for each step through the reactor and each step through time.

Tail gas catalyst activation at low temperature is recognised at the margin of the temperature and hydrogen partial pressure for effective activation. Application of information from recently published work in concert with TGU activation studies and field experience can lead to measures which can improve low temperature activation.

Heats of reaction are applied to metal sulphided, using ΔH from thermodynamics, proportioning along reaction pathway as the fraction of metal mass converted. Thermodynamics and kinetics for intermediates are not explicitly known. Kinetics are set to represent that initial reactions steps are vigorous (based on observed plant exotherms).

Experiments are almost always in temperature-controlled settings, whereas plant scale sulphiding is adiabatic. In plant settings, exotherms driven by heat from reaction must be managed. The heat of reaction is determined based on thermodynamic database for defined substances. Density functional theory suggests even energy distribution across intermediates for sulphur-oxygen exchange[8,15,16].

The model provides bed temperature profiles and degree of activation as a function of sulphiding parameters, including influence of gas temperature and rate, concentration of H_2S, H_2, and H_2O, as well as time of duration for activation. Case study results incorporate heat and mass transfer and activation reaction kinetics to assess the impacts of these variables.

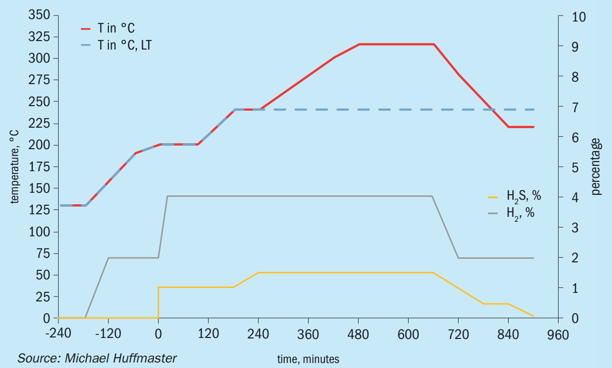
> For a Co/Mo catalyst the activation reactions are:
>
> $MoO_3 + H_2 \rightarrow MoO_2 + H_2O$ ΔH = -85,600 J/mol Kp = 4.1 x 10^{+8}
>
> $MoO_2 + 2H_2S \rightarrow MoS_2 + 2H_2O$ ΔH = -89,260 J/mol Kp = 3.2 x 10^{+10}
>
> $CoO + H_2S \rightarrow CoS + H_2O$ ΔH = -62,100 J/mol Kp = 3 x 10^{+6}
>
> With 10% metals (8% molybdenum and 2% Co) the temperature rise of the catalyst with no heat removal by the gas stream used during sulphiding would be:
>
> 1 kg catalyst
>
> Mo: 0.1*1 kg *1,000 g/kg /96 g/mol = 1.04 mole @ 174,860 J/mol = 182,145 Joule
>
> Co: 0.25 *1kg *1,000 g/kg /59 g/mol =0.42 mole @ 62,100 J/mol = 26,313 Joule
>
> Temperature rise:
>
> Cp – 955 J/kg-K Delta T = 208,458 J/kg / 955 J/kg-K = 218 K

Procedures

Catalyst activation procedures for gas phase HDS and traditional tail gas are similar. Initial steps are almost the same even for low temperature tail gas. Low temperature activation only achieves 240°C and does not raise the catalyst to the traditional 315°C temperature finish.

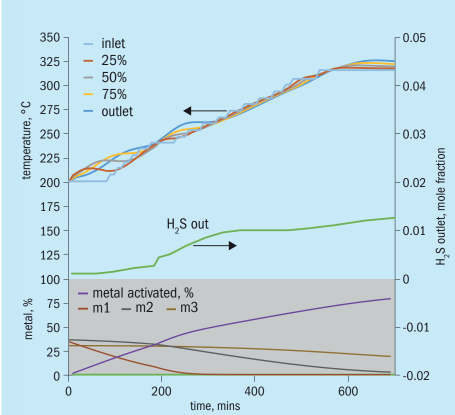
Tail gas procedures are conducted at atmospheric pressure and begun at 180 to 200°C. Sulphiding is initiated cautiously, with H_2S and H_2, and with control, to manage temperature rise from vigorous initial metal reactivity. A reference sulphiding procedure is presented, based on a 2007 presentation at Brimstone by Steve Massie[17].

Fig. 6: **Typical TGU sulphiding procedure, traditional and low temperature**



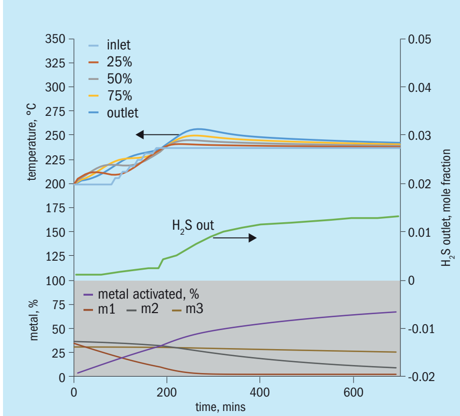
Source: Michael Huffmaster

Fig. 7: **Activation model profile for typical TGU sulphiding procedure, traditional, 320 nghsv**



Source: Michael Huffmaster

Fig. 8: **Activation model profile for typical TGU sulphiding procedure, low temperature**



Source: Michael Huffmaster

Traditional sulphiding procedure:

- Purge reactor to remove oxygen and establish (re)circulation at ~500 aghsv (320 nghsv)
- Ramp temperature to 130°C at 50°C/hr; hold for 1 to 2 hours to remove water from catalyst; water dew point should be controlled to 40°C in recirculation loop, removing water in quench column.
- Ramp temperature to 200°C at 50°C / hr: During this time hydrogen may reach 2% if a RGG is used for heating, firing at 95% stoichiometry.
- Introduce sulphiding gas: add H_2S at 1% and H_2 at 4%. Monitor bed for exotherms, not to exceed 30°C;
- Ramp temperature to 240°C at 20°C/hr and hold for 1 hour: Ensure H_2S out of bed is 3,000 ppm before increasing temperature further.
- Ramp temperature to 315 °C at 20°C/hr; increase sulphiding gas to 1.5% H_2S; hold for 3 hour heat soak.
- Total 12 hours at sulphiding conditions; once completed reactor can be cooled to 250°C and placed in service or standby.

The graphic in Fig. 6 depicts this procedure and low temperature adaptation. Fig. 7 presents activation model predicted temperature profile and activation effectiveness for the traditional sulphiding procedure and Fig. 8 presents activation model results for low temperature.

Typical low temperature TGU sulphiding follows this procedure except a final temperature and soak is at 240°C; this is indicated as a dashed line in the graphic.

Activation steps (noted for activation pathways from part 1):

- Initial sulphiding below 200°C - formation of oxy sulphides and MoS_3 morphs, MoS_2 and MoO_2 begins; exotherms create temperature waves in the bed.
- Temperatures are raised with sulphur uptake and production of MoS_2 and conversion of oxy sulphides.
- At 240°C Sulphur uptake is expected to be 50 to 75%. Hold to verify H_2S is penetrating the entire bed to ensure cobalt in the lower bed is not reduced by being in a hydrogen atmosphere without H_2S above 200°C.
- Temperatures are ramped to the critical 260°C transition. Transformation and completion of sulphiding follows, heating on at a controlled rate to 315°C final bed temperatures for another hold point to anneal and crystalise the MoS_2 nanoparticles.

Cautions and concerns

There are a few concerns to address regarding activation. The foremost concern should be for temperature in excess of 325°C due to strong exotherms. This peril arises during initial sulphiding period with vigorous reactions. If H_2S concentration is too high a lot of heat is released or if gas rates are low, insufficient heat is transported from the catalyst particles. This can cause temperature stacking and accelerated reactions at the elevated temperatures. Increasing the gas rate or reducing the H_2S will calm strong exotherms.

Another concern should be reduction of cobalt to metal. This agglomerates cobalt and reduces promotion and results in low activity for the catalyst. It is caused by exposure of catalyst to H_2 at temperatures above 200°C without the presence of H_2S. The risk during sulphiding is H_2S starvation, consuming H_2S in the upper bed with low concentrations of H_2S in the lower bed.

A similar and related concern is reduction of molybdenum; however, sulphiding conditions are not sufficiently strong to reduce MoO_3. Hydrogen alone will not reduce MoO_3 below 400 to 500°C[10] nor MoO_2 to metal until 1,100°C [NIST]. Moreover, water inhibits these reduction reactions.

Exposure of catalyst to H_2S in the absence of H_2 could potentially form MoS_3. This is a less active catalyst which needs to be reduced by H_2 or decomposed at 315°C.

Exposure of sulphide catalyst to hydrogen without H_2S has a risk of stripping sulphur. This is largely mitigated for TGU because of low partial pressures

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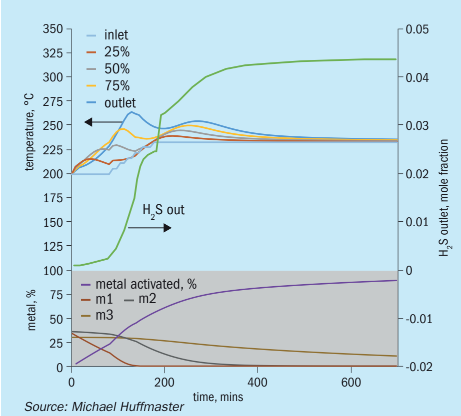
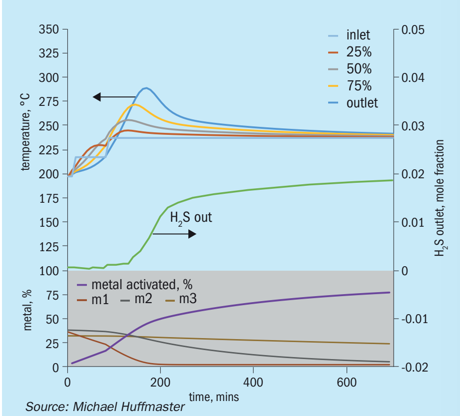
Fig. 9: Adjusted procedure low temperature activation: Gas rate, 370 nghsv (575 aghsv), 2 to 4.5% H_2S, 4 to 10% H_2, 10% H_2O



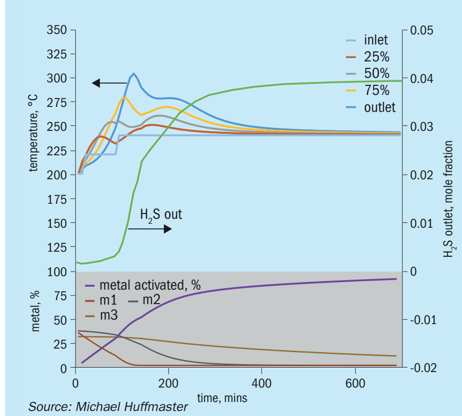
Source: Michael Huffmaster

Fig. 10: Adjusted procedure low temperature activation: Gas rate, 320 nghsv (500 aghsv), 1 to 2% H_2S, 4 to 10% H_2, 10% H_2O



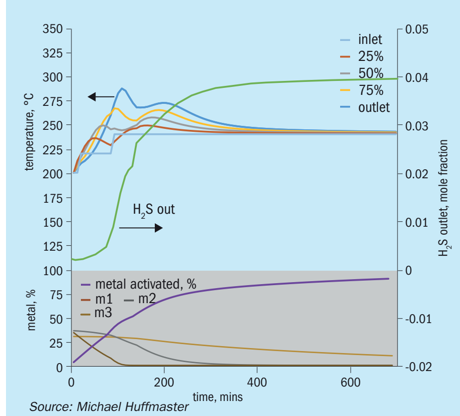
Source: Michael Huffmaster

Fig. 11: Adjusted procedure low temperature activation: Gas rate, 320 nghsv (500 aghsv), 2 to 4% H_2S, 4 to 10% H_2, 10% H_2O



Source: Michael Huffmaster

Fig. 12: Adjusted procedure low temperature activation: Gas rate, 385 nghsv (600 aghsv), 2 to 4% H_2S, 4 to 10% H_2, 10% H_2O



Source: Michael Huffmaster

of hydrogen, especially if temperatures are below 250°C. Addition of small amounts of H_2S offer further protection, with 100 ppm being quite sufficient.

Finally, there is concern of exposure to oxygen. If oxygen is present during sulphiding it will inhibit conversion of oxides to sulphide. Exposure of sulphide catalyst risks sulphation of support and oxidation of active metals, which can severely damage the catalyst.

Low temperature consequences

Low temperature tail gas diverges from traditional tail gas because bed inlet temperatures may be limited to 240°C and with restrained temperature ramp rate bed temperatures may not reach 250°C. Activation at maximum temperatures of 250°C has notable consequences on the activity potential of cobalt-molybdenum catalysts.

The consequence of not going through the 250 to 260°C transition may leave a significant fraction of metals not converted to sulphide. There will be higher valence molybdenum in oxy sulphide, MoO_2 and potentially MoS_3. Spectrographic tracking of activation revealed Mo+IV increased from 17 to 70% at this transition[7]. MoS_2 formed is amorphous and less effective as a catalyst.

Furthermore, a temperature above 260°C drives the transformation of amorphous MoS_2 to crystal slabs. At lower temperatures, the mobility of atoms and molecules is restricted, potentially affecting the dispersion and structural transformation of the catalyst metals. In particular, nucleation and crystallisation of MoS_2 may not occur and, absent MoS_2 slab, cobalt attachment at edge features and promotion may be reduced. The activation process is not as comprehensive as at higher temperatures, resulting in suboptimal active site formation and reduced catalytic performance. Thus, low temperature activations produce weak catalytic kinetic activity.

It is known that low temperature activation is partially successful as catalysts do function, albeit in diminished capacity, and units perform, although maybe at reduce catalyst life cycle. Thus, we know some formation of active slabs is occurring. What we want to know is if the activation step be managed to enhance and improve activation.

The critical factor is to achieve 260°C, or perhaps to target 270°C which allows some margin for reported transition temperature and offers allowance for low hydrogen partial pressures in tail gas applications. This should initiate the vital transition of amorphous MoS_2 and seeding nucleation sites for MoS_2 nanoparticles. Time is necessary for transformation of amorphous MoS_2 (coordinated with 4 sulphur) to MoS_2 crystalline (Mo coordinated with 6 sulphur). Also consider that nucleation in principle needs to occur in each independent nanoparticle.

Extending time in sulphiding conditions improves activity, so the indication is more slab development/promotion occurs. Although it may not be as effective as traditional temperatures, it is an enhancement which can be applied in LT TGUs. With transition achieved, annealing might proceed at lower temperatures. The rate of crystallisation is slower at lower temperatures, but with nucleation initiated, perhaps an acceptable level of slab formation will occur with extended time.

Case study examples

An activation process model for the outlined activation procedure is presented in the form of charts in Fig. 9 through Fig. 15. Several variations or adjustments to temperature ramping, gas rate and composition are assessed. A best case recommendation is offered and parametric adjustments of variables are made for sensitivity.

The charts each include temperatures for inlet gas and temperatures at bed quarter points including bed outlet across 12 hours, roughly the duration of a sulphiding procedure. Low temperature procedure duration would be extended for longer heat soak to further activation. Also tracked are outlet H_2S concentration, percentage of metal converted/activated and percentage of vigorous, moderate and difficult metal fractions.

The calculations are based on an alumina supported CoMo catalyst with 2.5 wt-% cobalt and 10 wt-% molybdenum in oxidic form. This is an illustrative catalyst, so can be considered either spherical or extrudate, although physical properties are more typical for high pore volume extrudate.

Reference sulphiding: procedure 200°C starting temperature, (re)circulation of sulphiding gas at 320 nghsv, 40°C water vapour for 10% water, 1.0 to 1.5% H_2S, 4% H_2, 15°C per hour ramp, 240°C hold for LT finish.

The rate of initial reactions is managed in part by the concentration of the sulphiding agent, e.g., H_2S and H_2 concentration. Increasing H_2S concentration initially and then stepping higher enhances bed temperatures. Reducing H_2 initially moderates reaction followed by stepping higher to drive more complete activation.

The rate of temperature ramping impacts bed temperature, as slow ramp rates allow more heat to depart with the gas. The step from 200 to 240°C accomplished in 1.5 hours increases bed temperatures, with a caution that gas rates must be sufficient.

A major control is gas rate. Lower gas rates increase bed temperatures but below 240 nghsv risk excessive exotherms. Higher gas rates, above 600 nghsv, suppress exotherms and elevated water levels dampen exotherms.

Discussion

A critical aspect of activation procedures is managing exotherm in the bed. Energy released by sulphiding reactions heat the catalyst and the sulphiding gas.

Gas rates traditionally used in the range of 1/4 to 1/3 operating design gas rate (280 to 360 nghsv) proved adequate to control bed temperature, and H_2S concentrations were set to reduce risk of strong exotherms. However, very low H_2S values are often found at the bed outlet, especially when H_2S is held to low levels. The level of 1% H_2S typically applied causes starvation in the lower bed, putting catalyst in the lower portion of the bed at risk of damage and impairment from reducing cobalt.

Development of low temperature catalysts achieved stronger kinetic activity at low temperatures and also increased metal levels to provide overall similar activity to that of more conventional catalysts. With the increase in metals, the magnitude of exotherms is amplified.

A facet of increased exotherm magnitude is the appeal of utilising this heat to raise bed temperatures during sulphiding. This could provide a means to improve the low temperature activation challenge, but excessive exotherms must be avoided as they can damage catalysts. Managing exotherm magnitude is important because of the risk it can self-reinforce or run-away. As the temperature of the bed is increased, the activation reactions are more vigorous and proceed faster which releases even more heat. Temperature stacking comes in with heat released in the bed raising the bed temperatures further along in the flow path. By adjusting (increasing) gas rates the exotherm may be managed.

A further consideration and challenge is the need to have most of the initial or fast reactions completed before moving to elevated temperatures. This is a consideration for preventing excessive temperature. Also, the initial sulphiding steps need to be mostly completed, forming MoS_2, before the 240 to 260°C transition which initiates nucleation of the MoS_2.

The ability of the metal sulphiding reactions to increase bed temperatures is mostly from the initial vigorous reactions. The reactions which follow are kinetically limited or have lower energy release, limited in ability to raise bed temperature in either case. The opportunity to use the higher metal levels of low temperature catalysts to raise bed temperatures requires finesse to have

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Fig. 13: **Adjusted procedure low temperature activation: Gas rate, 385 nghsv (600 aghsv), 2 to 4% H_2S, 4 to 10% H_2, 20% H_2O, dampened exotherm**

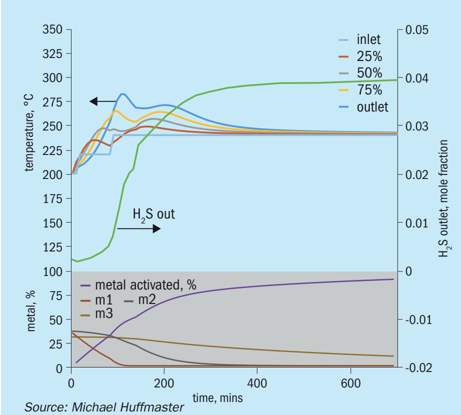

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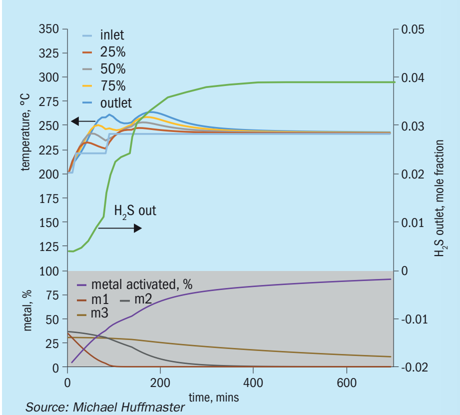
Fig. 14: **Adjusted procedure low temperature activation: High gas rate, 580 nghsv (900 aghsv), 2-4% H_2S, 4 to 10% H_2, 10% H_2O, suppressed exotherm**



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most of the initial high energy reactions completed before moving to higher temperatures.

The critical factor is to achieve a 240°C to 260°C transition temperature and 260°C or a target of 270°C in the bed for transformation. Although it may not be as effective as traditional temperatures, it is an enhancement which can be applied in LT TGUs. The rate of crystallisation is slower at lower temperatures, but with nucleation initiated, perhaps an acceptable level of slab formation will occur with extended time.

Options for plant owners

Plant owners can consider improvements to existing facilities and enhancing plant specifications to address activation requirements. Areas of focus should be process information and equipment constraints. These include:

- managing activation to utilise heat of sulphiding to achieve bed temperatures of 270 to 315°C:
  - to achieve a temperature above 260°C transition, one hour or preferably longer
  - to increase H_2S concentration of 2.5% initial to 5% during sulphiding with gas rate set appropriately to control exotherms;
- placing more thermocouples in one zone of bed to provide temperature tracking on a fine grid of 10 cm;
- setting specification for plant design that addresses minimum activation requirements:
  - minimum specifications sufficient for effective sulphiding, e.g., 275°C, preferably 300°C
  - creative utilisation of supplemental heating designed just for catalyst activation
  - including provision of proper supply of acid gas and hydrogen
  - providing proper metering of streams used activation, e.g., hydrogen, acid gas (H_2S), and recycle gas;
- employing pre-activated catalyst;
- utilising very high activity catalyst and accept partial activation;
- changing catalyst more frequently to avoid running at low activity of aged catalysts.

Conclusions and recommendations

- Low temperature TGUs often are constrained to temperatures in the range of 220 to 240°C.
- Lower temperature prolongs sulphidation; activity may be as low as 2/3 of full.
- Advancement in low temperature activation work incorporates published research on activation mechanisms and identifies pathways.
- Key sulphiding conditions identified are:
  - transition at 240 to 260°C, critical for molybdenum reduction,
  - transformation requires 260°C, seeding nuclei needed to initiate crystallisation.
- Modelling to represent sulphiding kinetics with heat and mass transfer for adiabatic conditions provides bed thermal profiles for assessment of activation procedures.
- Initial vigorous reaction must be managed to avoid excessive exotherms and H_2S starvation.
- Sulphiding procedure enhancement opportunities for low temperature TGUs are:
  - gas rate is major control, targeting 275 to 320 nghsv.
  - raise initiation temperature and accelerated ramping.
  - increasing hydrogen partial pressure; recommend 5% minimum and prefer 10%.
  - increasing H_2S partial pressure; initiation at 1 to 2%; ramp to 4 or 5%.
- Extending time at 240°C improves activation, but does not achieve activity of traditional 315°C temperatures.
- Operations has options to improve sulphiding:
  - manage activation to utilise heat of sulphiding to achieve bed temperatures 270 to 300°C.
  - set design specifications for effective sulphiding.
  - employ pre-activated catalyst.
  - utilise very high activity catalyst.
  - change catalyst more frequently.

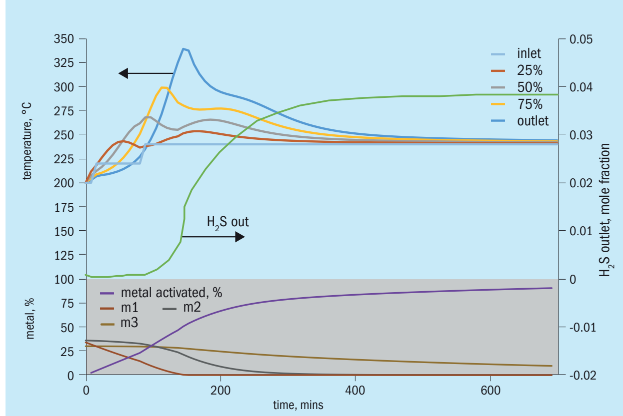
- Improving low temperature catalyst activation procedures enhances catalyst activity in the TGU reactor achieves low sulphur emission and environmental compliance.

Future work

Future work is needed:

- to develop thermochemical properties for reaction intermediates;
- to provide additional information on minimum effective H_2 partial pressure;
- to provide field verification of amended procedures and model predictions. ■

Fig. 15: **Adjusted procedure low temperature activation: Gas rate, 250 nghsv (400 aghsv), 2-4% H_2S, 4 to 10% H_2, 10% H_2O – excessive exotherm**



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