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SULPHUR

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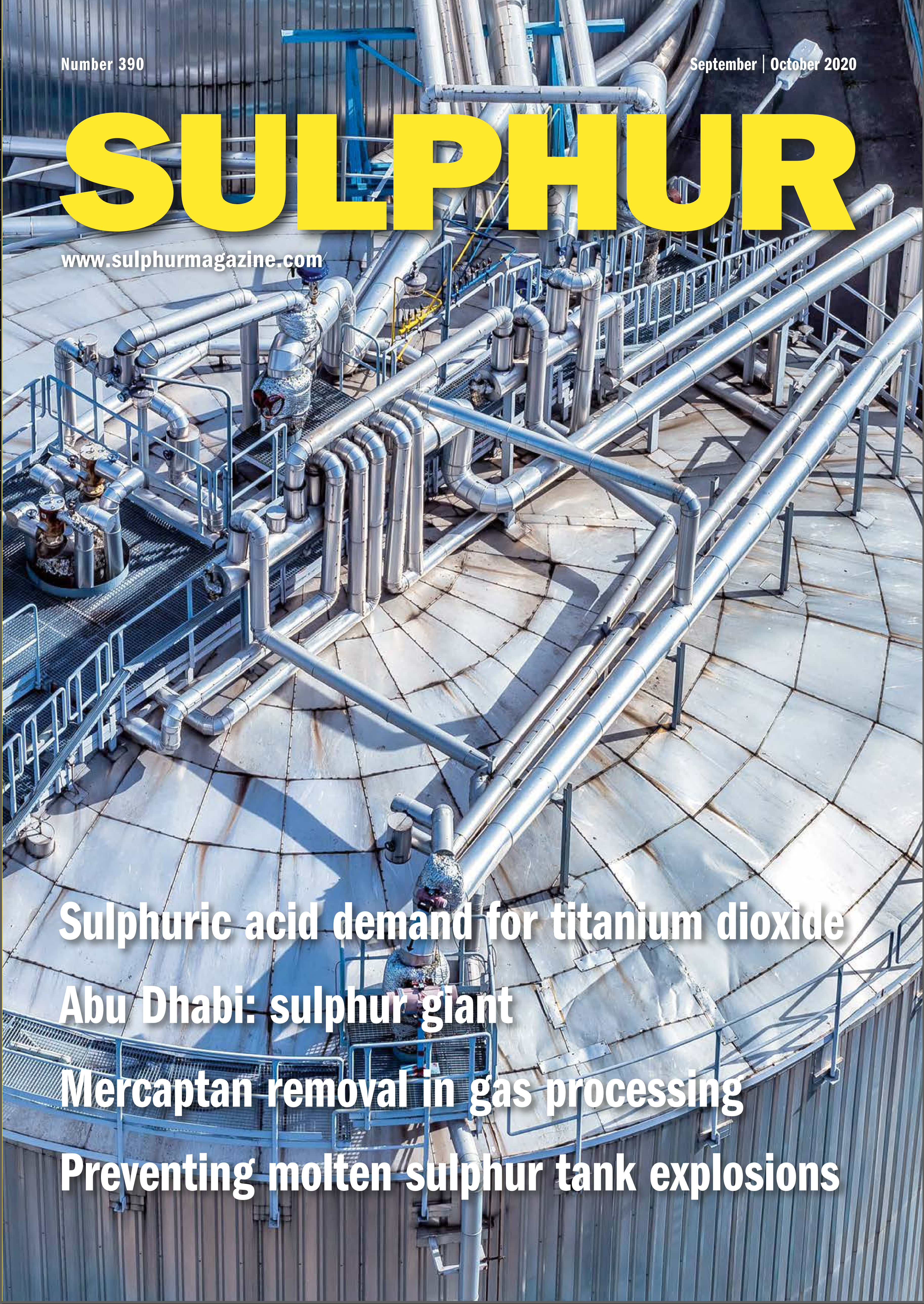

Sulphuric acid demand for titanium dioxide

Abu Dhabi: sulphur giant

Mercaptan removal in gas processing

Preventing molten sulphur tank explosions

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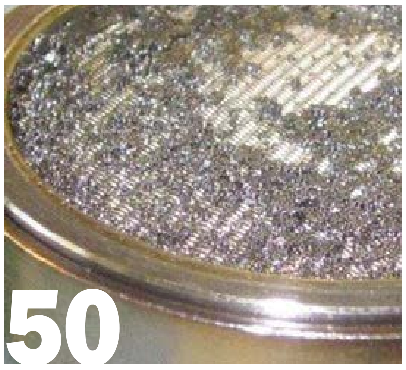
REGULARS

Titanium dioxide

Prospects for sulphuric acid demand.



Sulphur filtration

A new self-cleaning sulphur strainer now available.

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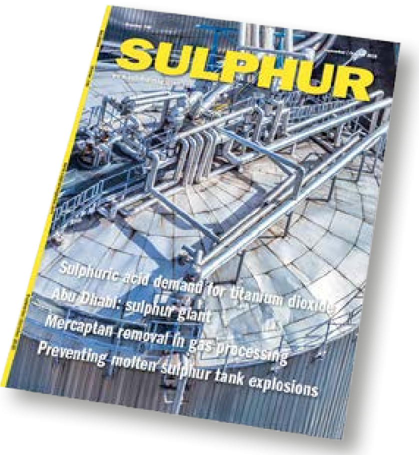

Is this Peak Oil?

Do you remember Peak Oil? This was the theory, driven by research originally conducted by petroleum geologist M.K. Hubbert in the 1950s, that oil production inevitably followed a bell curve, with supply eventually peaking as easier reserves were exhausted, leading to an inflexion point in production and a long tailing off. Originally Hubbert was talking solely about US oil production, and he seemed to have been borne out by the evidence. But a lack of discoveries of new large fields in the 1990s led to a revision of the theory that predicted a global production peak in 2005-6, potentially leading to rapidly rising oil prices until demand destruction occurred.

Of course, as we now know, advances in technology for unconventional oil extraction, especially tight oil, have upended all of those doom and gloom predictions, and the world now has more oil than it knows what to do with. Peak Peak Oil concern was probably somewhere in the period 2000-2005. So instead, over the past decade and a half, Peak Oil predictions have drifted away from the supply side of the equation and began to focus instead on the demand side. As the cost of renewable power falls and installations become more widespread, and there is an increasing take-up in electric- or hybrid-powered vehicles, together with fuel efficiencies and ageing populations who are less mobile, so, the theory runs, we will instead see peak oil production by default, as demand instead peaks and then begins to ebb away, and so prices fall and supply contracts with it. This would of course have major implications for the world's sulphur production, given that nearly 50% of it comes from the extraction of sulphur compounds from oil at refineries.

> **"The prospects for future oil demand start to look far more pessimistic."**

Until very recently, predictions for peak oil demand clustered around the medium- to long-term future; somewhere around 2030 or 2040, perhaps, once electric vehicles had started to make a significant impact on the demand for transportation fuels. But the Covid-19 pandemic has upset a lot of predictions this year, and as the shape of a world dealing with the virus on a longer term basis starts to become clear, so the prospects for future oil demand start to look far more pessimistic. The International Energy Agency (IEA) last month predicted 2020 oil demand would be down 8.1 million bbl/d on 2019. OPEC puts it at 9.1 million bbl/d down, and the prospects for a major recovery in 2021 seem to be fading. The most recent figures for oil consumption show that demand remains weak, and refining margins are low. US refinery utilisation rates fell from 93% at the start of the year to 67% in April, and even now are only at around 75%. Oil prices have slid below $40/bbl at the end of August, an unsustainable level for most OPEC producers, who rely on oil revenues to balance their books. OPEC cut output by 9.7 million bbl/d in April, albeit with a gradual slacking off of this as demand was expected to return, but in its absence it may find it needs to cut again.

Some of this, no doubt, is short term. But optimistic hopes of a vaccine have met a colder reality, and in the northern hemisphere winter may well bring a second surge in cases. Even now, air travel is down 40%, but avgas consumption is down more than 50%, as far fewer people are willing to risk long haul flights. The passenger ship market is at a standstill. And in Europe and North America people are commuting less. The longer that the pandemic persists, the more likely it is that it leads to permanent changes in behaviour. The move to home working and teleconferencing that has been forced by lockdowns will see some companies continue to operate that way after restrictions are lifted.

Bigger changes like protectionism and resource nationalism, and a general backlash against globalisation already present before the pandemic, but exacerbated by it, may also play a part. Likewise the weakening in Chinese growth that was already a feature of the world economy prior to 2020. And efficiency gains are also working to reduce demand – US oil demand peaked in 2005, and in spite of 10% more vehicle miles per year being travelled since then, efficiency savings mean overall consumption has continued to fall.

In 2007, OPEC predicted that global oil consumption would reach 118 million bbl/d in 2030. By 2019, however, it had revised this down to 108 million bbl/d. And with consumption for 2020 now forecast at only 91 million bbl/d, there seems an increasing chance that 2019's demand figure of 99.7 million bbl/d may be the highest that it ever reaches – that was the conclusion of a DNV GL report published just this week. Lower oil consumption of course means lower sulphur production. And even if there is a return to 100 million bbl/d, a surplus supply of oil may mean less of a premium (and so higher utilisation) for sweeter grades, and hence lower sulphur output even if demand does return. Perhaps the upside for sulphur in such a scenario is that a reduction in supply may at least make it more valuable. ■

Richard Hands, Editor

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Price Trends

MARKET INSIGHT

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

SULPHUR

Global sulphur prices were broadly stable through August. The holiday season contributed to the slower pace of price movement with limited trades confirmed. There has been increasing focus on firming processed phosphate prices to see if this will lend support to the sulphur market. Phosphate fertilizer demand has been healthy with the sustained uptick in prices reflecting the seasonal demand boost. The global pandemic is weighing on the economic outlook with uncertainty surrounding the possibility of a second wave in the coming months.

In Morocco, OCP has shown its ability to quickly adapt processed phosphates production output to meet demand. Lockdown measures in India introduced in March saw the shutdown of many plants reliant on Moroccan phosphoric acid, but with Indian demand bolstered by good rains and record plantings, OCP increased output of finished fertilizers. In late May, as Indian production normalised, OCP lowered finished fertilizer output, while boosting phosphoric acid shipments to compensate, keeping sulphur demand healthy over the disruption period. A spike in Moroccan Covid-19 cases led the government to introduce strict lockdown measures across several major cities. We understand that mining, logistics and fertilizer production operations are to remain unaffected in the country and the government is unlikely to impose restrictions that would impact OCP's operations. Moroccan DAP/MAP production is expected to increase in 2020 with an associated increase in sulphur consumption. There was a strong sulphur vessel line up at the port of Jorf Lasfar with 4.52 million tonnes of sulphur scheduled to discharge between 1 January and 25 August.

Looking to the nickel market, the outlook for Indonesian sulphur demand has been revised up with several high pressure acid leaching projects underway. The most imminent appears to be the Tsingshan, GEM and CATL joint venture. Plans are to produce 50,000 t/a of nickel and 4,000 t/a of cobalt. The facility will benefit from being constructed in Tsingshan's industrial site in Morowali, where a sulphur burner will likely be constructed and lead to an increase in sulphur imports. Start up is planned for late-2020.

Meanwhile in Madagascar the Ambatovy nickel mine shut down operations in March after workers contracted Covid-19. When operational, the mine produces 60,000 t/a of nickel and 5,600 t/a of cobalt as well as producing and consuming 2 million t/a of sulphuric acid. Sumitomo, which owns 48% of the project, expects the mine to remain closed until Q1 2021. This has led to a downward revision for sulphur imports and consumption for the short term. The majority of tonnes would usually be procured from the Middle East region. Sumitomo recognized approximately $500 million of impairment loss this July due to revenue losses tied to low nickel prices and production cuts.

Middle East producer pricing for August reflected a slightly softer tone since July with slight decreases posted across the board. In the UAE, ADNOC set its August monthly price at $58/t f.o.b. Ruwais, $2/t down on July, for shipments to the Indian market. KPC/Kuwait set its price for June at $54/t f.o.b. Shuaiba, down by $6/t on the previous month. State-owned marketer Muntajat set its June Qatar Sulphur Price (QSP) at $56/t f.o.b. Ras Laffan/Mesaieed. This was $2/t below July. The Muntajat spot tender in August was heard awarded in the high-$50s/t f.o.b.

Extensive supply disruption in the second quarter on the back of Covid-19 lockdowns has seen improvement in many regions but project delays appear to be emerging for new supply additions in the short term. In Kazakhstan operating rates at Kashagan are expected to improve from mid-September following the outage that began at the end of July. Production is likely to return to normal from the fourth quarter. In Kuwait, KNPC's Al Zour refinery was initially expected to be commissioned in the fourth quarter but sources close to the matter have said this is likely to be delayed, potentially pushing a start up to Q1 2021.

In its Q2 2020 financial results Saudi Aramco reported reaching full capacity rates at its Fadhili Gas plant at 2.5 scf/d after successfully completing its commissioning activities. Crude processing at the Jazan refinery is expected to begin in Q1 2021, a slight delay on previous estimates. Aramco's 325,000 bbl/day Ras Tanura refinery began maintenance in August, likely to last for a month, although this was unconfirmed. Upgrade work is set to be carried out at the facility.

Supply in the US faced temporary tightening with the arrival of Hurricane Laura. Refiners in Texas and Louisiana shutdown or reduced run rates, adding to the already tight market balance. No significant damage was noted to infrastructure however after the storm passed. Export prices out of the US Gulf were assessed at $56-60/t f.o.b. at the end of August. Data from the USGS for first half 2020 shows sulphur losses in the US were less than previously expected on the back of Covid-19 related disruption at refining operations. Total production was around 3% lower than a year earlier, equating to a drop of around 140,000 tonnes.

Supply has also been squeezed in parts of West Europe this year with refining capacity under pressure in the wake of the global pandemic's impact on refinery margins and inventories. Looking ahead, the Grossenkneten gas field is scheduled to undergo maintenance from 8 September to 13 October. During this period sulphur output will be halted. The erosion of Western European supply provides support to the prospects for sulphur remelters in the region. Logistics and Services company Saconix appears to be planning to complete construction and begin testing of its remelter project in Brake by the end of 2020. Operations are currently expected to begin in early 2022.

China sulphur imports in the first half of the year dropped by 28% to 4.2 million tonnes, a level not seen since at least 2011 according to trade data. The drop can be attributed to high inventory levels at major ports and the disruption to end users earlier in the year on the back of Covid-19 lockdowns. Operating rates at major processed phosphates producers in the Hubei province were down significantly in the first quarter. Port stocks surged to just over 3 million tonnes in February, remaining high through the first half of the year. Average port stocks have been around 2.8 million tonnes, much higher than 1.4 million tonnes in the same period in 2019. Sulphur prices in China have edged down by $6/t since the start of the year, averaging $57/t c.fr in the month of August. Pricing is expected to remain fairly stable through to the end of the year. Domestic production in China is forecast to rise in 2020, supporting the view for lower import demand in 2020 vs 2019.

SULPHURIC ACID

Average NW European export prices for sulphuric acid have dropped by 58% so far this year but proved to be the most resilient of the major exporters. Recovery has been slow and steady since drifting into negative netbacks. Prices ranged $9-17/t f.o.b. at the end of August, up from the lows of minus $18/t f.o.b. seen in April. Spot business concluded to the Americas led to firmer export prices in recent weeks. Smelters in the region are planning maintenance turnarounds in the third quarter, some were delayed from earlier in the year due to Covid-19 disruption. There is potential for a more balanced European market in the coming months, supporting stable prices with further recovery a possibility.

Contract business in Europe settled at decreases, with second half 2020 contracts concluded at €61-72/t c.fr, down from €67-78/ t c.fr in the first half. Third quarter contracts settled at €69-79/t c.fr, down from €74-86/t c.fr in the second quarter. The downturn was expected based on stable output from smelters and demand erosion from the industrial sector.

South Korea and Japan export prices were broadly stable through August with prices ranging minus $22/t to minus $12/t f.o.b. The gap between East and West export prices has remained steadfast with additional competition from Chinese exports weighing on the market. The downturn in demand from key markets alongside stable supply has put proven an obstacle to recovery. China is expected to remain a major global exporter of sulphuric acid in 2020 despite anticipated lower volumes compared with 2019. In the first six months of the year China exported just over 1 million tonnes of acid, down 9% on a year earlier. Morocco has been the main market, with volumes increasing by 34% to 389,000 tonnes. Indian demand has also shot up to 361,000 tonnes, with attractive prices an incentive in recent months. The main decline in trade has been to Chile, with trade down by 70% to just 142,000 tonnes versus a year earlier.

The pandemic is expected to erode global sulphuric acid consumption by 1.2% in 2020, with substantial rebound forecast from 2021. Africa is the main exception this year with increased demand forecast in the processed phosphates sector in Morocco. Phosphoric acid-based demand has remained more resilient than other sectors with government support through the pandemic. An increase of 500,000 t on 2019 levels is forecast reaching 102.1 million tonnes for the sector. Not all regions will see an increase – the Middle East will see a decline of around 500,000 t. Shutdowns across phosphate plants in the region will lead to a 1.5% drop in demand this year on 2019. After recovering next year, ongoing expansions at Ma'aden in Saudi Arabia will be responsible for the majority of acid demand increases in the outlook. Meanwhile in Latin America, while major consumers in the region have seen a significant contraction in sulphuric acid consumption from a demand shock for metals, Brazilian demand is predominantly phosphoric acid based. The September soybean planting season was forecast to be one of the largest on record amid strong sale prices and demand from China.

In Chile acid demand has been disrupted by the rise of Covid-19 cases in the country. Major copper consumers in Asia also entered lockdown in the first half of 2020, reducing copper refinery output and sulphuric acid consumption. Supply side shocks have also been developing over the past few months and major copper producers have reduced operations at mines as cases rose across the country. In June, copper output declined for the first time since the pandemic hit, coinciding with Codelco halting construction work at El Teniente and Chuquicamata. Codelco's mining operations continued, however the company idled its smelter at Chuquicamata at the end of June before restarting it earlier in August. Work at Chuquicamata has since resumed and expansion works at El Teniente are expected to restart later this month. We expect to see sulphuric acid imports to Chile dropping to around 2.6-2.8 million t/a in 2020, although this is dependent on the rate of recovery of the copper sector.

India looks set to become one of the worst affected countries by Covid-19. We expect a 15% decline in sulphuric acid demand across South Asia this year, almost all of which can be attributed to decreased phosphoric acid production. Despite a poor first half, declining sulphuric acid prices and a ramp up in fertilizer production as we enter a promising kharif season will aid in the recovery of sulphuric acid demand in India. ■

Price Indications

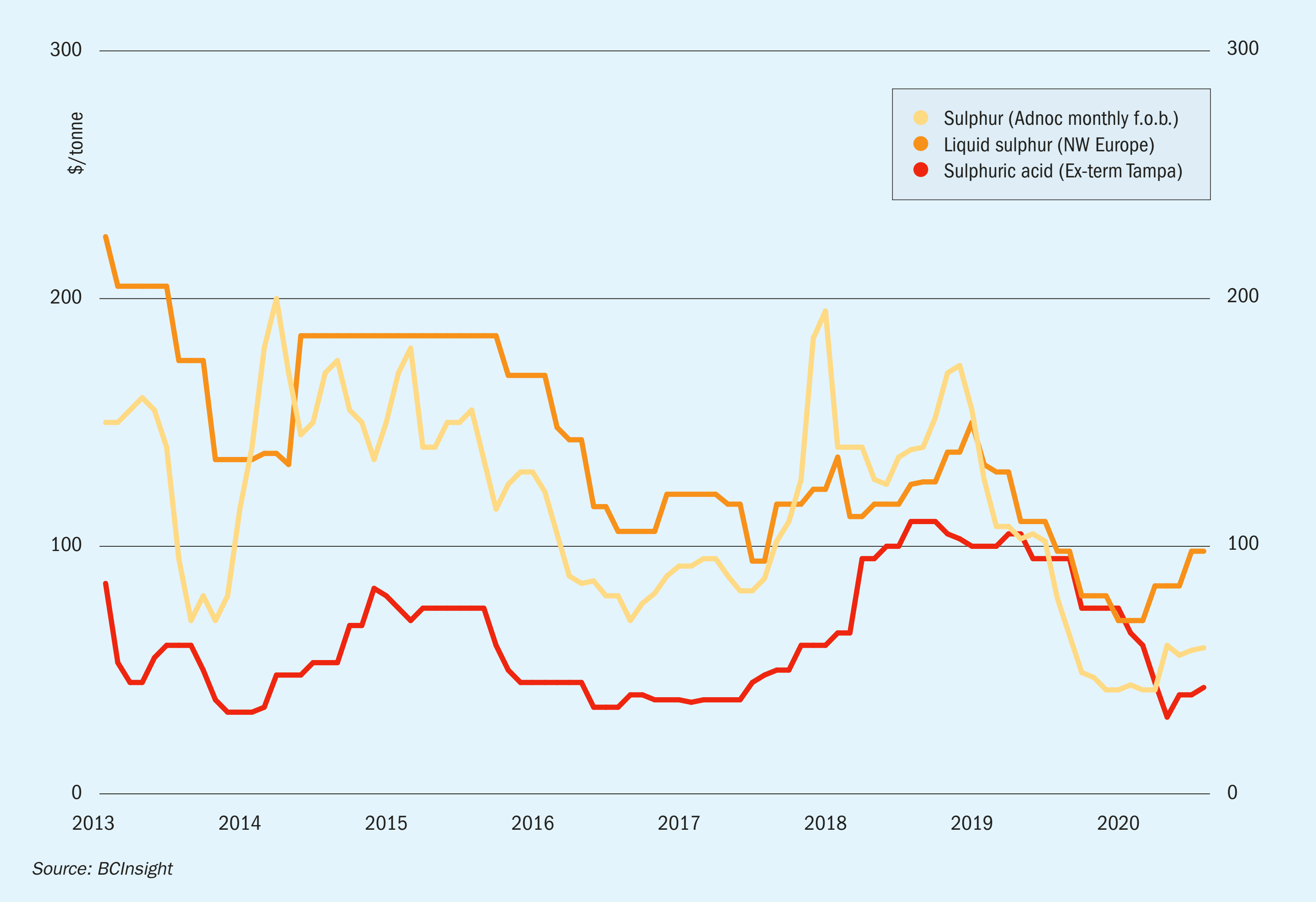
Table 1: **Recent sulphur prices, major markets**

Cash equivalent	March	April	May	June	July
Sulphur, bulk ($/t)					
Adnoc monthly contract	42	60	56	58	59
China c.fr spot	71	49	46	84	78
Liquid sulphur ($/t)					
Tampa f.o.b. contract	54	54	54	54	58
NW Europe c.fr	84	84	84	98	98
Sulphuric acid ($/t)					
US Gulf spot	45	31	40	40	43

Source: various

Market Outlook

Historical price trends $/tonne



Source: BCInsight

SULPHUR

- The risk of a second Covid-19 wave over the winter period continues to fuel the trend of forward trading of sulphur cargoes. Downward pressure in some sectors for demand is likely as the macro economic forecast remains challenging.
- Two Western European sulphur remelter projects are underway in Germany to ease the tighter balance that is currently forecast for liquid sulphur as gas based supply depletes and the refining sector remains under pressure.
- Indonesia is set to see significant ramp up in sulphur requirements if planned nickel leaching projects progress in the short and medium term. Sulphur imports are forecast to rise to meet demand.
- The development of the refining sector in China remains a major focus for the market as new production is forecast to rise to over 7 million t/a this year with the startup of projects including Sinopec's Zhanjiang refinery in Guangdong.
- **Outlook:** Project delays are anticipated on the back of disruption from Covid-19, pushing some new sulphur capacity additions into 2021. However, the short and medium term outlook still points to significant supply being added in the Middle East and China. The reduction in Chinese import demand requirements in the forecast would potentially lead to major shifts in trade patterns. Fourth quarter sulphur prices are forecast to see limited movement but some firming is possible within a small range.

SULPHURIC ACID

- DAP prices to remain steady to firm for remainder of 2020 and going into the new year, supporting sulphuric acid demand. DAP market expected to be in surplus from Q2 2021, leading prices to edge down.
- Indian import demand is set to reach record levels in 2020 at 1.9 million t/a. The Sterlite Tuticorin smelter is currently expected to remain closed through 2021, a key driver for sulphuric acid imports in the interim.
- Moroccan import demand is forecast to reach highs in 2020 at 1.9 million t/a, supporting trade through the remainder of the year.
- Planned smelter turnarounds appear to be below levels seen in recent years in 2020. This points to the likelihood of a busier schedule in 2021, potentially providing a floor to pricing during periods of weakness.
- The ongoing global pandemic remains a wildcard for the acid market. There is potential for further supply side disruption and demand losses over the year ahead.
- The sulphur supply forecast is expected to be an influential factor for acid prices. Increased sulphur availability from Middle East projects from 2021 may provide a ceiling on achievable acid prices.
- Industrial and metals markets are forecast to rebound from 2021 with a robust outlook for nickel and copper. The uncertain macroeconomic picture relating to Covid-19 remains a risk to demand growth.
- **Outlook:** Chile and Northeast Asian acid prices remain under pressure on the back of sustained weakness, limited demand and ample supply.

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Sulphur Industry News

DENMARK

Strategic alliance on *TopClaus*® technology

Haldor Topsoe and *Comprimo*® have announced a global strategic alliance to jointly license the *TopClaus* sulphur removal and recovery technology. *TopClaus* combines Topsoe's energy efficient wet sulphuric acid (WSA) process with the industry-standard Claus process, enabling plant operators to handle acid gases and achieve sulphur removal efficiencies of above 99.9%. The Claus part of the unit recovers elemental sulphur from acid gases, and the tail gases from the Claus unit are then treated in the WSA unit, where the remaining sulphur compounds are converted into sulphuric acid. The sulphuric acid is returned directly to the Claus reaction furnace for reprocessing to elemental sulphur, with no sulphuric acid left as by-product. However, sulphuric acid can be drawn off for specific uses or for sale as desired.

TopClaus can significantly reduce refinery CO_2 production as it eliminates the need to incinerate tail gas, while the WSA unit recovers as much as 90% of the process heat in the form of superheated high-pressure steam, which can be used in other refinery processes or for generation of electricity. The companies argue that this results in lower operating costs compared to conventional amine-based technologies that use steam for amine regeneration and which requires tail gas incineration.

"We are extremely satisfied to enter into this alliance. Topsoe is an industry leader, and we share their commitment to provide customers around the world with smarter and more sustainable solutions to protect the environment," said Frank Scheel, senior vice president, Comprimo. ■

A WSA plant such as this treat tail gas from the Claus unit to achieve more than 99.9% sulphur removal efficiency (SRE).

SWEDEN

IPCO celebrates 40 years of its *Rotoform* pastillation system

Sulphur processing and handling equipment manufacturer IPCO is celebrating 40 years' continuous production of its *Rotoform* sulphur pastillation system. The rotary drop-forming technology was first developed in 1980, and was a major innovation in sulphur solidification, producing a premium formed product with consistent size, moisture and friability specifications. As formed sulphur can be handled many times between solidification and subsequent reprocessing, often being shipped between continents, IPCO argues that this predictable quality is a major advantage for the producer, the transportation company and the final customer. IPCO says that *Rotoform* is the most widely used sulphur pastillation system in the world in terms of number of processing units, with more than 750 machines installed to date.

"We had been supplying flaking systems since the early 1950s," said Johan Sjögren, Managing Director of IPCO's Equipment division, "and our range now encompasses storage and handling solutions too, but the introduction of *Rotoform* was a defining moment for the company."

While the core principle – direct melt solidification on a steel belt cooler – remains unchanged, *Rotoform* technology has expanded over the years to include higher capacity versions, such as the *Rotoform* S8, with a capacity of 140 t/d, and the *Rotoform* HS, a high speed model with a capacity of up to 350 t/d.

A view inside the Rotoform machine, showing the deposition cylinder and steel water-cooled belt.

The machine consists of a heated cylindrical stator, supplied with molten sulphur via heated pipes and filter, and a perforated rotating shell that turns concentrically around the stator. Drops of the product are deposited by the nozzle bar across the whole operating width of a continuously running stainless steel belt. A system of baffles and internal nozzles built into the stator provides uniform pressure across the whole belt width, providing an even flow through all holes of the perforated rotary shell. This ensures that all pastilles are of uniform size, from one edge of the belt to the other.

The rotation speed of the machine is synchronised with the speed of the steel cooling belt to allow gentle deposition of the liquid droplets onto the moving belt. Heat released during cooling and solidification is transferred via the steel belt to cooling water sprayed underneath. This water is collected in tanks and returned to the water re-cooling system; at no stage does it come into contact with the product. After the drop has been deposited onto the steel belt, any product residue on the outer shell is returned to the Rotoform via a heated refeed bar which keeps the outer shell clean. The sulphur droplets are then discharged as solid, hemispherical pastilles at the end of

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the cooling system. To eliminate the possibility of damage to the pastilles during discharge, a thin film of silicon-based release agent is sprayed onto the steel belt.

IPCO argues that this process offers a number of advantages; as the cooling water never comes into direct contact with the sulphur, there is no risk of cross contamination. Secondly, solidification takes less than ten seconds so there is little time for H_2S to escape, resulting in very low emissions. And low levels of sulphur dust levels mean no need for exhaust air treatment.

CANADA

No long term effect on oil sands from Covid

Canadian oil sands production is expected to decline by nearly 175,000 bbl/d in 2020 as a result of Covid-19 – the largest annual decline on record. However, the longer-term forecast for oil sands production is expected to be little changed according to market analysts. IHS Markit projects Canadian oil sands production to reach 3.8 million bbl/d in 2030, nearly 1.1 million bbl/d higher than 2020 levels. This is down only slightly from previous forecasts of 3.9 million bbl/d in 2030. The oil sands patch is likely to see sustained but slow growth over the next decade, with transportation constraints such as a lack of adequate pipeline capacity and the resulting sense of price insecurity in western Canada weighing on new large-scale incremental investments.

Oil sands production is anticipated to rise over the back half of 2020 and into 2021 as curtailed production comes back online and existing installed capacity that has never been fully utilised ramps up. Should the Government of Alberta ease its regulated curtailment, by 2022 oil sands output could rebound from its Covid-induced declines to more than 300,000 bbl/d higher than 2019 levels.

Production would then proceed along a trajectory close to prior expectations, with most production growth to 2030 coming from Covid-19 recovery and ramp-up of already existing production capacity.

About half (over 500,000 b/d) of the rise in production is expected to come from incremental investments in new capacity, the majority of which will come from projects where some capital has already been deployed. Less than a third of anticipated growth to 2030 is expected to come from new projects that include entirely new greenfield operations or projects to expand existing facilities.

UNITED STATES

Evonik acquires Porocel

German chemical firm Evonik is acquiring the Houston-based Porocel Group for $210 million to accelerate the growth of its catalysts business. Porocel offers a technology for rejuvenation of desulphurisation catalysts, which are in increasing demand to produce low-sulphur fuel. Rejuvenation reduces CO_2 emissions by more than 50% compared with the production of new desulphurisation catalysts. In addition, Porocel has available production capacity, enabling Evonik to speed up expansion of its existing business with fixed-bed catalysts. Evonik says that it expects to increase sales of the combined catalyst business to significantly more than €500 million by the end of 2025 without the need for investment in new capacities. The acquisition gives Evonik access to major customers in the refinery and petrochemicals sector. Porocel's core competence is an efficient technology for purification adsorbents, sulphur recovery catalysts and hydroprocessing services highlighted by rejuvenation of used desulphurisation catalysts.

"This acquisition is the next logical step in the strategic development of our portfolio. Our focus is on stable and high-margin specialty chemicals," said Christian Kullmann, chairman of Evonik's executive board. "We are systematically expanding the share of our specialty businesses – and that at an attractive valuation."

"Sustainability and especially circular economy play a decisive role for us when it comes to acquisitions and the orientation of our portfolio," said Claus Rettig, head of the Smart Materials division. "With the acquisition of Porocel we are meeting increasing demand that is coming from a trend towards sulphur-free fuels as well as reducing CO_2 emissions and saving resources. The catalyst rejuvenation process results in significantly less CO_2 emissions than the manufacture of fresh catalysts, while yielding comparable efficiency and at a much lower cost."

Agriculture replaces fossil fuels as largest human source of sulphur

A new study has found that fertilizer and pesticide applications to crops are now the most important source of sulphur in the environment. Sulphur used to find its way into soils via sulphur dioxide emissions from burning fossil fuels and its uptake into 'acid rain', a phenomenon which gained attention in the 1960s and 70s when scientists linked degradation of forest and aquatic ecosystems across the northeastern US and Europe to fossil fuel emissions from industrial centres often hundreds of kilometres away. This research prompted the Clean Air Act and its Amendments, which regulated sulphur content of fuels and emissions by power stations, driving sulphur levels in atmospheric deposition down to low levels today.

Eve-Lyn Hinckley, assistant professor of environmental studies at University of Colorado, Boulder, said: "our analysis shows that sulphur applications to croplands in the US and elsewhere are often 10 times higher than the peak sulphur load in acid rain. No one has looked comprehensively at the environmental and human health consequences of these additions."

"Although sulphur is applied to agricultural lands to improve the production and health of crops, it can have detrimental effects to agricultural soils and downstream waters, similar to what occurred in remote forest landscapes under acid rain," added Charles Driscoll, a professor at Syracuse University and co-author of the study.

The researchers examined trends in sulphur applications across multiple important crops in the US, including corn in the Midwest, sugarcane in Florida, and wine grapes in California. Their models of surface water sulphate export demonstrated that while areas like New England show declining trends in response to recovery from historic atmospheric deposition, sulphate export from agricultural areas is increasing.

The researchers predict that increasing trends will continue in many agricultural regions around the world, including places like China and India that are still working to regulate fossil fuel emissions, and argue that it is time for the research community to apply lessons learned while investigating the effects of nitrogen and phosphorus fertilizers to studying the implications of high sulphur use in agriculture.

Marathon closes two US refineries

Marathon Petroleum is to permanently close 200,000 bbl/d of refining capacity because of the reduction in demand for transportation fuels caused by the Covid-19 pandemic. The company says that it will reduce its 166,000 bbl/d Martinez, California refinery to terminal operations and consider converting units to renewable diesel production. The company has no plans to restart its 27,000 b/d refinery Gallup, New Mexico, in any capacity. Both have been idled since April.

US gasoline demand fell by about 50% in the first months of 2020 because of the pandemic, and jet fuel consumption almost totally ceased. While there has been a recovery, with gasoline consumption now back up to about 10% below the same time as last year, jet fuel markets continue to be poor, with surplus fuel blended into diesel supplies, leading to inventory levels of ultra-low sulphur diesel being 30% up on average values.

"Our bigger view would be that we expected several million barrels to rationalise across the globe before this," Phillips 66 executive vice president of refining Bob Herman said. "The pandemic only pushes it forward, and we probably get it sooner than later."

North American refinery shutdowns have totalled 800,000 bbl/d in 2020, including Philadelphia Energy Solutions 330,000 bbl/d facility in Philadelphia, and Calcasieu Refining confirming that it will idle its 136,000 bbl/d refinery in Calcasieu, Louisiana, through at least August.

KUWAIT

Completion of clean fuels project in Kuwait

Fluor Corporation says that its joint venture with Daewoo Engineering & Construction and Hyundai Heavy Industries has successfully achieved final provisional turnover of the facilities for Kuwait National Petroleum Company's (KNPC) Mina Abdullah Package 2 (MAB2) Clean Fuels Project in southern Kuwait.

The Clean Fuels Program is being executed on the three KNPC-owned and operated refineries in Kuwait. As part of the program, KNPC plans to retire existing processing facilities at the Shuaiba Refinery and perform a major upgrade and expansion of the Mina Abdullah and Mina Al-Ahmadi refineries to integrate the refining system into one complex with full conversion operations. The MAB2 package consists of a hydrogen plant, sulphur block (sour water stripper, amine regeneration unit and sulphur recovery unit) and utilities, off-sites and non-process buildings. MAB2 includes 800 t/d of additional sulphur recovery capacity for the refinery.

Mark Fields, president of Fluor's global Energy & Chemicals business said: "It has been an honour to complete this megaproject alongside KNPC, training hundreds of their personnel and leveraging multiple local suppliers and contractors. We look forward to providing ongoing support to the refinery's commercial operations and helping KNPC deliver on its mission to strengthen Kuwait's economy by producing high-quality fuels to meet both local and international demand."

INDIA

Desulphurisation project to commission this year

Chennai Petroleum Corporation Ltd (CPCL), a subsidiary of the state-owned Indian Oil Corporation, says that it is planning to commission two major projects, worth $300 million, during the 2020-21 financial year. The company has successfully completed the BS-VI revamp project, adding 600,000 t/a of capacity via a new fluid catalytic cracker gasoline desulphurisation unit. Pre-commissioning activities have begun and mechanical completion

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is expected during this quarter. Commissioning is expected by 4Q 2020. The new sulphur recovery block is expected to be mechanically complete by 1Q 2021.

The expansion comes at a difficult time for India's refiners because of Covid-19. Several Indian refineries have scaled back operations, including CPCL's 211,000 bbl/d Manali refinery, where production is down by 40%.

AUSTRALIA

Cobalt project presents revised economic projections

Cobalt Blue Holdings has released a project update on its Broken Hill cobalt sulphide project. The update reports significant improvements in project economics compared to the 2018 pre-feasibility study. It also upgraded mineral ore probable reserves by 55% to 71.8 million tonnes with a grade of 710 ppm cobalt, expanding the targeted life of mine to over 17 years.

Cobalt Blue plans to mine up to 6.3 million tonnes of ore, generating 3,500-3,600 t/a of cobalt for electric vehicle batteries. The project will also produce up to 300,000 t/a of elemental sulphur from thermal decomposition of pyrites. A bankable feasibility study and final investment decision is expected to be completed in 2022.

CHINA

Saudi Aramco pulls out of Chinese refinery

Saudi Aramco has suspended a deal to build a $10 billion refining and petrochemicals complex in China, according to press reports. Aramco agreed last year to form a joint venture with Chinese partners China North Industries Group Corp and Panjin Sincen to build a 300,000 bbl/d refinery in the northeastern province of Liaoning. The joint venture, Huajin Aramco Petrochemical Co., would have taken 70% of its oil from Saudi Arabia for processing. However, the impact of Covid on oil prices and energy markets have evidently changed the calculations for Aramco, which faces deep cuts to its capital spending as it tries to maintain a $75 billion dividend amid low crude prices and rising debt. Reports indicate that the Chinese partners currently still intend to continue with the project, which also includes an ethylene cracker and a paraxylene unit.

VENEZUELA

Venezuelan oil production drops to near zero

In spite of having the largest paper oil reserves in the world, Venezuela's oil production is declining so quickly that it may soon reach zero, according to analysis by IHS Markit. Venezuelan crude oil production is currently estimated at around 100-200,000 bbl/d and falling. Production was around 650,000 bbl/d just a year ago and in 2017 was as high as 2 million bbl/d. The decline of the country's oil industry – Venezuela's main foreign currency earner – has been a catalogue of poor management, lack of investment and difficult security conditions, as well as a lack of domestic storage capacity, ongoing US sanctions and Covid restrictions. The country is now the third smallest producer among OPEC's 13 members. However, travel restrictions globally due to Covid mean that global oil markets are subject to poor demand and remain oversupplied in spite of the absence of Venezuelan capacity. Venezuela's refineries had been producing up to 700-800,000 t/a of sulphur at maximum output.

Sulphuric Acid News

CHINA

Hengli starts up new alkylation unit

DuPont Clean Technologies has announced the successful startup and performance test of a 300,000 t/a *STRATCO*$^{\circledR}$ alkylation unit licensed at the Hengli Petrochemical Company's new refinery complex on Changxing Island in the Harbour Industrial Zone, China. The new alkylation unit enables Hengli to produce high-quality alkylate from a 100% isobutylene feed stream, catalysed by sulphuric acid. This first-of-a-kind unit was developed through DuPont research into the best ways to maximise product octane and minimise end point with this feedstock. Hengli had awarded DuPont the contract for the new alkylation unit as well as a *MECS*$^{\circledR}$ sulphuric acid regeneration unit in 2015.

The alkylation unit uses patented XP2 technology by DuPont in the *STRATCO* reactor, designed to improve the acid/hydrocarbon emulsion flow path near the tube bundle heat transfer area of the reactor in order to realise significant process benefits and achieve optimal alkylate product quality.

"DuPont Clean Technologies could not be happier with its ability to enable Hengli Petrochemical Company to meet performance guarantees while processing a feed never before processed in an alkylation unit," said Eli Ben-Shoshan, Global Business Leader, DuPont Clean Technologies. "It's a groundbreaking achievement and we're very pleased to provide innovative technology and services that support the operational and business goals of Hengli." ■

INDIA

Vedanta appeals court ruling on copper smelter

Vedanta Ltd has appealed against the Madras High Court's refusal to allow the reopening of the Sterlite Copper plant in Thoothikudi, Tamil Nadu. The company's move follows a verdict that dismissed Vedanta's petition to reopen its copper smelter and upheld the state government's decision to shut it down. The closure of the unit has amounted to a monetary loss of around $820 million to the company, and has led to a surge in India's imports of sulphuric acid. The smelter's 1.2 million t/a acid plant supplied 30-40% of India's domestic needs for acid and its closure has turned India into a net importer of sulphuric acid.

The Sterlite plant was closed in May 2018 by order of the Tamil Nadu Pollution Control Board (TNPCB) amid a backdrop of protests against the unit that left 13 people dead when police fired on demonstrators. This PCB order set aside an earlier National Green Tribunal order that allowed the opening of the plant. Vedanta says that emission levels at the sulphuric acid unit were on a par with similar facilities in Europe, and that it had invested in a flue gas desulphurisation system for the smelter, over and above necessary compliance with emission control regulations, as well as monitoring ambient air quality through continuous monitoring stations in and around the plant as well as through a fence line monitoring system.

MOROCCO

OCP to double EMAPHOS production capacity

OCP Group and its partners, Germany's Budenheim and Prayon of Belgium, are to begin constructing a new purified phosphoric acid (PPA) plant at Jorf Lasfar, through their jointly-owned Euro Maroc Phosphore (EMAPHOS) subsidiary.

This new plant will effectively double EMAPHOS' annual production capacity to 280,000 tonnes P_2O_5 when it enters production during the fourth-quarter of 2022.

Basic engineering was completed in March with the project currently at the detailed engineering stage. Construction is, however, scheduled to start in the first-quarter of 2021. Equipment with long lead-in times will be ordered later this year in advance of construction commencing.

The major expansion project is part of an ambitious strategy by the three EMAPHOS partners to establish a world lead in PPA production. The development will also strengthen OCP's presence in the speciality phosphate market.

Budenheim, part of massive food conglomerate Oetker, specialises in high-value, phosphate-based food, pharmaceutical and technical products. Prayon, which is jointly owned by OCP Group and the Société Régionale d'Investissement de Wallonie (SRIW), is a world-leading phosphoric acid technology company and speciality phosphate producer.

CHILE

Codelco restarts copper smelter

Codelco has begun to restart the smelter at its Chuquicamata complex. It has also restarted work at the large scale construction projects at its Chuquicamata and El Teniente mines. Work was halted on all three sites in June due to an outbreak of Covid-19 among the workforce. However, the number of positive novel coronavirus cases among its workforce now appears to be falling. To reduce the risk of infection, the number of workers on-site was drastically reduced from March onward, shift cycles have been lengthened and many auxiliary activities, including mine development and maintenance, have been suspended. However, following a spike in the number of cases in June, with more than 3,000 workers infected, unions at Codelco threatened stoppages unless more was done to contain the pandemic, prompting more radical measures. To reduce the risk of infection, Codelco said it will continue to avoid using the airport at Calama, the nearest airport to Chuquicamata, and move workers from outside the city in sealed buses from airports in the nearby cities of Antofagasta and Iquique.

The smelter at Chuquicamata is one of Chile's largest with the capacity to handle 1.65 million t/a of copper concentrates and processes production from Codelco's Chuquicamata, Ministro Hales and Radomiro Tomic mines. The complex includes five sulphuric acid plants with a combined capacity of 10,000 t/d of acid (3.3 million t/a).

WORLD

Smelting at lowest level for two years

Global copper smelting activity fell to its lowest level in over two years in July, according to data from satellite surveillance of copper plants. Earth-i, which specialises in geospatial data, launched its SAVANT service late last year, tracking more than 100 smelters representing up to 90% of global production. It publishes a free monthly index of global copper smelter activity, which declined to an average of 41.5 in July, the lowest since March 2018 and down from 50.7 a month earlier. An index value of 50 indicates that the smelt-

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ers are operating at the average level of the last 12 months.

"The unusually swift decline coincided with a record amount of maintenance outages observed globally and follows a period of unusually low maintenance at Chinese sites relative to seasonal norms," the company said. Reuters also quoted Guy Wolf, global head of analytics at Marex, which helped develop SAVANT, as commenting: "Global activity levels overall have been propped up in recent months by the extremely strong readings coming out of China. "With China now seeing more maintenance, the weakness globally is starker. What is particularly striking is the sustained period of exceptionally low activity readings from North America. Physical traders will be on the alert in case that leads to strength in premiums in the second half of the year."

BRUNEI

Hengyi Industries to license alkylation technology

DuPont Clean Technologies has been awarded the contract to supply Hengyi Industries with licensing and engineering for a *STRATCO*® alkylation unit at the Brunei refinery in Pulau Murara Besar. The new refinery will not only supply the domestic market but also plans to produce refined fuel for export. In order to comply with the China VI standard of 10 ppm sulphur content for fuel, Hengyi commissioned DuPont for an 800,000 t/a (20,750 bbl/d) alkylation unit. The Pulau Muara Besar refinery and petrochemical plant has the capacity to refine 8 million tons of crude oil per year. The alkylation unit will enable Hengyi to generate low-sulphur, high-octane, low-Rvp alkylate with zero olefins that meets the criteria of the China VI standard. Startup is targeted for 2023.

KOREA

India imposes anti-dumping duty on phosphoric acid from Korea

India has imposed a five year anti-dumping duty on phosphoric acid from Korea in order to protect domestic manufacturers from cheap imports. The duty was imposed after the Commerce Ministry's investigation arm, the Directorate General of Trade Remedies concluded an investigation into alleged 'dumping' of "Phosphoric Acid of all grades and concentrations (excluding Agriculture or Fertilizer grade)" from Korea, and concluded that the acid was being sold at a price lower than that in the domestic Korean market. The anti-dumping duty is pegged at $137/tonne.

INDONESIA

New smelters delayed by lockdowns

The development of two $3 billion metal smelters mining firm PT Freeport Indonesia has fallen behind schedule because of the pandemic-related lockdowns, according to the company. The copper concentrate smelter – one of only two being developed in Indonesia – was 5.9% complete in July, behind the target of 10.5%, according according to Indonesia's Energy and Mineral Resources Ministry mining director general, Ridwan Djamaluddin. Meanwhile, the Freeport's gold and silver smelter had reached 9.79%, behind the target of 14.3%. The government expects Freeport to finish construction by 2023, in spite of the company's requests to extend the deadline to 2024. Indonesia's new Coal and Mineral Mining Law mandates all metal ore must be processed domestically by 2023. ■

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People

Chris Heaton has joined Baker Engineering and Risk Consultants, Inc. as Chief Executive Officer. Chris replaces Quentin Baker as part of BakerRisk's ownership and management succession plan. Baker will remain with BakerRisk, serving as chairman of the board, and will continue to support clients with incident investigations, engineering studies and research programs. Heaton has executive experience with risk engineering and consulting, fire protection engineering, life safety and incident investigation companies, and holds degrees in civil engineering and architecture.

SensoTech has announced a high level management restructuring which represents a generational change in leadership. **Robert Benecke** and **Hannes Benecke**, sons of the founder Dr. Ingo Benecke have become the company's new managing directors with immediate effect, replacing Dr. Ingo Benecke and SensoTech co-founder **Mathias Bode**, who have run the company for 30 years, developing and producing sonic velocity measuring instruments for liquid analysis which can be found in numerous industrial plants around the globe.

Robert and Hannes Benecke said that they are looking forward to the new challenges and tasks: "In a way, we grew up in the company and know many employees for a very long time. SensoTech GmbH has very well-functioning structures and we look forward to further developing the company. We would like to thank the previous managing directors for their trust and look forward to the new tasks." The objectives of the new management are the further development of the individual company divisions and the expansion of the international sales network. In this way, the successful course of the past years is to be further pushed.

Retiring director Dr Ingo Benecke said: "We would like to thank our employees, customers and business partners for the good, long-term cooperation. We had both good time and difficult. But even the difficult times were mastered through active commitment. With the handover to Robert and Hannes Benecke, we are banking on the future. The new management will tackle the tasks ahead with high motivation and determination and further develop SensoTech GmbH. We are convinced of this."

AMETEK Land has promoted **James Cross** to the role of global industry manager for the hydrocarbon processing sector (HPI). Having worked at AMETEK Land since 2018 and reporting to the Director of Development and Product Management, Cross will continue to carry out his existing role as regional sales manager – Middle East, whilst taking on new responsibilities for driving growth globally within the HPI sector. This includes working along the sales and marketing team to profile the market and gather customer data to steer the future product roadmap.

David Primhak, Director of Development and Product Management at AMETEK Land, said, "We are delighted to appoint James to the role of Global Industry Manager for HPI. He has a proven track record of developing new markets and his ability to understand customer requirements and provide innovative solutions will enable us to gain new business opportunities globally. HPI is a growing market for us and we wish James all the best in his new role."

Chemtrade Logistics says that **Mark Davis** has informed the board that he will retire as president and Chief Executive Officer (CEO) in 2021. **Scott Rook**, currently the Chief Operating Officer (COO), will replace Davis upon his retirement. Rook joined the organization as COO in September 2019 as part of Chemtrade's succession plan. Chair of the Chemtrade board, Lorie Waisberg, said: "Mr. Davis was instrumental in forming Chemtrade in 2001 and has served as its president and CEO since that time. Under his leadership, Chemtrade has substantially grown its business portfolio and organizational capabilities and has returned over $1.1 billion of capital to its unitholders."

Mark Davis said, "I am extremely proud of the organisation and business portfolio that my team built over the last 20 years. Recently, our resilience during the COVID pandemic has validated the strength of our culture and diversified businesses. Since joining Chemtrade, Scott has demonstrated genuine leadership and deep knowledge of our businesses. I will be leaving Chemtrade in good hands." ■

Calendar 2020

! The following events may be subject to postponement or cancellation due to the global coronavirus pandemic. Please check the status of individual events with organisers.

SEPTEMBER

15-16

17th Sulphur Industry Chain Summit,
SHANDONG, China
Contact: OilChem Overseas Sales
Tel: +86 533 2591773
Web: en.oilchem.net

15-17

Brimstone 'Virtual Vail' Annual Sulphur Recovery Symposium – Virtual event
Contact: Mike Anderson, Brimstone STS
Tel: +1 909 597 3249
Email: mike.anderson@brimstone-sts.com
Web: www.brimstone-sts.com

28-30

SOGAT 2020 – Virtual Event
Contact: Nick Coles, Dome Exhibitions
Email: nick@domeexhibitions.com
Web: www.sogat.org

OCTOBER

7-8

TiO2 World Summit, CLEVELAND, Ohio, US
Contact: Shannon Siegferth, Smithers
Tel: +1 330 762 7441
Email: ssiegferth@smithers.com

NOVEMBER

2-6

RefComm Galveston 2020 – Virtual event
Contact: Refining Community
Tel: +1 360 966 7251
Web: refiningcommunity.com/refcomm-galveston-2020/

9-11

Sulphur and Sulphuric Acid Conference 2020 – Virtual event
Contact: CRU Events,
Chancery House, 53-64 Chancery Lane,
London WC2A 1QS, UK
Tel: +44 20 7903 2167
Email: conferences@crugroup.com

17-18

European Refining Technology Conference – Virtual event
Contact: Sandil Sanmugam,
World Refining Association
Tel: +44 20 7384 7744
Email: sandal.sanmugam@wraconferences.com

24-25

European Sulphuric Acid Association Autumn General Assembly,
VIENNA, Austria
Contact: Francesca Ortolan, Cefic
Tel: +32 2 436 95 09
Email: for@cefic.be

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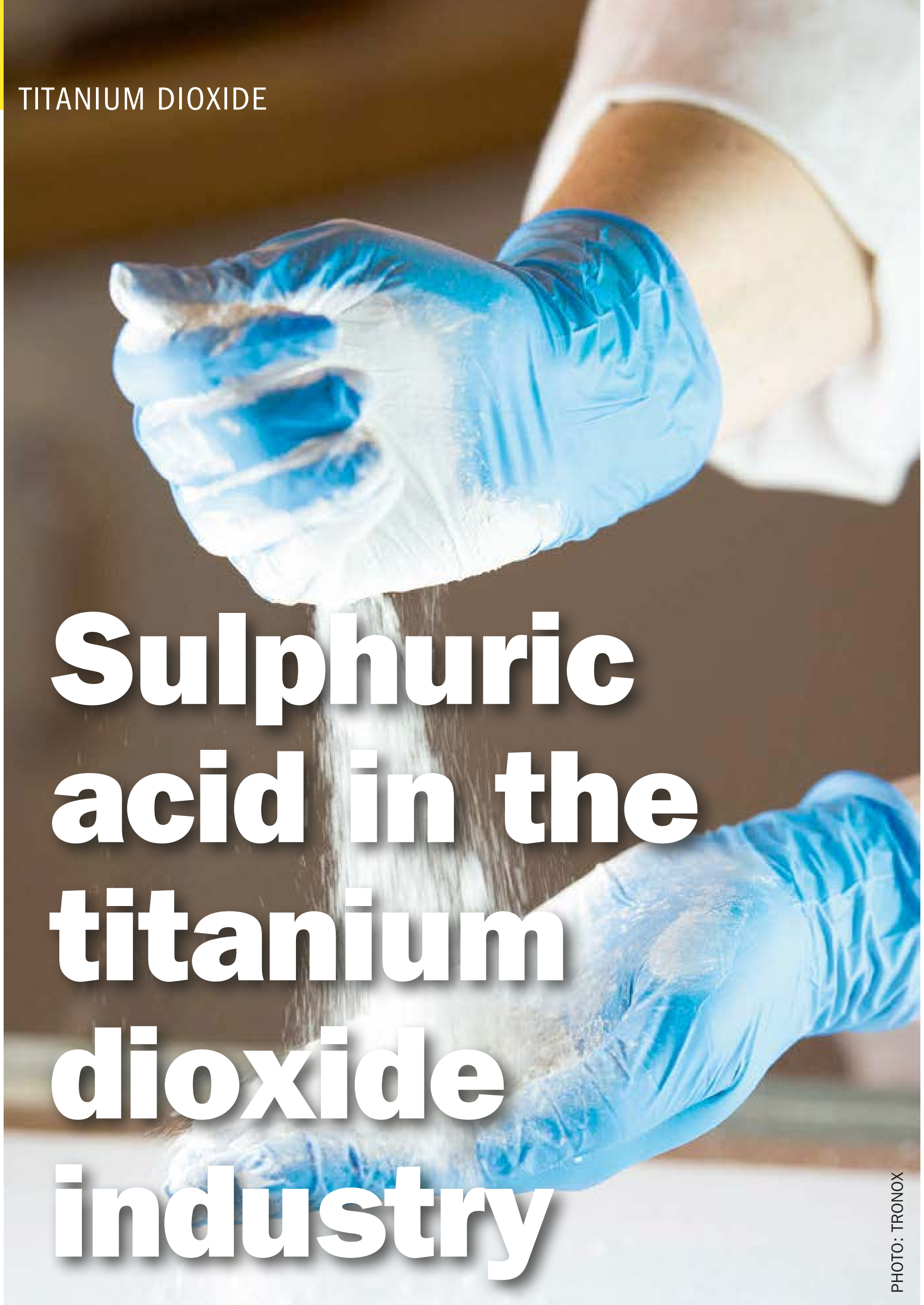

PHOTO: TRONOX

Sulphuric acid in the titanium dioxide industry

Reg Adams of pigments and titanium dioxide consultancy Artikol reviews the demand for sulphuric acid in the manufacture of TiO_2, and the prospects for consumption over the next few years.

Nearly 15 million tonnes of sulphuric acid (as 100% H_2SO_4) were used for the manufacture of titanium dioxide (TiO_2) last year. China's TiO_2 manufacturers accounted for about 77% of the total, while TiO_2 manufacturers in the rest of the world accounted for 23%.

Thanks to its high refractive index, its light scattering ability and its relative chemical inertness, TiO_2 is unrivalled as an opacifier and as a white pigment. In addition, TiO_2 has certain properties which make it extremely suitable as an ultraviolet absorber (for sunscreens and cosmetics), as a catalyst (for denitrification of exhaust-gases), as a photocatalyst (for self-cleaning and germicidal applications), as a delustrant (for synthetic fibres) and as a component of solar cells (for power generation). For many years, TiO_2 has been comfortably within the top 20 in the world league of inorganic chemicals – albeit with much lower consumption (in volume terms) than sulphuric acid and the major fertilizer products. At an average price of about \$3/kg, however, TiO_2 claims a place in the top ten inorganic chemicals in value terms; it is a \$20 billion industry.

Assured long-term demand

World consumption of TiO_2 amounted to 6.17 million tonnes in 2019, of which Europe (including Russia and the CIS countries) accounted for 17%, North America for 17%, Latin America for 7%, the Middle East and Africa for 4%, China for 37%, Japan for 4% and the rest of the Asia/Pacific region for 15%. Dry powdered TiO_2 has a very long shelf-life, given suitable storage conditions. This is one reason why world TiO_2 consumption, measured as aggregate manufacturers' shipments, fluctuates quite significantly from year to year as a result of variations in consumer inventories. Over the long term, however, say 1989 to 2019, the increase in world TiO_2 consumption has averaged 2.5% per annum. This is similar to the long-term average growth rate for global GDP. TiO_2 is difficult to recover from post-consumer waste or scrap, so there is no serious threat of recycled material troubling the consumption of virgin TiO_2. Also, there is no serious threat of substitution of TiO_2 in any of its important end-use applications.

Paint and plastics are the two major end-use sectors for TiO_2. In most countries, the paint industry accounts for 50-80% of TiO_2 consumption. In the world as a whole, paint accounted for 56% of consumption in 2019, plastics for 25%, décor paper for 7%, printing inks, textiles and catalysts for 3% each and sundry niche sectors for the remainder.

Chloride versus sulphate route

There are two groups of processes for manufacturing TiO_2: the chloride-route and the sulphate-route. Whichever route is chosen for making the "chemically pure" TiO_2, the final steps involved in converting this into a finished pigment are essentially the same. The aims of the pigment-finishing process are to break up aggregates and agglomerates, then to mill the material to a more or less uniform particle size, and then to coat the TiO_2 particles with various chemicals designed to improve durability, dispersibility, wettability and other properties suited to the specific end-use in paints, plastics, inks, etc.

It is generally acknowledged that higher-quality TiO_2 pigment can be manufactured at a chloride-route plant. Essentially, this is because the technology facilitates a narrower particle size distribution, which translates to better light-scattering, hiding power and brightness. For certain applications, e.g. automotive paints, consumers insist on chloride-route TiO_2. However, for many other applications, e.g. in paint and plastic formulations with a significant loading of pigment extenders (kaolin or calcium carbonate), good quality sulphate-route TiO_2 is fully competitive with chloride-route TiO_2 on performance and appearance. In

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fact, for printing inks, sulphate-route rutile-type TiO_2 pigments are generally preferred because they are slightly less abrasive. For certain niche applications, such as food colorants, catalysts and textile delustrants, anatase-type TiO_2 is required and this is only available from sulphate-route plants. Overall, about 10% of the world's total TiO_2 requirement can only be satisfied by sulphate-route TiO_2; about 10% can only be satisfied by chloride-route pigment; and the remaining 80% can be satisfied by either sulphate-route or chloride-route TiO_2, of suitable quality.

On the supply side, there are massive differences between the regions in terms of the chloride versus sulphate split. In China, where end-2019 capacity amounted to 4.05 million t/a (47% of the world total), 89% is sulphate route, 11% is chloride route. In the rest of the Asia/Pacific region, the split is 55% chloride-route, 45% sulphate-route. In Europe (including Ukraine and Russia), the split is 44% chloride-route, 56% sulphate-route. In North America, with a total capacity of 1.49 million t/a, 99% is chloride-route and only 1% is sulphate-route. In the rest of the world (namely Brazil, Mexico and Saudi Arabia), the split is 90% chloride-route versus 10% sulphate-route.

Chloride-route technology essentially involves reacting the TiO_2 feedstock with elemental chlorine in the presence of petroleum coke at a temperature of 800-1,000°C to produce titanium tetrachloride, then oxidising with oxygen to produce TiO_2. In several process designs, the oxidation stage is carried out at pressures of 400-600 kPa. Because of the highly corrosive nature of titanium tetrachloride, chlorine and chlorine oxides, equipment made from specialty alloys is required. The detailed chemical engineering is quite complex and the intellectual property associated with successful operation of a chloride-route TiO_2 plant has been remarkably well protected. Just four companies – Chemours, Kronos, Tronox and Venator – are responsible for the technology employed at all the world's 19 chloride-route plants currently operating outside China. Within China, the major chloride-route TiO_2 producers have plants which were designed and engineered by Ti-Cons (of Germany).

Sulphate-route technology essentially involves reacting the TiO_2 feedstock with sulphuric acid (typically 85-95% H_2SO_4) at a temperature of 100-150°C to produce titanyl sulphate and iron sulphates. This acid digestion step is followed by clarification of the cooled black liquor, with unreacted solids being filtered out. Elemental iron is added to the digest solution so as to reduce all the ferric ions to ferrous ions. The liquor is then heated so as to concentrate the sulphates and then the copperas (ferrous sulphate) is separated out as crystals. The titanyl sulphate is hydrolysed to produce a colloidal TiO_2 hydrate, which needs to be washed and filtered prior to feeding into a calciner at 900-1,250°C so as to produce TiO_2. If TiO_2-rich slag is used as the feedstock instead of ilmenite, the copperas removal step is not necessary.

Acid consumption

There is a wide variety of sulphate-route plants. At one end of the spectrum are the small-scale plants, running a series of batch-type processes, lacking automated control systems and producing TiO_2 with a significant content of iron impurity, which imparts a yellowish tinge to the final product. At the other end of the spectrum are large-scale plants and plants that are equipped with systems for very precise process control systems for the hydrolysis and calcination stages, producing high-quality white pigments and specialty grades of TiO_2.

The quantity of sulphuric acid consumed mainly depends on the type of feedstock. For plants using Kronos ilmenite (45% TiO_2 content) – such as the Fredrikstad (Norway) and Nordenham (Germany) plants – the consumption of acid (as 100% H_2SO_4) is 4.2 tonnes per tonne of TiO_2 output. For plants using Velta's Ukrainian ilmenite (55% TiO_2 content) – such as the Prerov (Czech Republic) plant – the consumption of acid is 3.5 tonnes per tonne of TiO_2 output. For plants using Rio Tinto's Sorel slag (78% TiO_2 content) – such as the Varennes (Canada) plant – the consumption of acid is 2.5 tonnes per tonne of TiO_2 output. Several plants use a blended ilmenite/slag feedstock, so that the acid requirement is around 3.0 tonnes per tonne of TiO_2 output.

The sulphate ion ends up in the copperas and in acid-rich waste effluent. At many plants, the copperas is converted into marketable by-product ferrous sulphate for use as a water-treatment chemical, soil-conditioner or cement additive. Copperas generated at Venator's Duisburg-Homberg TiO_2 plant is used to supplement the pyrite feedstock for the captive on-site acid plant. Copperas generated at Precheza's TiO_2 plant is used at the captive on-site iron oxide pigment plant. Acid-rich waste effluent – about 8-10 tonnes (at 20-23% H_2SO_4 content) – is generated at the hydrolysis stage. At several plants, this acid is cleaned and then converted into marketable by-products, such as white gypsum. Alternatively, it is piped for mixing with stronger acid as an input for local phosphate fertilizer or ammonium sulphate plants. At many other plants, the acid is neutralised with lime and dumped at suitable landfill sites. Historically, acid-rich waste effluent from many TiO_2 plants was discharged into major fast-flowing rivers or coastal waters; this practice is now confined to small plants in India and China. At a few TiO_2 plants, e.g. Venator's Krefeld-Uerdingen plant, waste acid concentration plants are operated for re-concentrating the acid to 70% or 90% strength and this acid is then recycled for TiO_2 production, thus reducing the requirement for virgin acid input by up to 50%.

China's surge in sulphate capacity

World production of TiO_2 has naturally increased in line with world demand, but there have been several major changes in the structure of the TiO_2 industry over the past 30 years. At the end of 1989, total world capacity was 3.32 million t/a, of which 43% was accounted for by chloride-route plants and 57% by sulphate-route plants. China's sulphate-route plants accounted for only 2% of the total, while sulphate-route plants in the rest of the world accounted for 55%. By the end of 2019, global capacity had increased to 8.61 million t/a. The global capacity split between chloride-route and sulphate-route was again 43:57, but now China's sulphate-route plants account for just under 42% of the total and plants in the rest of the world account for just under 15%. While sulphate-route capacity in the rest of the world has declined at a gentle rate of 1% per annum from 1.82 million t/a at the end of 1989 to 1.35 million t/a at the end of 2019, China's sulphate-route capacity has conversely surged at an average rate of 15% per annum from 62,000 t/a to 3.6 million t/a.

There are now 25 chloride-route plants in the world, of which six are in China. There are 68 sulphate-route plants, of which 40 in China and 28 in the rest of the world. The majority of the Chinese plants

The Lomon Billions sulphate-route titanium dioxide plant at Dayang, China.

PHOTO: LOMON BILLIONS

were built during the past 20 years. Altogether, there are 12 sulphate-route plants in China with a capacity of 100,000 t/a or more, located at: Binzhou, Jinan, Yantai and Zibo (all in Shandong province); Mianzhu and Panzhihua (both in Sichuan); Baiyin (Gansu); Maanshan (Anhui); Nanjing (Jiangsu); Jiaozuo (Henan); Qinzhou (Guangxi); Ningbo (Zhejiang). Elsewhere in the world, there are only three sulphate-route plants with a capacity of 100,000 t/a or more: the two Venator plants in the Ruhr Valley region of Germany and the plant at Armyansk (Crimea) owned by Group DF (a Moscow-registered company controlled by Dmytro Firtash).

Outside of China, there have been very few new greenfield TiO_2 plants built in the past 30 years. There was a wave of new chloride-route plant construction during the early 1990s, the latest in that wave being the KuanYin (Taiwan) plant of Chemours, which now has a capacity of 150,000 t/a. Three small sulphate-route plants were built in India – at Kalyani in 1993, Thoothukudi in 1994 and South Silukkanpatti in 2010. The latest world-scale sulphate-route plant – Venator's plant at Teluk Kalung (Malaysia), now running at 60,000 t/a – was commissioned in 1992. No new chloride-route plants have been built since 1994 and no new sulphate-route plants have been built since 2010.

Changes in ownership structure

The structure of ownership within the TiO_2 industry has also changed markedly over the past 30 years, particularly in recent years. Back in 1990, the major TiO_2 producers functioned as units within large multi-activity corporations, notably Bayer, DuPont, Hanson, ICI, Ishihara, Kemira, Kerr-McGee, Metallgesellschaft, NL Industries and Rhône-Poulenc. Between them, these ten companies controlled 85% of global TiO_2 capacity.

After a sequence of acquisitions and demergers, involving Rockwood, Millennium, Cristal, Huntsman and others, the major players in the TiO_2 industry today all derive a large portion, if not all, of their profit and revenues from TiO_2 and related products. The top five producers – Chemours, Tronox, Lomon Billions, Venator and Kronos – have a combined capacity of 4.37 million t/a, representing 53% of total global capacity.

Chemours, which was created by demerger from DuPont in July 2015, is the world's largest TiO_2 producer, with a capacity of 1.25 million t/a derived from four large chloride-route plants in the US, Mexico and Taiwan.

Tronox, which was created by demerger from Kerr-McGee in November 2005, has a total capacity of 1.08 million t/a, derived from six chloride-route plants in Australia, the Netherlands, Saudi Arabia, the UK and the US and three sulphate-route plants in Brazil, China and France. Tronox substantially raised its global prominence in April 2019 thanks to the $2.2 billion acquisition of Cristal's TiO_2 assets. The three sulphate-route plants – a 60,000 t/a unit at Arembepe; a 46,000 t/a unit at Fuzhou (Jiangxi province) and a 32,000 t/a unit at Thann – were all included in the Cristal acquisition.

Lomon Billions, the largest TiO_2 producer in China and the third largest producer in the world, was created in October 2016 when Henan Billions acquired the TiO_2 business of Sichuan Lomon. It now has a total capacity of 1.015 million t/a derived from a 300,000 t/a chloride-route plant at Jiaozuo (Henan), a 60,000 t/a chloride-route plant at Chuoxing (Yunnan), a 255,000 t/a sulphate-route plant at Mianzhu (Sichuan), a 250,000 t/a sulphate-route plant at Jiaozuo (Henan) and a 150,000 t/a sulphate-route plant at Xiangyang (Hubei).

Venator was created by demerger from Huntsman in August 2017. Huntsman itself had entered the TiO_2 industry in 1999 as a result of the acquisition of Tioxide, ICI's wholly-owned subsidiary. Under Huntsman's ownership, the company closed four sulphate-route plants in the UK (2009),

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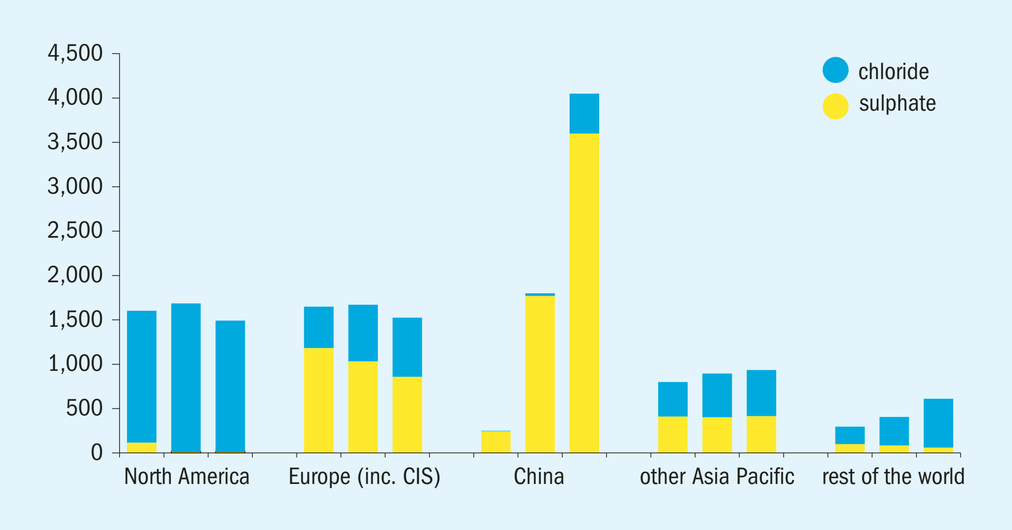
Fig. 1: **TiO_2 capacity, by region: sulphate vs chloride (end-year capacity, 1999-2009-2019, in '000 t/a TiO_2)**



Source: Artikol

France (2015), South Africa (2016) and Finland (2018) and acquired two sulphate-route plants in Germany (2014). Venator now has a total capacity of 657,000 t/a, of which 230,000 t/a is chloride-route and 427,000 t/a is sulphate-route. The chloride-route capacity consists of a wholly-owned 150,000 t/a plant in the UK and a 50% stake in a 160,000 t/a plant in the US. Venator has five sulphate-route plants: a 107,000 t/a plant at Krefeld-Uerdingen (Germany); a 100,000 t/a plant at Duisburg-Homberg (Germany); an 80,000 t/a plant at Scarlino (Italy); an 80,000 t/a plant at Huelva (Spain); and a 60,000 t/a plant at Teluk Kalung (Malaysia).

Kronos was created as a separate entity by demerger from NL Industries in 1989, but in fact NL Industries and affiliates within the Contran group still own directly or indirectly 75% of the equity of Kronos. It currently has a total capacity of 564,000 t/a, of which 422,000 t/a is chloride-route and 132,000 t/a is sulphate-route. Kronos has three wholly-owned chloride-route plants in Belgium, Canada and Germany plus a 50% stake in a 160,000 t/a plant in the US. Kronos also has four sulphate-route plants in Canada, Norway and Germany.

Most of the world's chloride-route TiO_2 plants are owned by one or other of the five majors. The only other owners of chloride-route plants are: Ineos (with two plants in the US), Ishihara (Japan), Kerala Minerals & Metals (India), Pangang, Citic Jinzhou, Yibin Tianyuan and Luohe Xingmao (all four in China).

The ownership of sulphate-route plants is much more widely spread. Of the 68 plants operating at the end of 2019, the majors own 15. Venator has five, Kronos has four, Tronox and Lomon Billions have three each. There are no other owners besides the five majors with sulphate-route capacity in North America, Latin America, the Middle East or Africa.

In addition to Lomon Billions, substantial owners of sulphate-route TiO_2 capacity in China (ranked in order, by size) comprise: CNNC HuaYuan, Jilin GPRO, Shandong Dongjia, China National Bluestar, Wuhan Fangyuan, Lubei Enterprise, Ningbo Xinfu, Panzhihua Taihai, Yunnan Dahutong, Shandong Dawn, Guangxi Jinmao and Guangxi Cava. Each of these companies controls at least 100,000 t/a of sulphate-route TiO_2 capacity.

In Europe, sulphate-route plants are operated by: Cinkarna (72,000 t/a at Celje, Slovenia); Group DF (110,000 t/a at Armyansk, Crimea); Grupa Azoty (45,000 t/a at Police, Poland); Khimprom Sumy (50,000 t/a at Sumy, Ukraine); and Precheza (62,000 t/a at Prerov, Czech Republic).

In Asia/Pacific, sulphate-route plants are operated by: Beach Minerals (15,000 t/a at South Silukkanpatti and 5000 t/a at Kalyani, both in India); Cosmo Chemicals (40,000 t/a at Onsan and 25,000 t/a at Incheon, both in South Korea); Ishihara (86,000 t/a at Yokkaichi and 13,000 t/a at Kobe, both in Japan); Sakai Chemical (60,000 t/a at Onahama, Japan); Tayca (60,000 t/a at Saidaji, Japan); Titan Kogyo (4,000 t/a at Ube, Japan); Travancore Titanium Products (18,000 t/a at Thiruvananthapuram, India); and VV Pigments (30,000 t/a at Thoothukudi, India).

Slow decline in acid consumption

What is the future for the TiO_2 industry and for the sulphate-route sector in particular? In fact, against the background of an anticipated 5-8% drop in TiO_2 consumption in 2020 and uncertainty about the pace of recovery in 2021/22, none of the existing TiO_2 producers has confirmed plans for expanding capacity. Chemours has deferred a previously planned 125,000 t/a capacity increase spread over its four chloride-route plants. Lomon Billions and Yibin Tianyuan had both announced ambitious plans for expanding their chloride-route capacity in China, but these will probably be scaled back. There have been no definitive announcements of significant expansion of sulphate-route capacity by any of the Chinese producers. Nor have there been any definitive announcements of retrenchment and the wave of closures of small sulphate-route plants that had failed to meet new pollution guidelines enforced by Central Government inspectors seems to have ended.

On the downside in Europe, Kronos has announced that it will close its 36,000 t/a sulphate-route plant at Leverkusen (Germany) by the end of this year and Venator has indicated that it is going to reduce capacity at its 100,000 t/a sulphate-route plant at Duisburg-Homberg (Germany).

On the upside worldwide, TNG Ltd. has a well advanced project for building a new 150,000 t/a sulphate-route TiO_2 plant at Darwin (Australia) and has awarded the design and engineering contract to Ti-Cons. Nyanza Light Metals plans to build a 70,000 t/a sulphate-route TiO_2 plant at Alton North, near Richards Bay (South Africa), with provision for doubling capacity in a second phase of the project. Velta (the Ukrainian ilmenite supplier) is planning to build a 40,000 t/a sulphate-route plant at Mishkor Rotem (Israel), with provision for raising capacity to 70,000 t/a as warranted by demand. Assuming that all these plans come to fruition, these projects would provide a significant boost to sulphuric acid consumption in the TiO_2 industry.

Overall, however, annual world consumption of sulphuric acid for TiO_2 production is more likely to decline than increase over the next 5-10 years, with chloride-route TiO_2 output gradually displacing sulphate-route TiO_2 output, especially in China. ■

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PHOTO: GEOMETRICA

Left: The sulphur storage dome at Ruwais, with the stacker-reclaimer.

Abu Dhabi: sulphur giant

In a few short years Abu Dhabi has grown to become the world's largest sulphur producer and exporter, and new sour gas projects will lead to additional sulphur recovery capacity, provided they can overcome economic challenges.

The oil-rich Emirate of Abu Dhabi, capital of the United Arab Emirates (UAE) has grown rapidly over the past decade to become the world's largest exporter of sulphur. Most of this sulphur has come as a by-product from sour natural gas processing, as the Emirate tried to produce enough gas to power its breakneck growth.

The pace of Abu Dhabi's growth has been astonishing. In 1970, the population of Abu Dhabi was 46,000. In 2016, including non-residents and resident non-citizens, this had mushroomed to 2.9 million, with the city of Abu Dhabi accounting for half of that. The city now sprawls far from the original island onto the mainland and across several neighbouring islands recovered from the sea. At the same time that its population has expanded, growing demand for electricity, for lighting, air conditioning, domestic power and desalination of sea water, has increased faster still, with peak demand rising sixfold from 3.3 GW in 2000 to 18.3 GW in 2020.

Meeting this rapid growth in power demand has been a considerable challenge. Abu Dhabi has great potential for solar energy, and has already completed a large 1.2 GW solar array at the Noor Abu Dhabi site, and in July gave the go-ahead for constructing a new 2 GW solar array at Al Dhafra, which is due to be operational by 2022. Likewise, Abu Dhabi has looked to nuclear power as a solution, and this August switched on the first of four reactors at the $32 billion 5.6 GW Barakah nuclear power site – the other three reactors are due to come on-stream over the next three years. However, building a nuclear power station has taken ten years, and in the meantime, the speed of increase of electricity demand has meant a concentration on natural gas as a solution – gas turbines are relatively quick and easy to set up. Consequently, at present, over 90% of Abu Dhabi's power generation comes from natural gas.

Natural gas

The UAE held the seventh-largest proved reserves of natural gas in the world at 215 trillion cubic feet (6.0 trillion cubic metres) in 2018, with most of this in the Emirate of Abu Dhabi. However, since then there have been a string of new gas discoveries which have moved it up to sixth place. In November 2019, Abu Dhabi's state-owned Abu Dhabi National Oil Company (ADNOC) announced the discovery of 58 tcf of conventional gas and 160 tcf of unconventional gas, in addition to new oil finds, and in February this year came news that this may have been added to with another 80 tcf (2.2 tcm) of gas, with the discovery of the shallow water Jebel Ali reservoir, between Abu Dhabi and Dubai. The new giant field has the prospect of being the largest single gas field discovery since Galkynysh was found in Turkmenistan 15 years ago. Both Abu Dhabi and Dubai will develop the field jointly, according to a statement by their respective rulers, over the coming decade.

In the meantime, however, most gas production in the UAE will remain in Abu Dhabi, from a combination of onshore and offshore fields. Gas production in the UAE rose to 62.5 bcm in 2019, running behind consumption at 76 bcm. The UAE as a whole has been a net importer of gas since 2008, with the growth of the city of Dubai having been equally as breakneck as that of Abu Dhabi but without – until now – the gas reserves to power it. As a result, a pipeline was constructed across the shallow waters of the Gulf from Qatar, which operates the largest gas field in the world – the North Field. The Dolphin pipeline has been supplying an average of 25 bcm of gas since 2008, although this figure dropped to 19.5 bcm in 2019. At the same time, since 1973, ADNOC has also been exporting natural gas as LNG from the offshore Das Island terminal. This was expanded to encompass a third LNG train in 1994, and exports ran at around 7.7 bcm in 2019. Of course, Das Island was set up before the UAE became a net gas importer, but now it remains locked into long term export contracts. Somewhat counter-intuitively, therefore, a floating LNG storage and regasification unit was

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also installed off Dubai in 2014, joined by a second in 2016, and Dubai imported 1.6 bcm of natural gas as LNG in 2019.

The UAE's rapid growth of gas demand for electricity production noted above soon outstripped the capability of the Dolphin pipeline to supply gas, and so Abu Dhabi has turned to its large onshore reserves of sour gas to make up the shortfall. The largest sour gas project has been Shah, detailed below, the completion of which has turned Abu Dhabi into the world's largest exporter of sulphur, but sulphur tonnages are also boosted by the processing of sour associated gas and sour gas from other fields at the Habshan complex.

The UAE's future needs for gas will be reduced by the start-up of the solar and nuclear power plants, which will be supplying 25% of the country's energy needs by 2023. However, recent years have also seen relations between the UAE and neighbouring Qatar sour over a number of issues, and in 2017 the UAE, together with Saudi Arabia and a number of other Gulf states, broke off relations with Qatar. Though things have thawed a little in the intervening years, there is a general consensus in the UAE to try and end its dependence on Qatari natural gas imports, and so new sour gas projects will vie with additional LNG imports as potential sources of gas for the nation.

Oil and refining

The UAE holds 6% of the world's proved oil reserves, and 96% of those reserves are in the Emirate of Abu Dhabi. Reserves were increased by 7 billion barrels in November 2019 with the new offshore oil and gas discoveries. The country produced 4.0 million bbl/d of petroleum and other liquids in 2019, of which about 3.1 million bbl/d was crude oil and the remainder was condensate, natural gas liquids, and refinery processing gain. This makes the UAE, and particularly Abu Dhabi, the third-largest oil producer in OPEC after Saudi Arabia and Iraq. The state-run Abu Dhabi National Oil Company (ADNOC) plans to increase this to 5 million bbl/d by 2030, primarily by using enhanced oil recovery (EOR) at the company's existing oil fields.


EMIRATES WATER & ELECTRICITY COMPANY

The Noor Abu Dhabi solar plant, largest of its kind in the world.

There are four downstream refineries in the UAE. The largest complex is at Ruwais in the west of Abu Dhabi, with a capacity of 837,000 bbl/d, divided into two refineries, the older Ruwais Refinery East (420,000 bbl/d) and the more modern Ruwais Refinery West (417,000 bbl/d), completed in 2015. The other three smaller refineries are at the Emirates of Jebel Ali (140,000 bbl/d) and Fujairah (82,000 bbl/d) and there is another smaller refinery, Umm Al-Narr, in Abu Dhabi city itself (85,000 bbl/d).

There was a plan to expand the Fujairah refinery, which sits on the UAE's Indian Ocean coast, east of the Straits of Hormuz, by 250,000 bbl/d, with Brooge Petroleum & Gas Investment (BPI) and Sahara Energy Resources DMCC involved, but this has now been scaled back. Instead BIA is completing a more modest 25,000 bbl/d refinery designed to produce low-sulphur fuel oil that complies new IMO new regulations requiring ships to use marine fuels with a sulphur content below 0.5%.

Meanwhile, ADNOC announced plans in May 2018 to develop Ruwais into the world's largest refining and petrochemicals complex by increasing refining capacity to 1.5 million b/d by 2026, at a cost of $45 billion. Wood Group has been working on the FEED project, and OMV and Eni – who are also partners in ADNOC Refining – have taken stakes in the venture. The expansion will take place in two stages, adding 200,000 bbl/d of capacity by 2024, and building a new 400,000 bbl/d greenfield refinery at the site by 2026. In the meantime, ADNOC is changing the configuration of the existing refinery to allow it to process up to 420,000 bbl/d of ADNOC's heavy, sulphur-rich Upper Zakum grade, freeing up the more desirable light sour Murban grade for export. This $3.5 billion upgrade is expected to be complete by 2022, and was reported by the company in August 2020 to be 73% complete. As part of the upgrade, ADNOC Refining has contracted China's Wison Engineering Services Ltd to replace ageing sulphur recovery units at the Ruwais refinery with more efficient units.

Sour gas

As previously mentioned, Abu Dhabi's turn to its major sour gas reserves has been due to a combination of factors, from a

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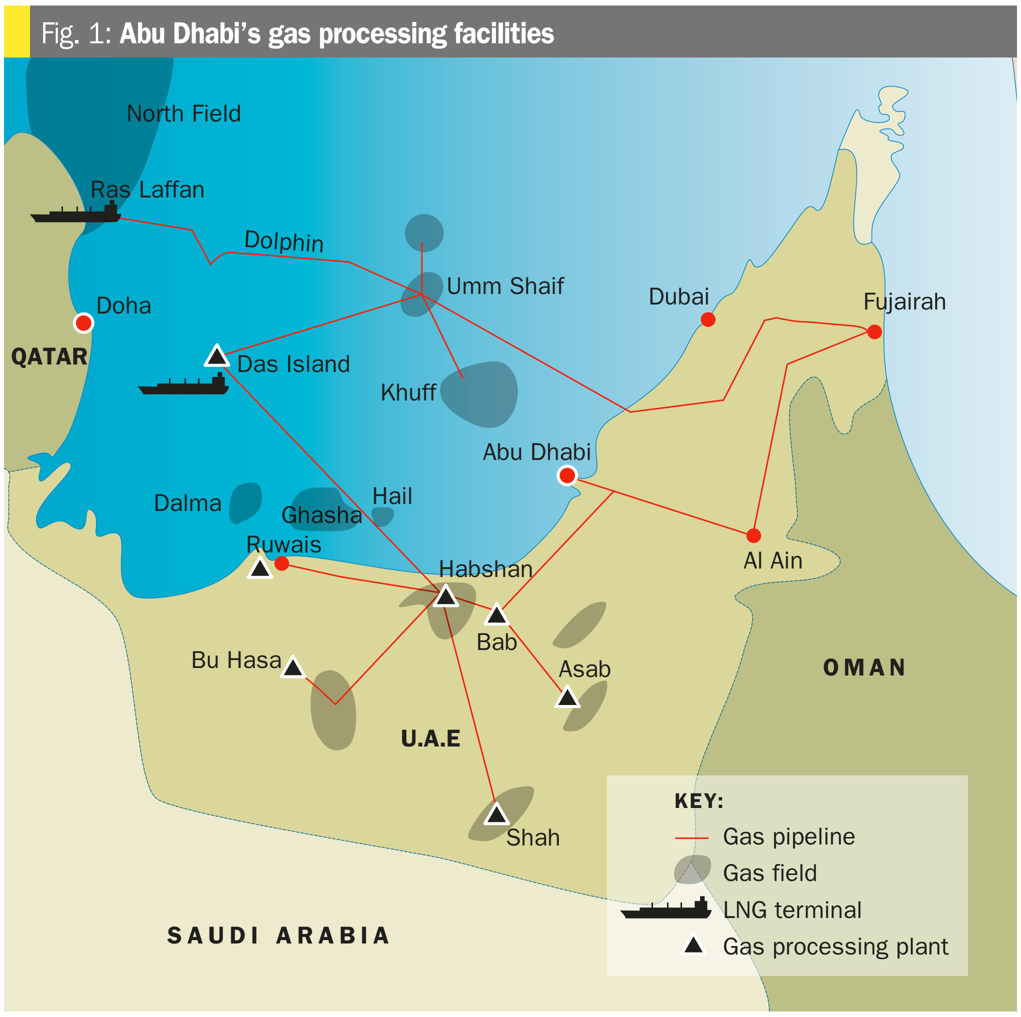
Fig. 1: **Abu Dhabi's gas processing facilities**



need to process associated gas from sour crudes and avoid flaring, to a need for additional gas to feed power production, and a desire to achieve self-sufficiency in gas production.

Sour gas and liquids processing happens at several sites in the Emirate (see Figure 1).

- Asab ('Asab-0') began life as a natural gas liquids plant, debottlenecked and uprated to a capacity of 450 million scf/d. In 2000, it was joined by the Asab Gas Plant, 7 km away, with a capacity of 870 million scf/d of non-associated gas from the condensate-rich Asab reservoirs. The gas here is reinjected for pressure maintenance, while the condensate is sent by pipeline to the Ruwias refinery for processing.
- Bab is also a natural gas liquids extraction train processing 150 million scf/d from oil production in the neighbouring oil field. Acid gas separated from processing operations is sent to Habshan for further treatment and sulphur recovery.
- The Buhasa natural gas liquids plant has two trains each designed to process 300 million scf/d of associated gas, with the plant typically exporting 7,500 tons per day of NGL to the Ruwais fractionation plant. In addition, Buhasa exports sales gas, with surplus gas being routed to Habshan for injection.
- Das Island processes gas for export as LNG. Liquid sulphur is produced which is taken by a dedicated 9,200 dwt liquid sulphur tanker, the Janana.
- The Habshan gas plant was built in 1983. Continuous expansion has taken it to 10 gas processing trains, 10 sulphur recovery units and eight gas injection compression trains, with the capacity to process and sweeten 4.73 million scf/d of feed gas from onshore reservoirs. The latest phase, Habshan-5, is sited 11 km away from the main Habshan Gas Plant, and was completed in 2013 by Tecnimont. It includes 'rich' and 'lean' streams, processed separately. Rich processing facilities constitute two trains designed to process 1.3 billion scf/d of gas from offshore gas from Umm Shaif, as well as onshore associated gas from the Thamama-B and Thamama-G reservoirs, to produce gas liquids and sales gas. The 'lean' facilities comprise two trains designed to 850 million scf/d of gas from the main Habshan Gas Plant (HGP) to sweeten and dehydrate the gas before sending it back to HGP.
- The Ruwais natural gas liquids plant is located within the Ruwais refinery complex, where it receives gas liquids from HGP, Habshan-5, Bab, Asab and Buhasa as well as raw LPG from the Ruwais refinery for treatment and fractionation. Ruwais refinery also recovers sulphur from acid gas and sends this to the sulphur terminal for export.
- Thammama C has a 450,000 scf/d gas gathering and processing plant which recovers and granulates sulphur. The sulphur, around 800 t/d, is taken by road shipment to the terminal at Ruwais.

Shah

While all of the foregoing generate sour gas and hence sulphur, the largest step change has come from the Shah sour gas field development, about 210km southwest of the city of Abu Dhabi. The $10 billion project is being developed by ADNOC Sour Gas, a 60-40 joint venture between Adnoc and Occidental Petroleum. Shah processes 1.0 billion scf/d of highly sour (23% H_2S) gas to generate 500 million scf/d of sales gas, as well as condensate and NGLs, and 10,000 t/d of sulphur. The four sulphur recovery units – the largest in the world – each have a capacity of 2,500 t/d of sulphur production.

Recovered sulphur is taken by pipeline 11 km to a sulphur granulation plant, and from there it is loaded onto rail wagons for transport 265 km to the export terminal at Ruwais. In 2018 ADNOC Sour Gas installed a sulphur remelter at the Shah granulation plant to recover sulphur lost during transportation via conveyors and transport operations.

ADNOC gave the go-ahead to a 50% expansion of capacity at Shah in 2018, expanding it to 1.5 billion scf/d of gas processing, with an additional 5,000 t/d of sulphur production. The project was due for completion in 2023, but Covid disruptions and ADNOC's review of its operations could push that back.

Investment delays

Indeed, Abu Dhabi has started to scale back some of its planned sour gas project developments this year, as falling oil and gas prices and prospects for lower demand cause a rethink of projects. One of the major casualties has been the Ghasha megaproject, an umbrella for the Hail, Ghasha, Dalma, Nasr, and Mubarraz offshore sour gas schemes, designed to turn Abu Dhabi into a net gas exporter, and involving the construction of 10 artificial islands

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and two causeways. Italy's Eni, Germany's Wintershall, and Austria's OMV have taken major stakes in the project, and Petrofac was awarded the $1.65 billion EPC contract for Dalma in February, only to find the contract cancelled in April. The project was due to begin production of another 1.0 billion scf/d of sour gas by 2024, but the high development costs have been causing anxiety among ADNOC's partners, and a delay now looks certain.

Another planned project was the Bab sour gas project, originally designed to be on a similar scale to the Shah project (1.0 billion scf/d of sour gas), with a price tag estimated at $10 billion, and a joint venture development company with majority ownership by ADNOC. The gas at Bab is even sourer than at Shah, with an average H_2S content of 33%. It has been suggested that up to 20,000 t/a of sulphur may need to be extracted in order to process the gas. However, partner Shell exited the project in 2016, and so far no announcement of a revised tender has been announced.

Sulphur output

Most of Abu Dhabi's sulphur output now comes from Shah and Habshan. Up to 4,500 t/d of liquid sulphur was originally sent by truck from HGP to Ruwais for granulation and export, but there is now a pipeline to take the sulphur to Habshan-5, where there are an additional four sulphur recovery units to process the separated acid gas from both rich and lean streams to produce 5,200 t/d sulphur. The Habshan Sulphur Plant handles all of this sulphur, granulating up to 10,000 t/a for onward transport along the rail line for export at Ruwais. Habshan-5 also features the capacity to store up to 180,000 tonnes of sulphur in a covered stockpile.

Shah adds another 10,000 t/a of sulphur granulation capacity, and this is taken by rail to the Ruwais port terminal.

The Ruwais Sulphur Handling Terminal has facilities for handling road deliveries of liquid sulphur via an unloading pit, from which sulphur is transported to a 40,000 tonne capacity liquid storage tank. Liquid sulphur in the storage tank is pumped to a day pit through sulphur filters via a transfer pump, from where the sulphur is pumped to granulation units. There are nine granulation units each with a capacity of 1,000 t/d. Each granulator is provided with its own dedicated wet scrubber. Sulphur product from the granulators is collected at conveyors equipped with dust collection systems and transferred to bulk storage. There are two bulk storage buildings, one circular, with 40,000 tonnes capacity and a linear warehouse with 110,000 tonnes of capacity. There is also a truck loading facility.

Rail deliveries of up to 22,000 t/a can be handled from the granulation plants at Habshan-5 and Shah. There is an additional 400,000 t/a arriving as liquid sulphur from the Das Island LNG facility, and 100,000 t/a from the next door Ruwais refinery.

Granulated sulphur is exported to ships through a shiploader system on a conveyor at the rate of 1,100 t/h. The 300m jetty can take vessels of up 65,000 dwt. The marine terminal is also used to unload liquid sulphur coming from the Janana liquid sulphur vessel in batches of approximately 8,000 tonnes. It is unloaded and transferred to storage tanks.

For export, ADNOC Logistics and Services operates a shipping fleet, including four very large crude carriers, 7 refined products tankers, 8 LNG vessels and three container ships. In 1993, the company launched the business of molten sulphur transportation with the acquisition of sulphur carrier Janana. The company also operates seven bulk carriers for delivery of ADNOC's sulphur exports to North Africa and other locations. ADNOC signed a deal with Morocco's OCP in 2017 for the supply sulphur out to 2025 for OCP's phosphate production. In 2018 OCP received 2.6 million tonnes of sulphur from ADNOC.

A pause not a break

Abu Dhabi's sulphur output has quadrupled over the past decade, from 1.7 million t/a in 2010 to over 7.1 million t/a today, catapulting it into the ranks of the world's largest sulphur producers, such as China, Russia and the US, and – with little to no domestic demand to absorb this – in the process making it the largest exporter of sulphur in the world. In so doing, ADNOC has made a virtue of a necessity, and decided to focus on the whole sulphur value chain, treating sulphur as a valuable commodity in its own right rather than an unwanted by-product. It has begun to try to develop markets for sulphur, including sulphur-coated urea (ADNOC is also a urea producer, in conjunction with partner OCI), as well as phosphate fertilizer ventures in Africa, Asia, South America and Australia.

The current collapse in oil and gas prices, coupled with the completion of solar and nuclear power facilities, may have temporarily put the brakes on sour gas developments in Abi Dhabi, but commitments to increase oil production by 1 million bbl/d and become a net exporter of natural gas once more mean that this is likely to be a pause, rather than a break. It seems likely that by 2030, with the completion of projects such as the Shah expansion and the Ghasha sour gas project, we will be seeing even larger volumes of sulphur coming from Abu Dhabi, possibly turning it into the world's largest sulphur producer. ■

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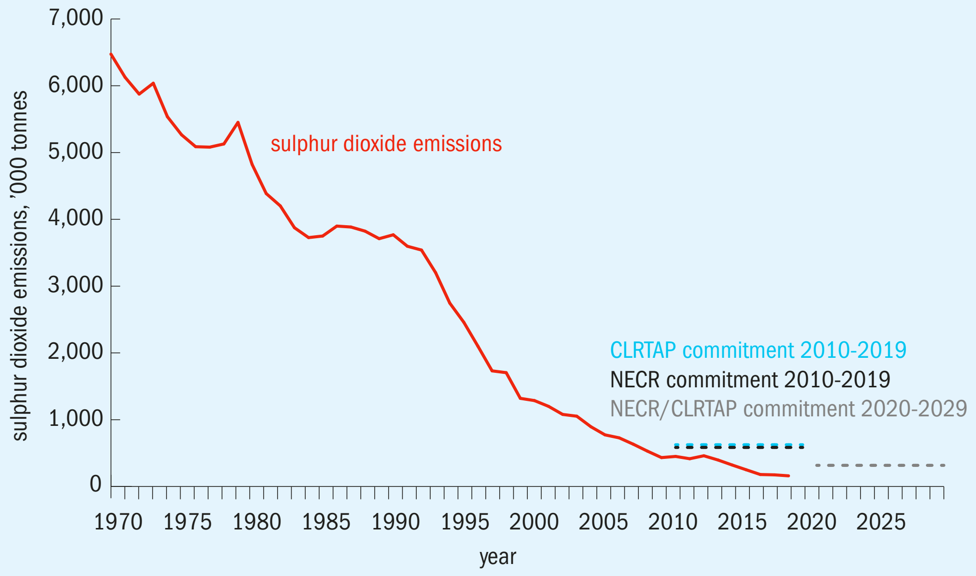
47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64

SO_2 emissions control

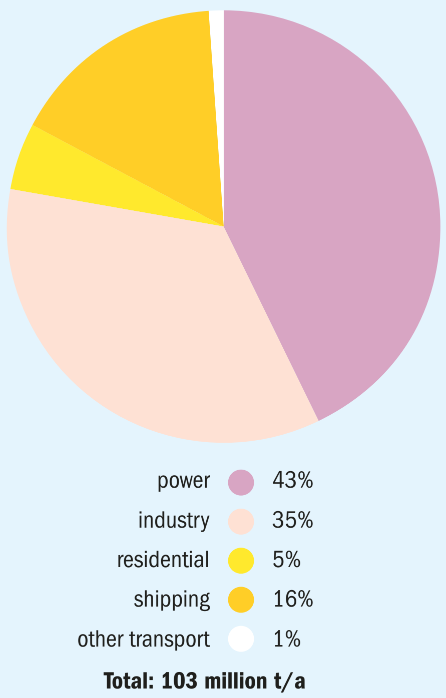
Legislation to control emissions of sulphur dioxide continues to tighten, via vehicle exhausts, and refinery and smelter emissions, leading to increased recovery of both sulphur and sulphur dioxide.

Fig. 1: **Reduction in SO_2 emissions for the UK, 1970-2018**



Source: UK Department for the Environment, Food and Rural Affairs

Fig. 2: **Major sources of global SO_2 emissions, 2014**



Source: Zhong et al, College of Urban and Environmental Sciences, Beijing University.

The sulphur industry has arguably achieved its present form due to atmospheric sulphur dioxide pollution, and attempts to control it. Flaring of acid gas recovered from sour gas in places such as Alberta led to SO_2 plumes and a move to recover the sulphur prior to combustion back in the 1950s, and the beginnings of recovered sulphur as a major source of brimstone.

During the 1970s and 80s, the 'acid rain' phenomenon in Europe and North America was traced to SO_2 from coal burning power plants and industrial locations, and the move to rein in SO_2 began in earnest, via a combination of measures, including encouraging switching away from coal-burning power stations towards natural gas or other cleaner sources, and the installation of flue gas desulphurisation (FGD) technology at remaining coal-fired power stations, and the mandating of progressive reductions in sulphur content of liquid vehicle fuels.

The effect has been dramatic. As Figure 1 shows, UK SO_2 emissions have fallen by something like 98% in the period from 1970 to 2018. Comparable figures from the US Environmental Protection Agency likewise show a 92% reduction in man-made SO_2 emissions over the period 1980-2019 due to the US Clean Air Act. The EU has seen a 74% reduction from 1990-2011 via its National Emission Ceilings Directive. The UK has achieved this reduction primarily from switching from coal to natural gas and more recently renewable power generation, and FGD – around 75% of 1970 emissions came from coal-fired power stations.

These reductions have not only prevented the acidification of lakes and forests from acid rain, but also improved human health, as the evidence of SO_2 aerosols as damaging to lungs even at relatively low levels continues to increase.

However, global SO_2 emissions still remain relatively high. Figure 2 shows figures collated by Chinese researchers in 2014, which put anthropogenic SO_2 emissions to atmosphere at around 103 million t/a. This is approximately equivalent to emissions from natural sources, mainly volcanoes, but also large scale forest fires, which is around 75-100 million t/a.

Remaining SO_2 sources

Figure 2 identifies three major remaining sources for human SO_2 emissions; power generation, 'industry' – mainly smelting and refining – and shipping. The latter, of course, is what has led to the International Maritime Organisation's concentration on reducing sulphur in bunker fuels, which has seen a maximum sulphur fuel concentration of 0.5% overall, and 0.1% in designated emission control areas, mainly the Mediterranean and Baltic Seas and the east and west coasts of North America.

Other transportation, meanwhile, is now only a relatively small slice of overall emissions. Reductions of sulphur content of road vehicle fuels have brought sulphur levels to 15 ppm or less in most nations,

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and those that don't are likely to reach at least a level of 50 ppm. As Figure 2 shows, transportation emissions excluding international shipping are already only 1% of global anthropogenic SO_2 emissions.

The greatest gains that remain to be made are from the power and industrial sectors. While flue gas desulphurisation is widely used in OECD countries, its use is patchy outside of this, and SO_2 pollution from power plants has become a major issue in some countries which rely upon coal for power generation, particularly India. In 2019 India was named as the world's largest emitter of SO_2 in a Greenpeace report, responsible for 15% of global SO_2 emissions. It was striking that the lockdown of Indian power plants earlier this year due to the Covid pandemic led to a temporary 40% fall in SO_2 concentrations across the country. India's Ministry of Environment, Forest and Climate Change introduced SO_2 emission limits for coal-fired power plants in December 2015, but the deadline for the installation of the FGDs in power plants have been shifted from 2017 to 2022. This contrasts with China, where widespread use of FGD has reduced SO_2 emissions by 75% this century in spite of a 50% increase in coal-fired power generation.

Outside of power generation, it is evident that industry still remains a major polluter, especially the metal refining sector. The largest peak emissions source in the world according to satellite monitoring is the Norilsk Nickel refinery, responsible for 1.9 million t/a of SO_2 emissions on its own in 2018. Nor are smelter emissions confined to the developing world. Canadian figures show that between 1990 and 2017, SO_x emissions decreased by 69% to 954,000 t/a in 2017. However, of the remainder, 28% of the emissions are from smelting operations, compared to only 6% in the United States, and for the province of Ontario, the smelting contribution is 72%.

Another 26% of Canada's emissions came from the oil and gas industry, and this sector also remains a major emitter of SO_2. Numbers 3 and 4 on the list of global SO_2 'hotspots' are the Zagroz petrochemical complex in Iran and the Rabigh complex in Saudi Arabia, and installations in Mexico and the UAE are also in the top ten. Saudi Arabia is actually another of the countries where SO_2 emissions are still rising.

Implications for sulphur

While FGD in the power sector generates gypsum as a by-product, and hence is tangential to the sulphur industry, sulphur dioxide emissions control at refineries and gas plants will generate additional sulphur, and, from metal smelters, sulphuric acid. At present, SO_2 abatement measures are responsible for generating 65 million t/a of elemental sulphur worldwide, and another 80 million t/a of sulphuric acid from smelters (equivalent to 26 million t/a of sulphur). However, as Figure 2 shows, industrial emissions still represented another 36 million t/a of SO_2 in 2014, equivalent to 18 million t/a of elemental sulphur. This means that further reductions in sulphur emissions from smelters – which has become a contentious issue in many countries, from India's Vedanta smelter to La Oroya in Peru – and further reductions in flaring of sulphur-rich gas from the Middle East and elsewhere still have the potential to drive large increases, as SO_2 emissions legislation continues to tighten. ■

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Unlocking the potential of gas processing assets

G. Bowerbank and **W. Blas** of Shell Catalysts & Technologies discuss low cost strategies to maximise value at existing gas processing facilities. Changing solvents, introducing advanced column internals or a combination of both are relatively simple and cost-effective options for boosting production or revenue with minimal investment.

As 2019 drew to a close, the global gas market was poised for a period of healthy growth, with no fewer than 50 new projects at the pre-final investment decision stage. The change in the first quarter of 2020 could not have been more dramatic, with a sharp fall in oil prices and economic uncertainty linked to the Covid-19 pandemic. Consequently, it appears that only 10 of the 50 projects will now go ahead.

Lockdowns have reduced gas demand by about half in the three largest markets in Europe and lower oil prices have slowed gas imports to India. The drop in demand is likely to be temporary and to reverse once lockdowns end. The effects of the deferrals and cancellations of pre-final investment decision projects, however, will be felt for years to come. How will the major gas suppliers respond? How will countries adapt to meet their energy transition targets?

For most gas producers, long-term disruption of site activities is an unfamiliar problem. For some, it may provide an opportunity to implement improvement or debottlenecking projects or to take an "opportunity shutdown" that will help them maintain their competitive position once the market starts to recover. Despite the uncertainty and a much more cautious approach to capital investment, there is some upside for gas and liquefied natural gas producers.

Make the most of what you've got: The case for revamps

Revamping, repurposing or upgrading existing assets can be more capital efficient than adding new units or trains and can provide operators with more margin for their expenditure. Projects of this kind often require small, incremental investments, which can be highly appropriate in today's market, as they carry a low investment risk, generate credibility with investors and provide the ability to respond flexibly as market conditions change.

These projects seek to reuse existing equipment and any new items purchased, such as new column internals, heat exchangers, small pieces of equipment and upgraded solvent systems, generally have a modest capital cost. The revamping team can also seek synergies with units that are already in place, which further enhances the return on investment or helps to manage changes to expected feed gas sources, rates and compositions.

The implementation of revamp projects is generally more challenging than implementing grass-roots initiatives. Project planners must ensure that the revamp does not disrupt the continuing operation of the facility and align their implementation plans with shutdown time constraints.

A proven approach in uncertain times

Changing solvents, introducing advanced column internals or a combination of both are relatively simple and cost-effective options for boosting production or revenue with minimal investment. The potential benefits include:

- increased capacity;
- reduced energy consumption;
- deeper removal of contaminants;
- reduced solvent degradation rate; and
- improved performance for managing increased levels of contaminants.

Operators in upstream oil and gas facilities often have to deal with increasing feed gas contaminant levels caused by changes in field characteristics or the addition of hydrocarbons from new reservoirs or fields. There is also the challenge of meeting more stringent treated gas specifications. Most of the solvent swap opportunities that Shell has evaluated over the past decade have been driven by these changes, along with capacity increases resulting from higher amine loading capacity. Solvent swaps can be performed on- or offline. The choice depends on the similarity of the solvents. For example, swapping from aqueous methyl diethanolamine to Sulfinol-X can be done "on the run" if the existing solvent is of acceptable quality, but a swap from Sulfinol-D to ADIP-X or Sulfinol-X has to be performed offline.

Changes in feed often mean increasing contaminant levels, which can lead to reduced capacity. To address the need for enhanced absorption performance, Shell developed Shell Turbo Trays. These provide additional benefits for existing assets by increasing the hydraulic capacity and contaminant handling capacity. In addition, the trays offer substantial operational benefits, including increased operational flexibility, reduced fouling and increased resilience to foaming.

The examples below demonstrate the value of revamp solutions at four different assets.

Case study 1

Processing higher levels of feed gas contaminants[1]

In this example, the new feed to a gas plant had double the hydrogen sulphide (H_2S) content and 30% more carbon

Table 1: **Feed gas composition and treated gas specifications**

	Original design	**New conditions**
Feed gas H_2S content, mol-%	1.0	2.0
Feed gas CO_2 content, mol-%	2.5	3.3
Relative feed gas flow, %	100	100
Treated gas H_2S specification, ppmv	3.5	

Table 2: **Unit performance modelling results for Sulfinol-X relative to Sulfinol-D**

Sulfinol-X (as % of Sulfinol-D)	
Feed gas flow	100
Solvent circulation flow	100
Acid gas flow	133
Reboiler duty	109*
Steam consumption	109*

**The increase in the reboiler duty and steam consumption is a result of the higher acid gas content in the feed.*

dioxide (CO_2) than the plant had been designed to handle (Table 1). The operators had to find a way to process this new feed while meeting the same treated gas specifications. The existing process configuration used Sulfinol-D solvent, as shown in Fig. 1.

The plant operator asked Shell Catalysts & Technologies to look at potential solutions. Two options were considered: installing a new pretreatment acid gas removal unit (AGRU) or a solvent swap.

Option 1

Installing a new pretreatment AGRU would reduce the feed gas H_2S and CO_2 content to the design values for the existing Sulfinol-D system. However, depending on the resultant acid gas quality, an acid gas enrichment section might also be required (Fig. 2). This optional equipment would require considerable capital investment and plot space, and add operational complexity, which would likely reduce unit reliability.

Option 2

Swapping the existing Sulfinol-D solvent for Sulfinol-X was also considered (Fig. 3). This approach had the potential to improve unit performance for a minimal investment and without needing major modifications or new equipment.

The revamp team modelled the unit performance improvement for Sulfinol-X compared with the existing solvent (Table 2). This showed that the treated gas H_2S, CO_2, carbonyl sulphide (COS) and mercaptan specifications could be achieved with a similar solvent circulation rate. The lean solvent temperature to the absorber column would also be similar. Reboiler duty and steam consumption would be about 9% higher owing to the much higher acid gas flow. However, the higher duty was within the equipment design specifications, so there would be no need to modify the reboiler. The evaluation work showed that the solvent change would not require any major equipment modifications.

As Sulfinol-X has similar fluid properties to Sulfinol-D, the swap would have no impact on pump seals or seal material and the solvent circulation would be within the operating range of the pumps.

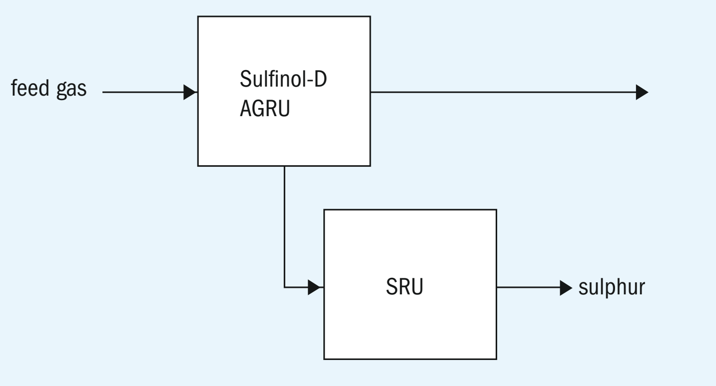
There would be substantial benefits derived from this solvent swap. Sulfinol-X has a higher loading capacity than Sulfinol-D, which means that higher amounts of H_2S and CO_2 can be removed from the feed gas at the same solvent rate. Methyl diethanolamine (MDEA) reacts 1:1 with CO_2 whereas diisopropanolamine (DIPA) reacts 2:1. This makes it possible to load an accelerated MDEA-based solvent more (up to 1 mol CO_2/mol amine) compared with a DIPA-based solvent (up to 0.5 mol CO_2/mol amine).

Increased loading provides operational cost savings, as less solvent pumping and a lower heating duty are required, and helps to debottleneck capacity for existing Sulfinol-D units.

The swap would require very little capital expenditure, as there would be no major equipment modification. The operating costs would also be considerably lower than for a new pretreatment unit and the solvent swap would not increase the operational complexity.

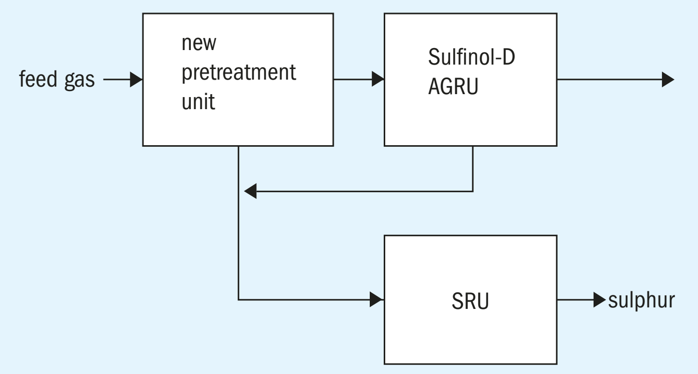
The evaluation concluded that a solvent swap to Sulfinol-X would be the most attractive option for meeting the new feed gas contaminant levels. It would provide the existing unit with the means to treat more highly contaminated feed gas at considerably lower capital investment and operating expenditure than the alternative while maintaining the same level of operability and reliability.

Fig. 1: **The existing process line-up**



Source: Shell Catalysts & Technologies

Fig. 2: **New AGRU (Option 1) process line-up**



Source: Shell Catalysts & Technologies

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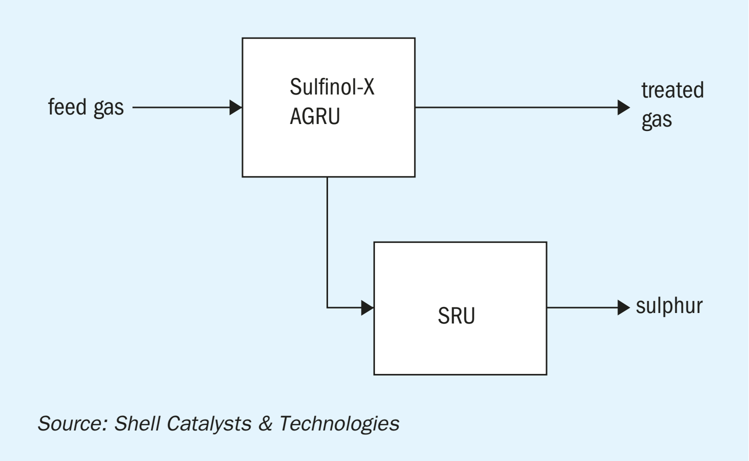
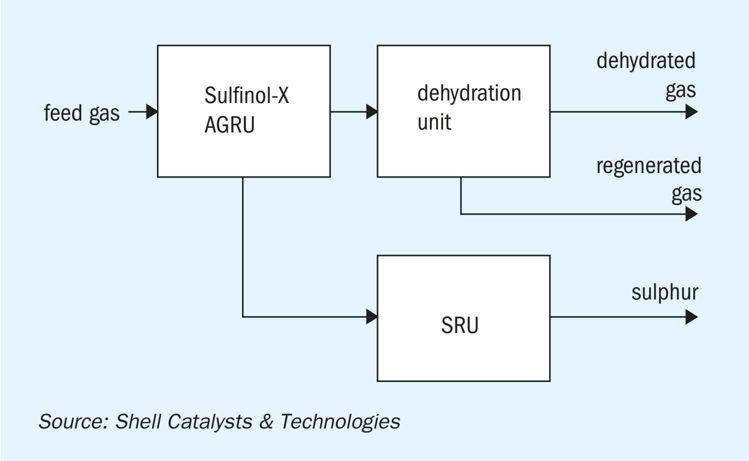
Fig 3: **Solvent swap (Option 2) process line-up**



Source: Shell Catalysts & Technologies

Fig 4: **Proposed line-up**



Source: Shell Catalysts & Technologies

Case study 2

Mitigating solvent losses and degradation to reduce operating costs[1]

An operator in the Middle East had been using a DIPA based solvent for a gas-sweetening unit, but increasing amounts of CO_2 in the feed gas were going to result in unacceptable rates of solvent degradation. DIPA reacts with CO_2 to form carbamate, which then reacts irreversibly to form oxazolidone. In this case, the increased partial pressure of CO_2 would have accelerated the build-up of oxazolidone and other related degradation products.

A solvent swap to Sulfinol-X was proposed to combat this problem. With Sulfinol-X, the gas-sweetening unit met the required specifications for CO_2 and sulphur (H_2S, COS and mercaptans) removal using a similar solvent circulation rate. Compared with Sulfinol-D, Sulfinol-X requires a lower reboiler duty for the same sulfolane content to remove the same amount of CO_2 in the regenerator, as the overall heat of reaction for the accelerated aqueous methyl diethanolamine is lower than that of DIPA. In this example, the reboiler duty was about 10% lower compared with the Sulfinol-D case.

The DIPA-based Sulfinol solvent had been performing well, but continuing to use this solvent with feed gas that contained high volumes of CO_2 would have meant higher operational expenditure as a result of frequent solvent replenishment or the additional capital cost of a new solvent reclamation unit because of DIPA's contribution to the solvent degradation.

The solvent swap was made without additional capital cost and required no equipment modification in the gas-sweetening unit or the downstream units. The solvent circulation requirement was within the operating range of the pumps and had no effect on pump seals or seal materials. The composition chosen for Sulfinol-X was within the material selection guidelines for sulfolane-based solvents, so there was no impact on material selection from the solvent change.

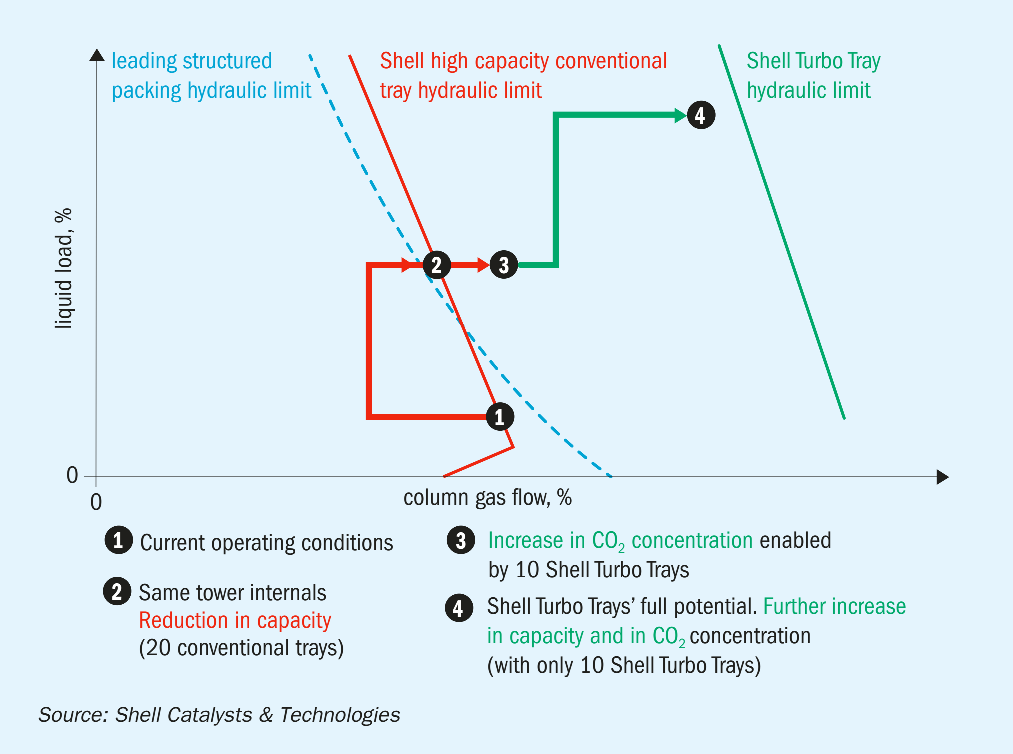
The performance of the unit was checked for a higher gas throughput. The unit can handle 10% additional gas throughput with about a 12% higher solvent circulation rate. The solvent composition for Sulfinol-X has lower sulfolane content compared with Sulfinol-D. This gives a lower solvent temperature in the reboiler and, hence, increased reboiler capacity. In this case, the reboiler duty was limiting the capacity. So, instead of reducing its duty (steam requirement), the reboiler was kept close to full capacity to increase the gas processing capacity. This unit has now been running successfully with Sulfinol-X for several years.

Case study 3

Improving performance to meet tighter specifications[1]

A gas processing operating company wanted to reduce the total sulphur content of its final product to meet tighter gas specifications. In collaboration with Shell Catalysts & Technologies, a solvent swap from diethanolamine to Sulfinol-X was proposed. The feasibility study showed that using Sulfinol-X in the AGRU (Fig. 4) would

Fig. 5: **Comparison of hydraulic limits for a leading structured packing, conventional high capacity tray and Shell Turbo Trays**



Source: Shell Catalysts & Technologies

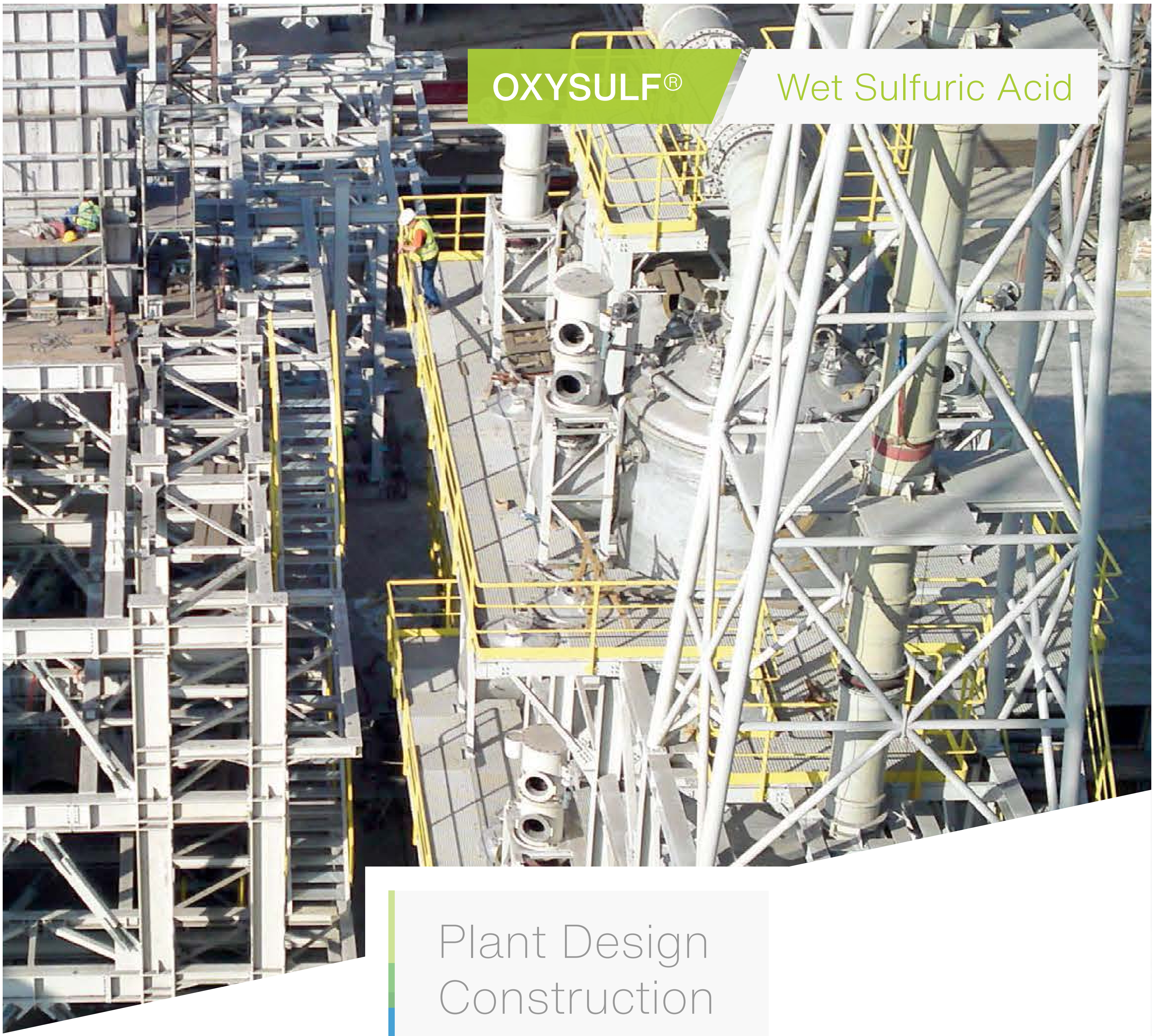


Table 3: **Replacing proprietary solvent and conventional trays with Shell Turbo Trays and ADIP ULTRA**

Results	Current trays	Shell Turbo Trays
Number of trays	25	12
Maximum gas flow	Base	Base + 82%

reduce the total sulphur content in the treated gas to the target levels.

Modelling also demonstrated that Sulfinol-X would remove H_2S, CO_2, mercaptans, COS and organic sulphides to the required treated gas product specifications in a single process.

With diethanolamine, the process was achieving more than 100 ppm total sulphur in the product; the higher performance of the Sulfinol amine enabled treating down to 5 ppm total sulphur.

By opting for a solvent swap, the operator would maintain the same equipment count, in contrast to the alternative multi-process line-ups, and avoid unnecessary capital costs. Without the need to invest in additional equipment, there would be no impact on availability and reliability. Operating costs could also be reduced, as Sulfinol-X has a lower steam requirement for stripping of the absorbed acid gases compared with alternative aqueous amine solvents.

Case study 4

Increasing throughput and CO_2 handling capacity[2]

A liquefied natural gas facility was facing an imminent rise in feed gas CO_2 concentration from about 1 to 4 mol-%. The plant was using a proprietary solvent and conventional trays. An initial assessment concluded that a solvent swap to ADIP ULTRA would be feasible. However, increasing contaminant levels would mean a 25% reduction in the gas processing capacity, even when the existing design margins on the unit were utilised (point 2 in Fig. 5). Shell Catalysts & Technologies was then asked to consider what maximum throughput the facility could achieve at 4 mol-% CO_2 concentration with minimal capital investment.

Shell Turbo Trays offered a higher mass transfer benefit that enabled increased solvent loading without other equipment changes. The new trays would provide an 18% increase in the gas throughput for only the capital cost of the trays (point 3 in Fig. 5). The subsequent limitation at this point was the reboiler capacity, which the client investigated for potential debottlenecking.

On the assumption that additional regeneration capacity could be added, the maximum gas throughput that could be processed by the absorber at the higher CO_2 concentration was simulated and was determined to be 182% of the original design throughput (point 4 in Fig. 5). The revamp would, therefore, deliver a substantial increase in maximum gas flow with fewer trays (Table 3).

The key principle behind Shell Turbo Tray technology is the combination of contacting and separation zones in an integrated tray package. This integrated tray design offers two distinct advantages over conventional trays and packing for the same column cross-sectional area:

- higher gas and liquid handling capacity with effective gas–liquid separation achieved at each tray; and
- improved mass transfer, as near equilibrium is achieved owing to the higher liquid–gas ratio and the intense contacting in the contacting boxes.

Fig. 6 shows a schematic of gas and liquid flows on a single Shell Turbo Tray through the contacting (a) and separation (b) zones.

Conclusions

Solvent swaps can increase the potential of existing gas processing trains with little or no capital expenditure. The case studies above show that major performance benefits can be obtained without purchasing equipment or extensive modifications. The combination of a solvent swap and the installation of Shell Turbo Trays has been shown to deliver cost-effective debottlenecking solutions in challenging operating conditions.

Effective planning and execution are important for the success of solvent swaps in brownfield assets. In certain circumstances, an on-the-run solvent swap, which avoids shutting down the unit, can be performed with appropriate procedures and monitoring. ■

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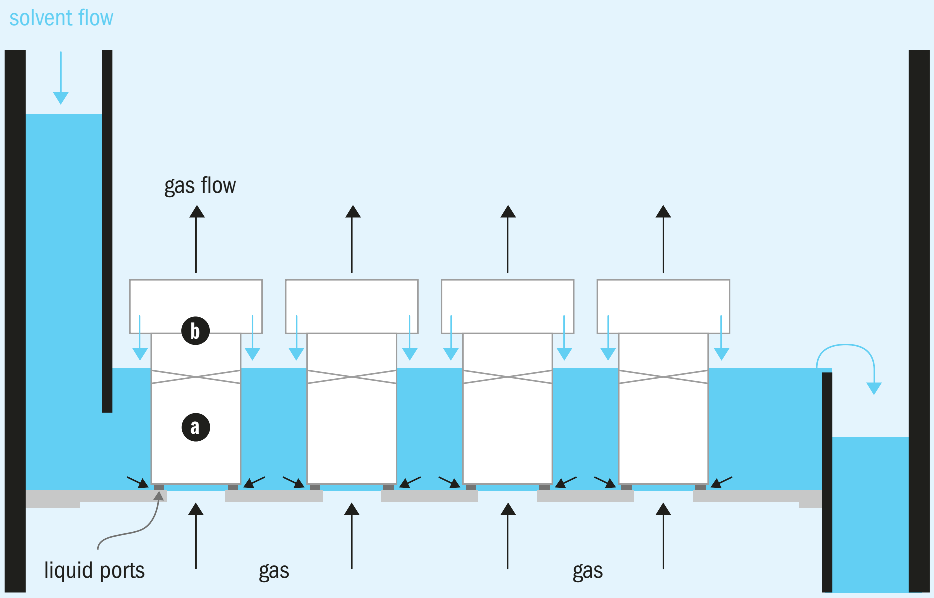
Fig. 6: **Schematic of gas and liquid flows on a single Shell Turbo Tray through the contacting (a) and separation (b) zones**



Source: Shell Catalysts & Technologies

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One size does not fit all

K. Hanlon Kinsberg and **J. Lewis** of Comprimo review the main approaches for mercaptan removal in gas processing plants, based on past project experience and generally accepted industry practice.

Mercaptans are a common contaminant in the feed to gas processing plants, along with H_2S, CO_2, carbonyl sulphide, mercury and water. Just as gas plants themselves come in a wide variety of process configurations driven by differing gas export specifications dependent on local market conditions, so too can there be an array of contaminant removal methodologies[1].

The best mercaptan removal process for a given site with defined feed conditions will depend on many factors. First and foremost, it is recommended that this evaluation is done holistically, considering the impacts on the overall gas plant configuration. Mercaptan removal can govern the entire gas-side configuration of a processing train[2], and it is a significant example of the interdependence between hydrocarbon processing and impurities removal. Depending upon the functional requirements of the gas plant, the design engineer needs to ask where the best place is to remove the mercaptans.

There are several gas processing options available for mercaptan removal, with the most common including solvents, adsorption with molecular sieves and NGL recovery with liquids treating. Each process has its advantages and disadvantages depending on the level of mercaptan removal required and how the removal integrates with the overall gas conditioning required.

Importance of accurate fluid analysis

The first step in determining the most suitable mercaptan removal approach for a new plant design is ensuring a rigorous reservoir fluid analysis is available. Understanding both the level of mercaptan contamination as well as the species distribution is critical when evaluating technology selection for the gas processing plant. Too often, projects make fundamental assumptions on the design basis if field data is either limited or incomplete, without appreciating the consequences of those assumptions.

The feed composition details are pivotal and can have tremendous ramifications on the process configuration and ultimately the overall plant performance. One design approach is to be "conservative" in the assumptions, and then proceed with technology selection from that baseline. But unfortunately, that conservativism could inflate the overall project cost due to over-design or it could misdirect the technology selection process. It is acknowledged that reservoir fluid characteristics can change over the life of a field, which sets the expected operating boundary for the processing plant, but there still needs to be solid analysis data at the technology selection phase for the best design foundation.

For example, solvent selection for acid gas removal depends upon the concentrations and species of contaminants expected. Such a fundamental design decision is increasingly difficult to alter as the project progresses through the engineering phases and into construction and start-up, if new field data reveals significant changes to the original design basis.

Case study

Impact of uncertainty of mercaptan levels[3]

In this study a hybrid solvent, containing amine for H_2S removal and concomitant CO_2 reduction, and a physical component for removal of organic sulphur species, primarily mercaptans, was used in the gas sweetening unit to treat a natural gas stream. The use of a physical component resulted in some absorption of hydrocarbon components, which were released in the high-pressure flash drum and the solvent regeneration facilities and subsequently lost, thus contributing to the acid gas stream routed to the SRU.

During plant operation the concentration of mercaptans in the feed gas was much lower than that used in the design basis for the facility resulting in a suboptimal design. Opportunity was seen to reformulate the solvent to address this by reducing the physical component concentration to reduce the physical absorption of hydrocarbon components, leaving them in the treated gas stream, thereby reducing the flash gas rates and improving the quality of the acid gas stream to the SRU. Other advantages achieved were higher CO_2 slip in the H_2S absorber, lower emissions, reduced power consumption, reduced entrainment of gas bubbles in the rich solution and improved performance of the flash drums.

In order to prove that the installed plant could operate with the reformulated solvent, checks were made on each component. Table 1 contains a summary of solved related parameter changes. There was essentially no change in the reboiler and lean/rich solvent exchanger duties.

This example serves to illustrate that the removal of contaminants in gas streams should not be considered independently from the requirement to process the hydrocarbon components to meet the product specifications. The degree of interdependence for an optimum overall processing scheme will differ for each application and

Table 1: **Summary of solvent parameters**

Parameter	Original solvent	Reformulated solvent
Circulation rate, m^3/h	135	115
Absorber residence time, mins	2.9	3.4
Gas entrainment in rich solvent, calculated bubble micron size	500	320
Solvent viscosity, cP	20	9

Source: Comprimo

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must be carefully considered during the design phase.

Mercaptan removal options

The gas processing plant complexity increases when reviewing how best to remove mercaptans; three main approaches can be used[1]:

- in the AGRU with a hybrid solvent (i.e., chemical and physical solvent combined);
- from NGL condensed in the NGL recovery unit, using a caustic-based process;
- combined with dehydration in a molecular sieve process, with additional treatment on the molecular sieve regeneration gas.

Some less commonly applied processes include gas caustic treating, scavengers/ inhibitors and membranes, but there can be instances where they are best suited to the plant conditions.

Solvent processes

When reviewing the processes for mercaptan removal, determine if the mercaptans can be removed along with the acid gas species, primarily H_2S and CO_2. Several solvent technologies are available for this purpose with varying degrees of mercaptan removal. See Table 2 for a comparison of common solvent types available.

Natural gas liquids recovery and liquids treating

There can be situations where it is considered more efficient to remove mercaptans from the natural gas liquids (NGL) rather than the inlet gas streams. It can be expected that the NGL volumes will be significantly lower than the total gas throughput of the plant, and the mercaptan concentrations higher in the liquid stream. These higher concentrations make the mercaptan removal easier than at dilute levels in the total gas. Once in the liquid phase, there are various options to consider for the mercaptan treating. For an in-depth review of technology selection for NGL treatment refer to a 2017 paper from the Laurance Reid Gas Conditioning Conference (LRGCC)[6]. A recent development is the Exion LT system for mercaptan removal from hydrocarbon condensates and NGL streams. The patented technology utilises a non-regenerable chemical additive within the process to capture H_2S and mercaptans. Initial pilot plant testing results were presented at LRGCC in 2016[7].

Table 2: **Comparison of solvents[2]**

Solvent type	Examples	Mercaptan removal
Chemical	Generic amines Sterically hindered amines Activated amines	Only partial
Physical	Selexol Purisol Fluor solvent IFPEX-2 Morphysorb (all licensed processes)	High levels
Hybrid (mix of chemical & physical)	Sulfinol UCARSOL™ HYBRID Series 900 (all licensed processes/products)	Partial or total depending on the solvent choice

Source: Comprimo

Adsorption processes

If the required level of mercaptan removal is not possible or feasible with solvents, another common approach is to consider fixed-bed adsorption. Options include:

Regenerable processes with molecular sieves/silica gel

- Gas composition dictates the quantity of adsorbent required and therefore the subsequent vessel size.
- The adsorption process offer a two-fold application, as are also used for gas dehydration.
- If molecular sieves are already required for gas dehydration, it would be only an incremental cost of the extra bed depth for mercaptan removal. In some instances, the quantity of molecular sieve needed for mercaptan removal could be higher than that for dehydration, depending on the relative concentrations.
- Regenerable adsorption is a well-established technology.
- The main challenge is how to manage the regeneration gas. From experience it has been found that the cost of dedicated regeneration gas treatment with a physical solvent can be equivalent to the cost of the molecular sieves themselves. In the past, incineration of the regeneration gas was a reasonable option. That is not generally feasible in the current era of stricter emissions controls where total sulphur discharge is measured. Extra focus is required to find the most appropriate treatment option for the regeneration gas depending on overall gas plant configuration.
- Adsorption is favoured by high partial pressure and lower temperatures.

Non-regenerable solid adsorption

- Chemical adsorbent.
- Used for only trace amounts of mercaptans.
- Similarly to the regenerable adsorbent the volume of adsorbent required is proportional to the mercaptan content.
- Two main disadvantages for non-regenerable adsorbents: whether they can meet specification and whether they can handle the capacity of mercaptans.

Gas caustic treatment

Suitability of this process depends on the CO_2 content of the inlet gas. If the CO_2 is too high, it reacts irreversibly with the caustic catalyst. To make this process viable the upstream amine unit would have to be adapted to remove CO_2 in the gas for mercaptan removal to very low levels.

Caustic is more typically used for treating hydrocarbon liquids. It's important to note that H_2S and CO_2 will consume caustic, so this process should be used downstream of the bulk acid gas removal process.

Within the context of caustic treatment, of special note are the findings presented at LRGCC in 2014 regarding the chemistry and predictability of mercaptan removal from gas streams with amines and caustic[8]. The referenced paper highlights three considerations when designing a mercaptan removal unit which can meet a treated gas performance guarantee; selecting the proper processing strategy, understanding the chemistry and effect on phase equilibrium, and using the right simulation tool in the process design. Simulation tools have greatly advanced in recent years in their ability to better estimate mercaptan removal performance, when given the most accurate feed conditions available.

Scavengers/inhibitors

Scavengers/inhibitors are used for polishing, with low levels of H_2S and mercaptans to be removed. There is limited data available regarding mercaptans performance. CO_2 can consume the chemical in some formulations.

Membranes

Membranes have a well-established performance history for bulk CO_2 removal and are not usually used for other acid gases. There have been recent developments in the use of membranes for mercaptan removal. Chevron has patented a pair of systems where the mercaptan-selective membranes are installed on the cooled regeneration gas stream from the molecular sieves for dehydration, and upstream of the fractionation unit[9]. This methodology of removing the mercaptans from the gas stream is designed to meet the LPG sales specification while avoiding caustic treatment.

Another development is rubbery membranes which have been recently commercialised and demonstrate mercaptan removal not previously possible with the traditional glassy membranes common in CO_2 removal[10].

Conclusions

- Accurate reservoir analysis is needed to avoid over-design or errors in technology choice.
- Use a holistic approach in technology selection for mercaptan removal in concert with fixing the overall plant configuration.
- Sales gas specification and further downstream processing have impacts on mercaptan removal. ■

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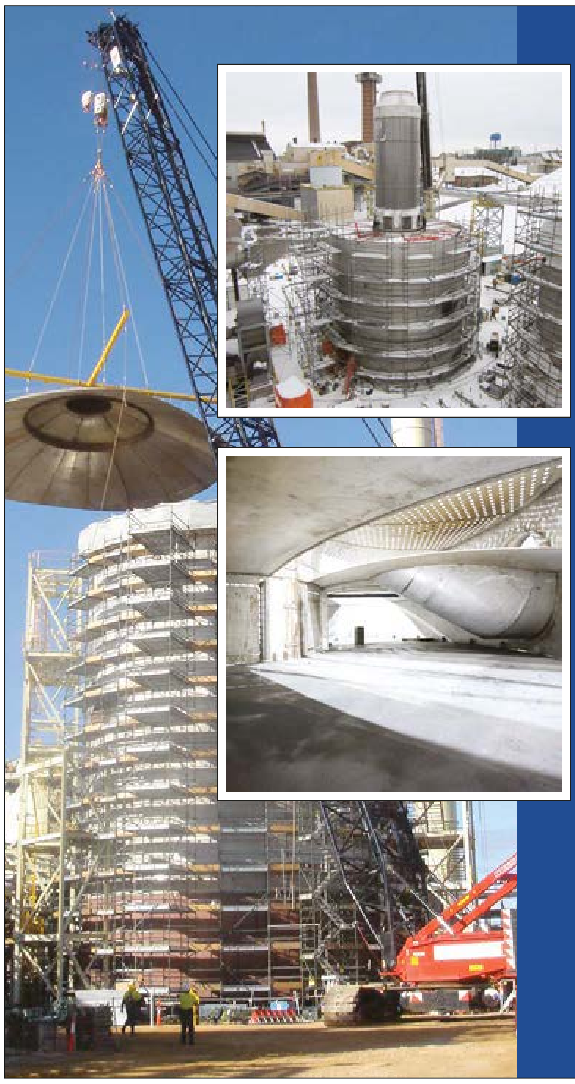

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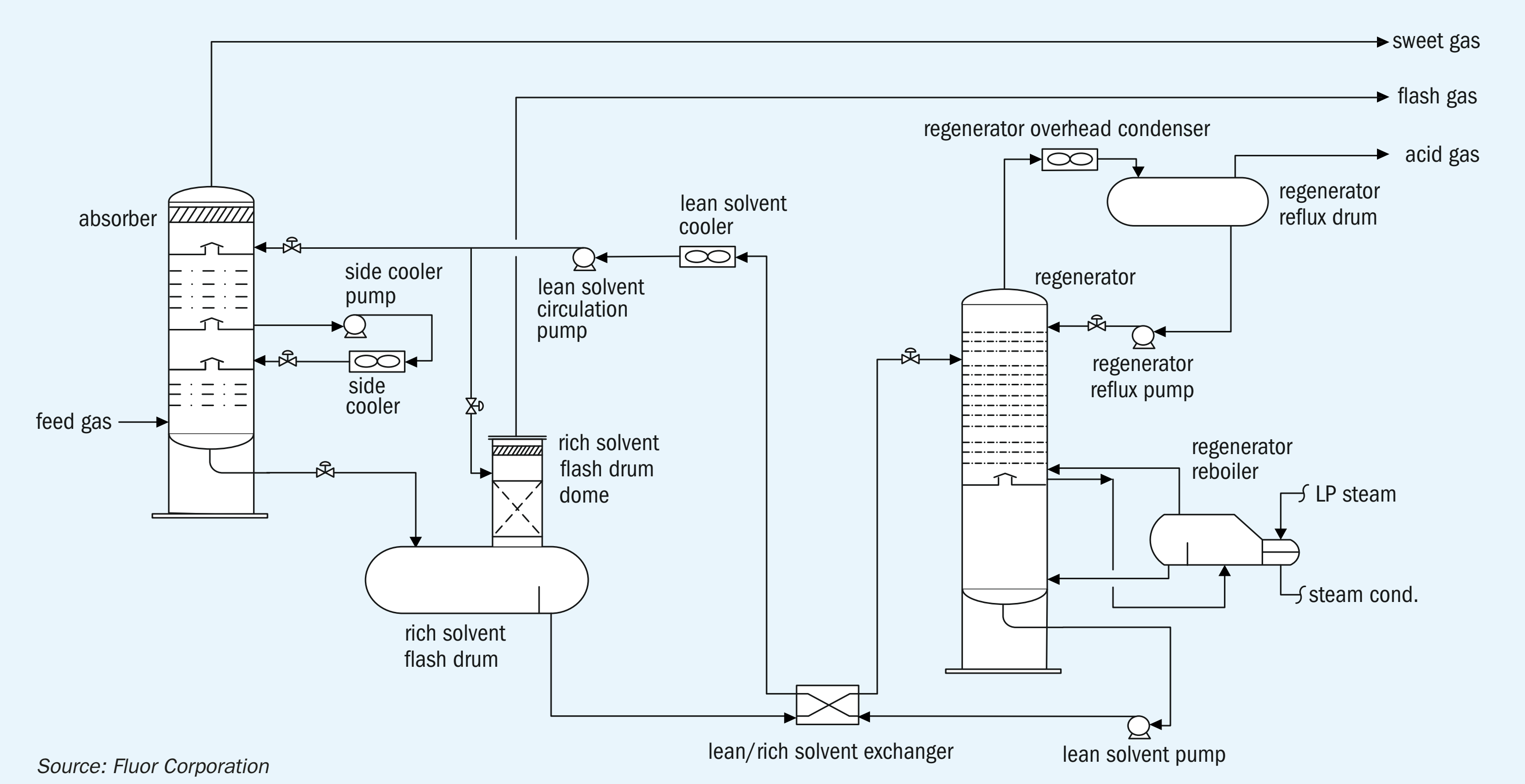
Two-stage absorption for mercaptan removal

Fluor's case study of recently constructed ultra-sour gas treating facilities provides new information about the operation of DGA-based AGRUs. **B. Lynch** and **C. Graham** of Fluor Corporation discuss how using this knowledge and leveraging the recent improvements to process simulators in the gas sweetening space, Fluor has developed an efficient, flexible, and cost effective solution in the two-stage absorption process to maximise mercaptan removal from ultra-sour gases with minimal equipment.

Fig. 1: **Typical improved Econamine flow scheme**



Source: Fluor Corporation

As the depletion of sweet gas reserves continues, development of ultra-sour gas fields (20%+ H_2S) is integral to meeting the increasing global demand for natural gas. Many sour reserves that had been left untouched due to technological and economic challenges are now being reevaluated in light of recent advancements.

This is especially true in the Middle East, where a large percentage of the region's gas reserves are sour. Currently, only a very limited number of facilities process ultra-sour feeds, and an even smaller number do so on a large scale. Development of these ultra-sour fields are hindered by challenges such as varying acid gas concentrations from well to well and the presence of organic sulphur species (e.g. COS and mercaptans) that must be removed. The number of producers in this space will surely grow rapidly in the coming years; therefore, it is imperative that acid gas removal solutions are effective, flexible, and cost efficient. Fluor's recent experiences with its licensed acid gas removal units (AGRU) have led to insights and innovations for ultra-sour gas treating that offer flexibility and cost savings over conventional AGRU designs.

Acid gas removal with DGA

Alkanolamines are commonly used as chemical solvents to remove acid gases (H_2S and CO_2) from sour hydrocarbon gas streams. Diglycolamine (DGA) is a type of alkanolamine that couples the stability and reactivity of monoethanolamine (MEA) with the low vapour pressure and hygroscopicity of diethylene glycol, which allows for more concentrated solutions and thus lower solvent flow rates. DGA has proven to be very effective at treating large volumes of gas at both high and low absorption pressures.

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Table 1: **Facility design conditions**

Design characteristic	Value
AGRU feed gas rate per train, million std ft³/d	250
H_2S content in feed gas, mol-%	23.4
CO_2 content in feed gas, mol-%	9.7
COS content in feed gas, ppm mol	390
Total mercaptans in feed gas, ppm mol	150
Absorber pressure, barg	66
Solvent DGA content, wt-%	55
Solvent circulation rate per train, m³/h	1,645
Lean solvent temperature, °C	60
Treated gas H_2S specification, ppm mol	< 20
COS removal specification, %	> 90
Absorber diameter, m	6.1
Solvent regenerator diameter, m	8.0
Design ambient air temperature, °C	50

Table 2: **Design feed gas versus average actual feed gas composition**

Components	Design	Actual
H_2S, mol %	23.38	25.07
CO_2, mol-%	9.68	9.38
N_2, mol- %	0.02	0.27
H_2, mol-%	0.14	0.22
Methane, mol-%	57.74	55.65
Ethane, mol-%	4.45	4.47
Propane, mol-%	1.96	2.22
Butanes, mol- %	1.52	1.63
C_{5+}, mol-%	1.10	1.00
COS, ppm mol	390	300
Mercaptans, ppm mol	150	330

Table 3: **Average sweet gas composition**

Components	Value
H_2S, ppm mol	< 1
CO_2, ppm mol	< 1
N_2, mol-%	0.01
H_2, mol-%	0.32
Methane, mol-%	86.84
Ethane, mol-%	6.25
Propane, mol-%	2.94
Butanes, mol-%	1.97
C_{5+}, mol-%	1.67
COS, ppm mol	< 1
Mercaptans, ppm mol	< 4

Even at high ambient temperatures, DGA can produce sweet gas with below 4 ppmv H_2S[1]. Unlike selective amines that result in CO_2 slip into the treated gas, DGA can also remove CO_2 down to ppm levels. CO_2 removal improves the heating value of sales gas and is imperative to prevent freezing in downstream low temperature units such as NGL recovery and LNG liquefaction. Another benefit of DGA is removal of COS and CS_2 from the feed gas. Removal efficiency for these components can exceed 90%. As such, DGA is the solvent of choice for the Fluor Improved Econamine^{SM} process. Fig. 1 provides a process flow diagram of a typical Improved Econamine^{SM} flow scheme.

Experience treating ultra-sour streams with DGA

Due to the small number of facilities that treat ultra-sour feeds on a large scale, there is limited experience regarding the design and operation of such facilities. Recently, a high capacity AGRU based on Fluor Improved Econamine DGA technology, was constructed and commissioned. Table 1 provides basic design information and operating conditions for the facility.

As Table 1 shows, this facility provides a unique challenge of treating a large volume of very sour gas (almost 35 mol-%) down to a standard sales gas specification in a very hot climate. More information is available on the design of these units in Reference 2.

Performance of this unit, after a successful start-up and stable operation, provided valuable data for a detailed analysis of the AGRU. This study has yielded new insights into ultra-sour gas treatment utilising DGA. Table 2 provides a comparison between the design sour gas composition and the average actual sour gas composition during operation. The actual sour gas composition was determined by laboratory analysis of samples taken at site.

Although the H_2S content in the actual feed gas is greater than design, the unit effectively removes all acid gases as shown by the extremely low treated gas H_2S and CO_2 content in Table 3. The 25.1 mol-% of H_2S and 9.4 mol-% of CO_2 in the feed gas are treated to less than 1 ppm(mol) in the sweet gas, demonstrating that DGA is an extremely effective solvent for ultra-sour feed gases.

A challenge with ultra-sour gas treatment is the removal of organic sulphur species such as carbonyl sulphide (COS), carbon disulphide (CS_2), and mercaptans. These organic sulphur species are present in many sour gases and must be removed to meet total sulphur specifications for the sales gas and NGL products. Operating experience has proven that DGA is effective for COS removal above 90% in the majority of applications, thus prompting the COS removal guarantee listed in Table 1. DGA has also proven ability to remove mercaptans, but no data existed for the extent of removal at conditions similar to the referenced facility. As such, a mercaptan removal guarantee was not made and downstream provisions for mercaptan removal were included in the design.

Table 3 also shows low concentrations of COS and mercaptans in the sweet gas, indicating that for this system, DGA removed not only the majority of COS in the feed, as expected, but the majority of the mercaptans as well. To prove the long-term sustainability of organic sulphur removal, daily sample data for the organic sulphur content of the feed gas and treated sweet gas was collected over a 14 month period. This data has been consolidated into Fig. 2 and Fig. 3.

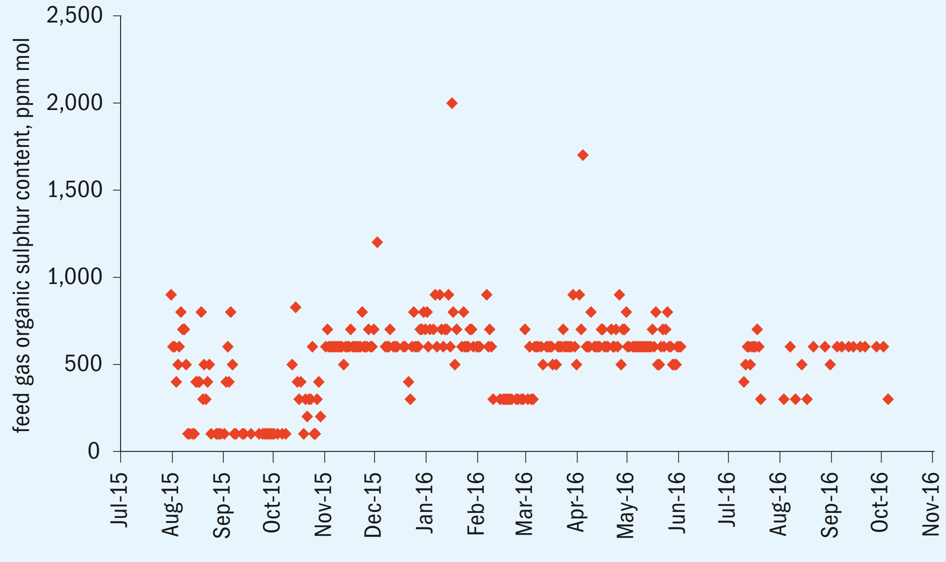
Fig. 2 shows that the feed gas organic sulphur content ranges between 500 ppm (mol) and 800 ppm(mol) for the majority of operation. Once treated, the organic sulphur content in the gas is consistently below 10 ppm (mol) as shown in Fig. 3. Table 3 shows that the average COS content in the sweet gas is less than 1 ppm (mol), so the remaining organic sulphur in the sweet gas are mercaptans. This corresponds to a total mercaptan removal efficiency of well over 90%.

Mercaptan removal by DGA occurs through both chemical and physical absorption. The dominating mechanism varies from system to system and is dependent on the operating conditions and the specific types of mercaptans in the feed gas. From a chemical perspective, mercaptans have acidic properties, like H_2S, but because of the hydrocarbon functional group, they are much weaker acids than H_2S. Mercaptans behave less like acids and more like hydrocarbons as the hydrocarbon chain length increases. Due to their acidic properties, mercaptans chemically react with amines, but these chemical bonds are weak and are readily dissociated by more acidic compounds (e.g. H_2S and CO_2). The solubility of mercaptans in amine solutions increases with increased solvent alkalinity (less absorbed H_2S and/or CO_2), and decreases with increased temperature[1]. Similarly to other physical absorption systems, the rate of physical absorption of mercaptans by DGA increases with an increase in absorber pressure. This is due to the increased partial pressure of mercaptans in the gas.

The extent of mercaptan absorption in this system can most likely be attributed to the following:

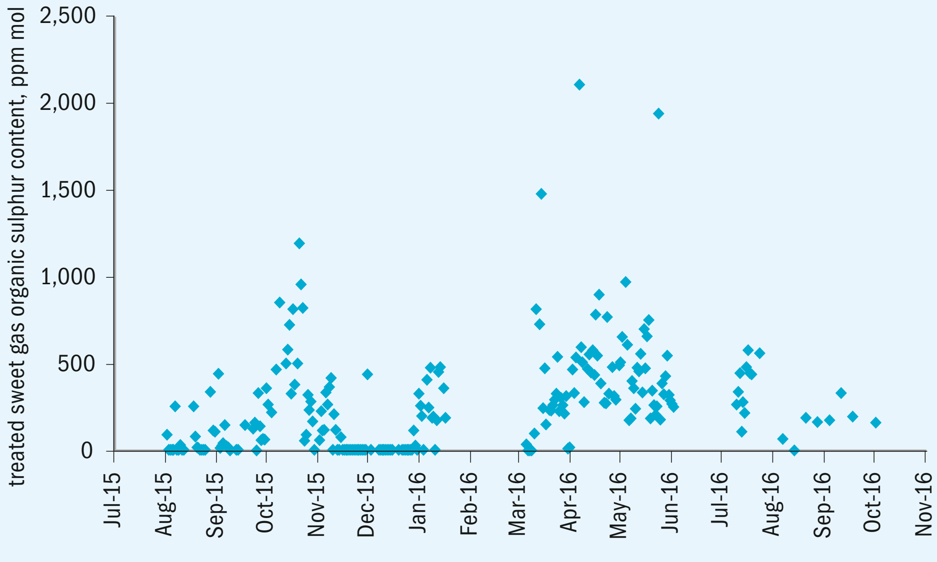
- high absorber pressure (66 barg) promoting physical absorption;
- high solvent circulation rate to ensure H_2S and CO_2 removal;
- limited chemical absorption competition by H_2S and CO_2 in the upper trays.

Fig. 2: **Feed gas organic sulphur content**



Source: Fluor Corporation

Fig. 3: **Treated sweet gas organic sulphur content**



Source: Fluor Corporation

Simulation validation

Using insights gleaned from the operating data, a simulation model of the AGRU process was built. Developing an accurate model (if possible) is imperative to any optimisation efforts or future design improvements for ultra-sour facilities. It should be noted that at the time that this facility was designed, process simulators were limited in their application to the extreme conditions in which these units operate. Recently, however, simulators such as Bryan Research and Engineering ProMax v4.0 (released in 2016) have seen major improvements in mass and heat transfer based absorption models, resulting in improved accuracy and consistency with operating data. Table 4 compares operating data for August and September of 2016 to ProMax v4.0 simulation results of the AGRU.

Based on the comparison in Table 4, the new mass + heat transfer column models in ProMax v4.0 can provide accurate results for large, ultra-sour facilities using DGA solvent. Predicted acid gas removal is in line with operational results with virtually no error.

The predicted column temperature profile, which is an accuracy indicator of tray-by-tray acid gas absorption, also agrees well with operational data. The model slightly under predicts the absorption in the bottom tray and shifts some absorption up to the second tray, as seen by the smaller temperature differential between the trays compared to actual results. However, by the third and fourth trays, the predicted profile is in line with observed results.

For mercaptan removal prediction, the model is not as accurate. Predicted methyl mercaptan (C_1-mercaptan) absorption is very accurate (99.8% vs > 99% in actual operation). However, predicted ethyl mercaptan (C_2-mercaptan) and propyl mercaptan (C_3-mercaptan) removal is much less than observed removal (64% vs > 99% and 26% vs 99%, respectively). The accuracy decreases as the hydrocarbon chain length on the mercaptan increases. This is most likely due to under-prediction of the chemical absorption influence of heavier mercaptans. The accurate prediction of methyl mercaptan removal should prove to be important in future designs as methyl mercaptan often makes up a large fraction of the total mercaptan content in sour gas. This is evidenced by the much better agreement of predicted total mercaptan removal to operating data when compared to predicted ethyl and propyl mercaptan pickup.

The comparison in Table 4 shows that the improvements to ProMax v4.0 prove that the simulator will be an important design tool for future ultra-sour developments. While the mercaptan removal predictions could be improved, they currently provide a solid starting point. At the very least, they will contribute to slightly conservative designs, which is much preferred to the alternative. The accurate results also allowed for further optimisation and improvement of Fluor's Improved Econamine process, as discussed in the following sections.

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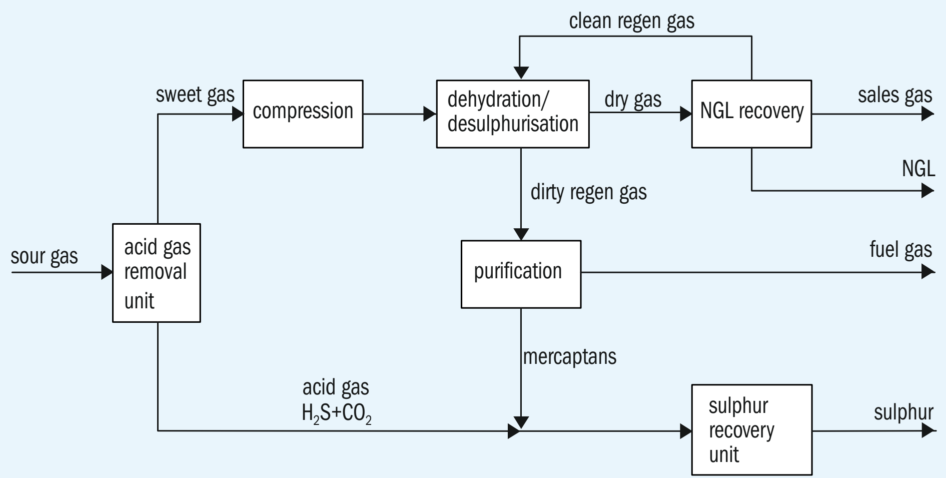
Table 4: **Comparison of operating data to simulation results**

Property	Operating data	Simulation result
Sour feed gas flow, million std ft^3/d	275	275
DGA solvent circulation rate, m^3/h	1,715	1,715
Feed gas H_2S content, mol-%	25.1	25.1
Feed gas CO_2 content, mol-%	9.4	9.4
Feed gas C_1-mercaptan content, ppm mol	230	230
Feed gas C_2-mercaptan content, ppm mol	60	60
Feed gas C_3-mercaptan content, ppm mol	30	30
Feed gas total mercaptan content, ppm mol	330	330
Treated gas H_2S content, ppm mol	< 1	0.1
Treated gas CO_2 content, ppm mol	< 1	0.3
Treated gas C_1-mercaptan content, ppm mol	0.7	0.7
Treated gas C_2-mercaptan content, ppm mol	1.0	33
Treated gas C_3-mercaptan content, ppm mol	0.7	35
C_1-mercaptan removal efficiency, %	> 99	99.8
C_2-mercaptan removal efficiency, %	> 99	64
C_3-mercaptan removal efficiency, %	> 99	26
Total mercaptan removal efficiency, %	> 99	86
Absorber bottoms temperature, °C	100-105	101
Absorber tray 2 temperature, °C	70-80	83
Absorber tray 3 temperature, °C	60-65	66
Absorber tray 4 temperature, °C	60-65	64
Absorber tray 6 temperature, °C	60-62	62
Absorber tray 8 temperature, °C	60-62	61

Fig. 4: **Typical single-stage absorption unit line-up**



Source: Fluor Corporation

Design for low pressure ultra-sour streams

This case study has demonstrated that high pressure absorption using DGA solvent is effective in removing mercaptans from ultra-sour gases. However, high pressure processing of ultra-sour gases carries major health, safety, and environmental (HSE) risks and impacts such as the following:

- large exclusion zones and unit setbacks leading to larger facility plot areas and increased site preparation requirements;
- requirement to use self-contained breathing apparatus (SCBA) or hard line air requirements when entering sour gas processing units;
- stringent design requirements;
- strict operating and maintenance procedures.

Reference 4 provides a detailed description of the various requirements for safe processing of very sour streams. These restrictions may be manageable for small facilities in more remote locations, but can have significant design and operability impact for larger facilities. For ultra-sour feed gases with a relatively low gathering system pressure (either due to HSE or reservoir limitations), the costs and risks are greater since the feed gas must be compressed to a higher pressure before treating. In an instance such as this, the sour gas compressors would be constructed of expensive metallurgy and carry additional risk due to the higher number of potential leak points. To mitigate these risks, treating of ultra-sour gases is typically performed at low pressure. However, operating experience has shown that low pressure systems suffer from poor mercaptan removal efficiency. As a result, a separate system for mercaptan removal is usually required, adding complexity and cost to the design. One example is the use of a downstream molecular sieve unit to remove both mercaptans and water moisture. Including mercaptan removal in the molecular sieve requires more sieve volumes as well as the need for an auxiliary purification system (e.g. Selexol) to remove the mercaptans from the regeneration gas. Fig. 4 shows the typical line-up of units required for an ultra-sour feed gas with mercaptan removal using molecular sieves.

A more attractive solution is the patented Fluor two-stage absorption[5] process. The two-stage absorption process was developed to take advantage of improved mercaptan removal at higher pressures in a way that maintains the health and safety advantages of the low pressure absorption configuration. The improved mercaptan removal will reduce or, in some scenarios, completely eliminate the need for downstream mercaptan removal. The auxiliary purification system can also be reduced or eliminated, resulting in significant cost savings for the overall facility. Fig. 5 shows the optimised line-up of units made possible through the two-stage absorption process.

The newly developed process is comprised of two stages. The first stage

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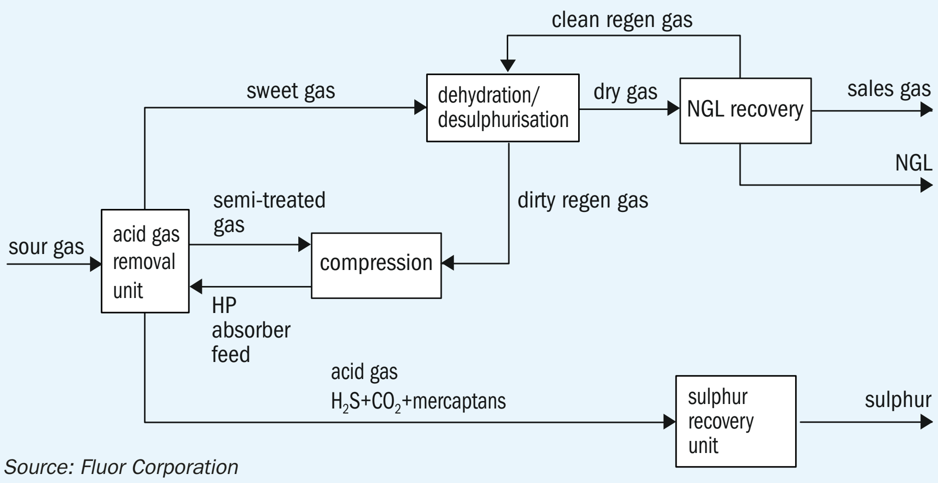
removes the bulk of H_2S at the lower feed gas pressure. The semi-treated gas, with relatively low H_2S partial pressure, is then compressed to the higher pressure second stage at which the remaining H_2S, CO_2, and organic sulphur species are removed to achieve treated gas specifications. Fig. 6 shows a process flow diagram for the Fluor two-stage absorption process.

The feed gas is fed to the LP absorber where it is contacted counter-currently with a semi-rich solvent stream from the HP absorber to remove the majority of the acid gases. The level of acid gas removal in the LP absorber depends on the operating pressure of the HP absorber and HSE requirements. The semi-treated gas leaves the top of the LP absorber and is sent to the semi-treated gas compression train. Once the semi-treated gas is compressed, it is fed to the HP absorber where it is contacted counter-currently with lean solvent from the solvent regeneration system. The lean solvent removes the remaining H_2S and CO_2 in the semi-treated gas along with a significant amount of the mercaptans. The treated gas leaves the top of the HP absorber for further processing. The semi-rich solvent from the bottom of the HP absorber is flashed across a control valve and then routed to the LP absorber. The rich solvent leaving the bottom of the LP absorber is regenerated in a typical AGRU solvent regeneration system.

Although the Fluor two-stage absorption process requires two absorber columns, the total number of trays required can be identical to a single-stage process. In some instances, the HP absorber can be a smaller diameter than the LP absorber due to the higher pressure and the bulk removal of H_2S and CO_2 occurring in the LP absorber.

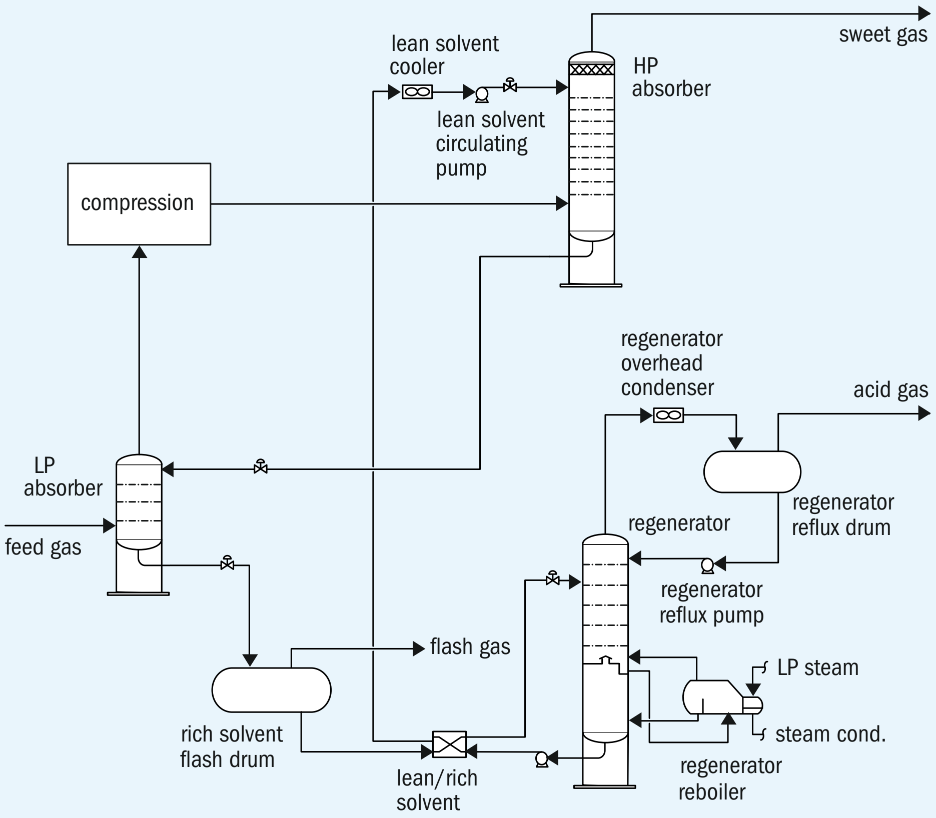
Table 5 compares the simulation results between a low pressure, single-stage absorption process and the Fluor two-stage absorption process. The data is based on a feed gas that contains approximately 22 mol-% H_2S, 10 mol-% CO_2, 100 ppm mol methyl mercaptan, 40 ppm mol ethyl mercaptan, and 160 ppm mol total mercaptans. The feed gas enters the system at 20 barg and 35°C. For the single-stage process, the absorber operates at roughly 20 barg. For the two-stage process, the LP absorber operates at roughly 20 barg and the HP absorber operates at roughly 70 barg. The absorber in the single-stage process has 23 trays. In the two-stage process, the LP absorber has five trays, and

Fig. 5: **Fluor two stage absorption unit line-up**



Source: Fluor Corporation

Fig. 6: **Fluor two stage absorption process**



Source: Fluor Corporation

Table 5: **Single-stage absorption versus two-stage absorption**

Component	**Feed gas**	**Sweet gas** **Single-stage LP absorption**	 **Two-stage absorption**
H_2S, kmol/h	2755	0.00	0.00
CO_2, kmol/h	1190	0.01	0.00
Methyl mercaptan, kmol/h	1.31	0.69	0.01
Ethyl mercaptan, kmol/h	0.51	0.45	0.42
Total mercaptans, kmol/h	1.99	1.28	0.57

the HP absorber has 18 trays, for a total of 23 trays. The lean solvent concentration is 55 wt-% DGA and the solvent circulation rate is the same for both scenarios. The lean solvent temperature is 58°C for both scenarios, which is typical for air-cooled solvents in the Middle East.

Table 5 shows that the single-stage process results in 47% methyl mercaptan removal, 12% ethyl mercaptan removal, and 36% total mercaptan removal. The two-stage process results in over 99% methyl mercaptan removal, 18% ethyl mercaptan removal, and 71% total mercaptan removal. These results indicate that the two-stage system provides a significant advantage in methyl mercaptan removal, which leads to roughly twice the total mercaptan removal from the feed gas. However, operating experience for single-stage, high pressure absorption systems (as described in a previous section) shows that ethyl and heavier mercaptans exhibit higher removal efficiencies than indicated in the simulation results. This further supports the notion that a two-stage system has appreciable mercaptan removal capabilities compared to a single-stage, low pressure system.

The Fluor two-stage absorption process can offer several benefits compared to the typical single-stage absorption process such as the following:

- improved mercaptan removal;
- similar equipment count in AGRU;
- minimal HSE risks and impacts;
- reduction in size or elimination of downstream mercaptan treatment units which saves capex and opex:
    - molecular sieves
    - regeneration gas treatment
    - Merox units in a NGL recovery unit;
- reduced plot space compared to single-stage, high pressure treatment

Conclusion

As the number of sweet gas reserves continues to decline, the development of ultra-sour gas reserves is essential to meet the global natural gas demand. Development of these ultra-sour reserves encounters many technical challenges, including organic sulphur removal, that were previously met with conservatism due to limited operational experience. Fluor has developed a two-stage absorption process utilising DGA to maximise mercaptan removal from ultra-sour gases with minimal equipment.

Moving forward, innovative solutions such as these will be crucial to meet the growing need for ultra-sour gas development. ■

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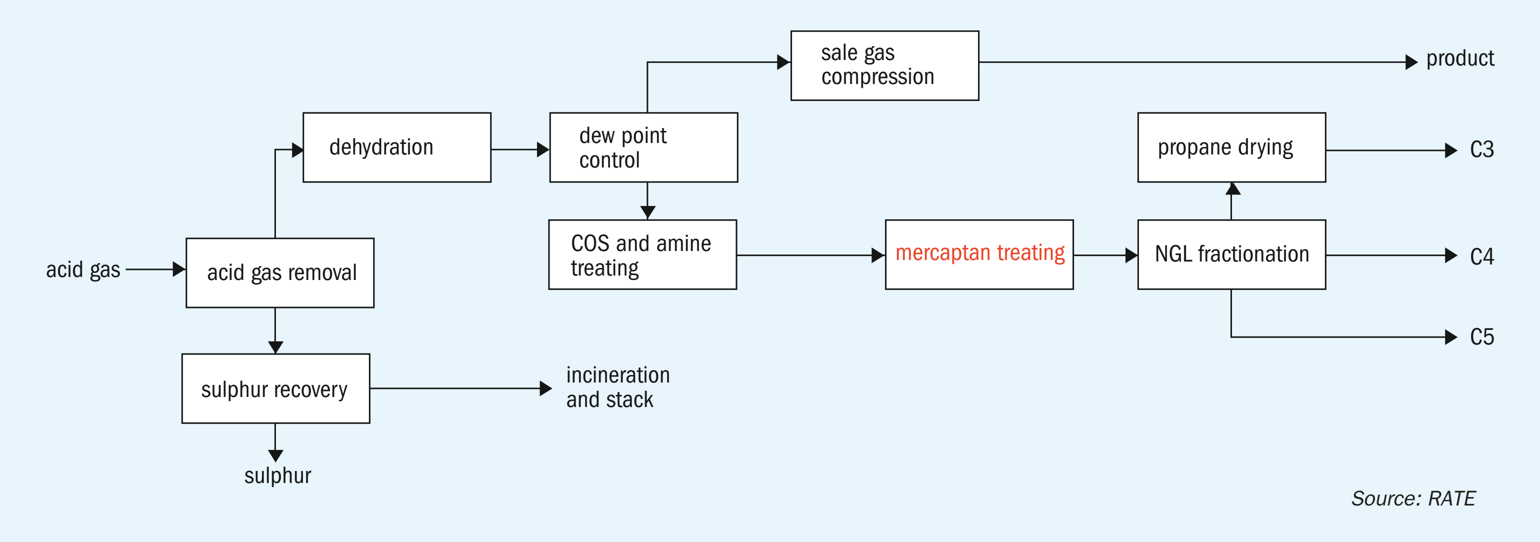
Meeting sulphur specs

An advanced mecaptan removal process has been developed and implemented by RATE. The RATE-Oximer process is an oxidative air-based regeneration process, designed to remove mercaptans from liquid and vapour phases. **M. Rameshini** of RATE describes the key features of the process and its applications.

Fig. 1: **A typical sour gas processing scheme with mercaptan treatment**



Source: RATE

A typical sour gas processing scheme highlighting the mercaptan treatment unit is shown in Fig. 1. Often mercaptans can be removed by proper selection of a formulated amine solvent, but sometimes, e.g. where there are higher volumes of mercaptans, further processing may be required to meet the specification of the treated sales gas or pipeline criteria.

In some cases the removed mercaptans are sent to the sulphur recovery unit for processing and destruction, but for small amounts of mercaptan removal catalysts and scavengers are typically used.

The RATE-Oximer process is an efficient and economical catalytic process developed for the chemical treatment of petroleum fractions to remove sulphur present as mercaptans or to directly convert mercaptan sulphur to less objectionable disulphides. This process is used for liquid phase treating of liquefied petroleum gases (LPG), natural-gas liquids (NGL), naphtha, gasolines, kerosene, jet fuels, and heating oils. It also can be used to sweeten natural gas, refinery gas, and synthetic gas in conjunction with conventional pretreatment and post treatment processes.

The principle of the RATE-Oximer process is to use dilute caustic to absorb the mercaptan from the feed stream and then to use air over a liquid sulphonated cobalt phthalocyanine catalyst in the oxidiser reactor to regenerate the caustic. Catalyst consumption is in the range of 250 to 350 ppm, based on the concentration and volume of the caustic.

In the extractor fresh feed is charged to the column, where mercaptans are extracted by a countercurrent caustic stream. The caustic absorbs mercaptans and then flows to the oxidiser which is injected with catalyst to oxidise the absorbed mercaptan to disulphide, which is insoluble in caustic. The disulphide is then separated from the caustic and the lean caustic is recycled to the extractor.

The key features of the liquid sulphonated cobalt phthalocyanine sweetening catalyst are:

- completely miscible with caustic;
- good chemical and thermal stability;
- convenient to use;
- higher catalytic activity;
- longer cycle.

It is especially suitable for the liquid-liquid sweetening of heavy oil catalytic cracking gasoline, hydrogenation refined gasoline and LPG sweetening, processing materials including gasoline, LPG, synthesis gas, coal gas, natural gas and for the removal of hydrogen sulphide and mercaptans (deodorisation) in the gas phase.

The RATE-Oximer process has been designed for applications with and without an upstream amine unit. Those that include an amine unit have used generic DEA or MEA amine solvent. The catalyst is supplied through RATE.

The extractor can be applied to both gaseous and light liquid hydrocarbon streams. The degree of completeness of mercaptan extraction depends on the solubility of the mercaptan in the alkaline solution which, in turn, depends on the following:

- molecular weight of mercaptan;
- degree of branching of mercaptan molecule;
- caustic soda concentration;
- temperature of the system.

Mercaptan solubility in the alkaline solution decreases with increasing molecular weight of the mercaptan and with increasing branching of the mercaptan molecule.

RATE performs simulation modelling case by case based on feed composition.

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Process description

In the first step, the feedstock is contacted in the trayed or packing extractor vessel with an aqueous caustic solution. The caustic solution reacts with mercaptans and extracts them. The reaction taking place in the extractor is:

$$2RSH + 2\ NaOH \rightarrow 2NaSR + 2H_2O$$

In the above reaction, RSH is a mercaptan and R signifies an organic group such as a methyl, ethyl, propyl or other group. For example, the ethyl mercaptan has the formula C_2H_5SH.

The second step is referred to as regeneration and involves heating and oxidising of the caustic solution leaving the extractor. The oxidation converts the extracted mercaptans to organic disulphides (RSSR) which are liquids that are water-insoluble and can be separated and decanted from the aqueous caustic solution. The reaction taking place in the regeneration step is:

$$4NaSR + O_2 + 2H_2O \rightarrow 2RSSR + 4NaOH$$

After decanting the disulphides, the regenerated "lean" caustic solution is recirculated back to the top of the extractor to continue extracting mercaptans.

The net overall caustic treating reaction covering the extraction and the regeneration step can be expressed by the following equation:

$$4RSH + O_2 \rightarrow 2RSSR + 2H_2O$$

The feedstock entering the extractor must be free of any H_2S. Otherwise, any H_2S entering the extractor will react with the circulating caustic solution and interfere with the caustic treating reactions. Therefore, the feedstock is first "prewashed" by flowing through a batch of aqueous caustic to remove any H_2S. The reaction that takes place in the prewash vessel is:

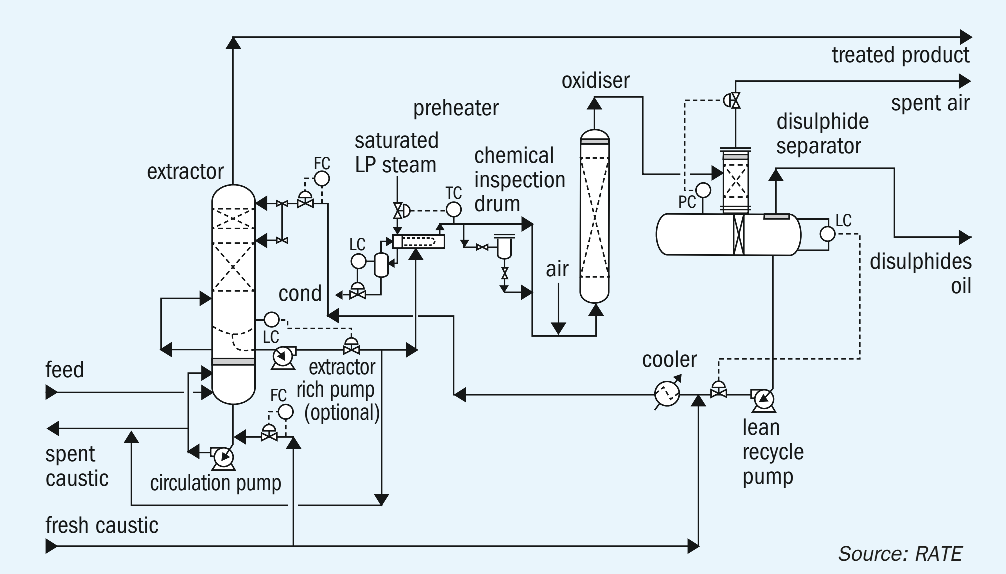
$$H_2S + NaOH \rightarrow NaSH + H_2O$$

The batch of caustic solution in the prewash vessel is periodically discarded as "spent caustic" and replaced by fresh caustic as required.

The caustic solution leaving the bottom of the mercaptan extractor (rich caustic) flows through a control valve which maintains the extractor pressure needed.

It is then injected with liquid catalyst (on an as needed basis), flows through a steam-heated and is injected with compressed air before entering the oxidiser vessel where the extracted mercaptans are converted into disulphides. The oxidiser vessel has a packed bed to keep the aqueous caustic and the water-insoluble disulphide well contacted and well mixed.

Fig. 2: **RATE-Oximer process shown without an amine unit**



Source: RATE

The caustic-disulphide mixture then flows into the separator vessel where it is allowed to form a lower layer of lean caustic and an upper layer of disulphides. The vertical section of the separator is for the disengagement and venting of excess air and includes a Rasching ring section to prevent entrainment of any disulphides in the vented air. The disulphides are withdrawn from the separator and routed to fuel storage or to a hydrotreater unit. The regenerated lean caustic is then pumped back to the top of the extractor for reuse.

The caustic and excess air mixture from the reactor flows into the top section of the disulphide separator. Here the air and any hydrocarbon vapour are vented to the incinerators and the caustic flows to the lower section or settler section where it is coalesced and separated. All separations are based on physical characteristics only; no chemical reactions are involved.

The caustic settler or disulphide separator is designed with sufficient residence time to handle upsets and to break down foam. A demister section at the top of the dome minimises carryover of liquid droplets in the vent gas. The vent gas leaving the dome is diluted with fuel gas to ensure that the vent gas mixture is always in the nonexplosive range.

The volume of fuel gas added is equal to 120% of the process air injection rate to the air diffuser. The minimum amount of oxygen required to support combustion in this type of mixture is about 11 vol-%. The 1.2:1 ratio of fuel gas to air reduces the oxygen content to at least 9.55 mol-%, even if no oxygen is consumed in the reactor.

It is important to mention that in the "RATE-Oximer" process if the feedstock is a vapour disulphides are not a problem, however, in the liquid phase if the specification is very tight some oil injection may be required to absorb the disulphides.

If the facility does not have caustic storage, it may be beneficial to have a small caustic inventory for the RATE-Oximer process. To date, in all projects the project specification has been met without using any oil. The low consumption of caustic and catalyst makes the process very economical. There is no product deterioration as a result of side reactions and no addition of undesirable materials to the treated product. The advantages include: a low operating cost, the caustic and the catalyst are cheap and available worldwide, the process is highly efficient, easy to operate and reliable, there is minimal waste unless excess components like CO_2 come from the amine unit, and the product meets specification and environmental regulations.

If LPG contains significant disulphide an additional packing column is provided using oil as the solvent to absorb disulphides. Fig. 2 shows a process flow diagrams of the RATE-Oximer process without an amine unit.

RATE has designed several RATE-Oximer units in South America and in Russia and has supplied the process design package (PDP) to several EPC contractors. The proprietary RATE-Oximer process design is licensed by RATE with performance guarantees. ■

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New self-cleaning sulphur strainer

For the protection of nozzles in sulphur forming plants it is important to prevent larger particles from entering the forming machinery and possibly blocking the nozzles. In normal operation, pipeline strainers are used. Sulphurnet has designed a new system which is suitable for continuous or batch operations and has lower maintenance costs. **J. Hermans** of Sulphurnet introduces the self-cleaning sulphur strainer.

Process filtration may give the impression of being an easy step, but today's demanding requirements for high filtration quality, automation and reduction of operational and investment costs makes filtration a field for special study.

Over the years, strainers have been placed in-line with process piping to remove large solid contaminants from the flow. A wide variety of filter materials can be used to achieve the required product quality. The most frequently used filter materials are perforated screens, screens covered with filtration mesh and wedge edge filter elements. However, pipeline strainers have a limited filtration area and have high maintenance costs, which calls for a review of this filtration process.

Environmental considerations such as emissions and safety in the workplace also play an important role in the decision for new investments, since manual cleaning of strainers is becoming less acceptable. All of these factors influence production targets, customer satisfaction and companies' profits.

Sulphurnet has designed a system, called a Self-Cleaning Sulphur Strainer which is suitable for continuous, as well as batch-operations, has low maintenance costs and takes into account the criteria mentioned above.

Strainer function

The heart of the Self-Cleaning Sulphur Strainer is an asymmetric edge-gap strainer element located centrally in a pressure vessel. The liquid flow is from the inside of the edge-gap strainer to the outside, keeping the particles on the inside. For cleaning purposes the strainer has a rotating axis with various impellor blades which rotates inside the strainer to remove the collected debris.

The edge-gap strainer is totally cleaned due to the particular design and rotation of the impellor. The impurities are pushed downwards and accumulate in the concentration chamber. After a pre-set number of cleaning cycles the solids are discharged by means of a drain valve in the bottom of the filter.

The filtered liquid leaves the filter through a side outlet. The filter housing is only in contact with the filtered liquid. The filtration, cleaning and the concentrate discharge cycles are carried out continuously, and are sequenced by a PLC.

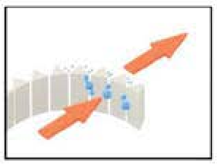
The cleaning cycle is carried out by an electrical motor which is activated either by a pre-set pressure differential or by running on time valves; alternatively the operations can run continuously.

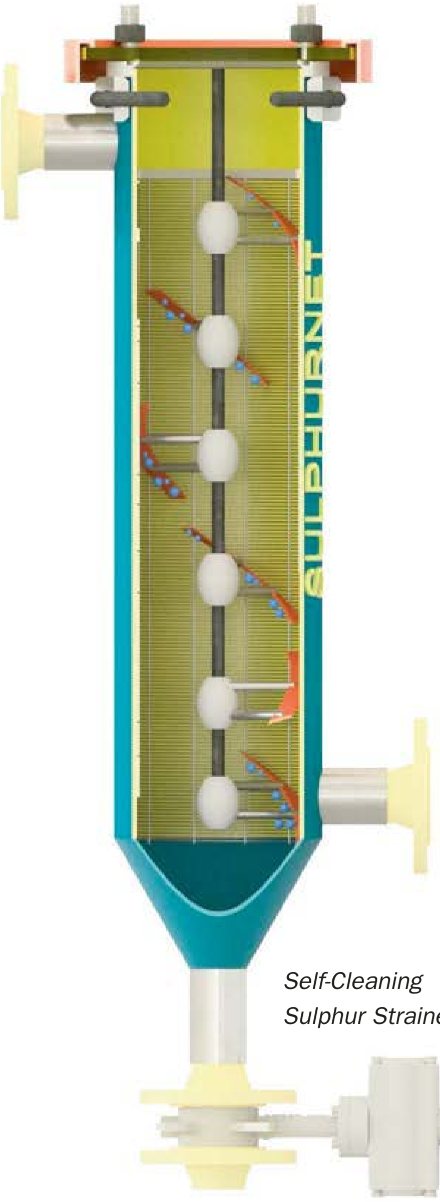
The frequency of operation of the drain valve is set by the number of cleaning cycles or time regulated.

The opening time of the drain valve can be set as required. This means a maximum concentration of solids can be achieved which results in a minimal loss of product. During the cleaning cycle filtration continues, which means that the process is not interrupted.

Edge-gap strainer

The Self-Cleaning Sulphur Strainer filter utilises an edge-gap strainer which is





Self-Cleaning Sulphur Strainer.

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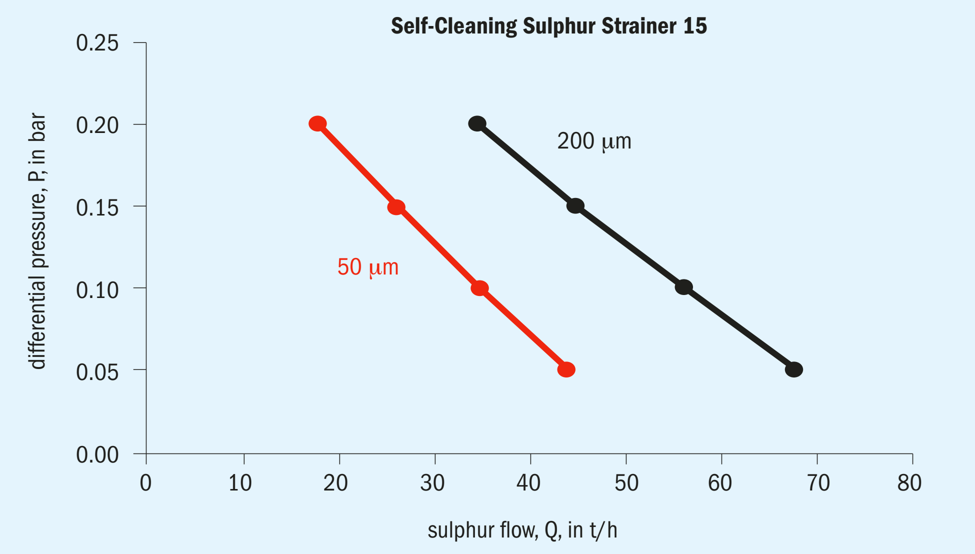
specially machined on the inside so that solid particles cannot attach to it. The rotating agitator knives scrape the impurities from the filter-element which means that the flow is uninterrupted.

The use of edge gap strainer offers the following advantages:

- high mechanical strength;
- self-supporting structure;
- retention from 50 micron and above;
- relatively high open area;
- non plugging surface;
- low maintenance cost;
- low operational cost.

Fig. 1: **Flow characteristics of the Self-Cleaning Sulphur Strainer**



Source: Sulphurnet

Sulphur polluted with steel.

Laboratory filtration.

Residue on filter mesh.

Clean sulphur.

PHOTOS: SULPHURNET

Due to the continuous cleaning cycle, a low-pressure differential is achieved which results in a constant flowrate. The flow characteristics of the Self-Cleaning Sulphur Strainer are shown in Fig. 1.

In current practice, two pipeline-strainers are typically installed, with one in operation and the other one in a cleaning cycle or in standby position. These strainers have to be cleaned manually which is not only time consuming, but also a hazardous operation; spilling of hot sulphur can cause severe burn wounds.

Cleaning of the strainer basket is also difficult, carsul and the solidified sulphur are hard to remove from the strainer basket and in most cases it should be replaced.

The Self-Cleaning Sulphur Strainer operates continuously, even during the cleaning cycle. The system is fully jacketed so the internals are kept at the correct temperature to ensure sulphur remains in liquid form.

The lack of clarity in the filtration market makes it difficult to decide on the best solution for a given application. Before making the selection it is important to carry out a thorough evaluation of costs, both operational and investment, and to take into account both process conditions and environmental issues.

The unique Self-Cleaning Sulphur Strainer is an efficient filter system for filtration tasks in sulphur processing, fulfilling stringent requirements.

Typical application

Elemental sulphur produced by the Claus process contains both physically dissolved H_2S and chemically bound H_2S in the form of hydrogen polysulphides. The principle of sulphur degassing is the removal of the dissolved H_2S from the liquid sulphur. Degassing is carried out as a batch or continuous process in the dedicated pit. The actual degassing takes place by bubbling air through the liquid sulphur. The SS air nozzles ae subject to corrosion and particles are released in the liquid sulphur. These particle need to be removed before sulphur forming.

Laboratory tests showed the required retention to obtain a clean sulphur product. Two options were possible, stop the process and repair the air nozzles, or install a self-cleaning strainer. The self-cleaning option was selected and successfully installed.

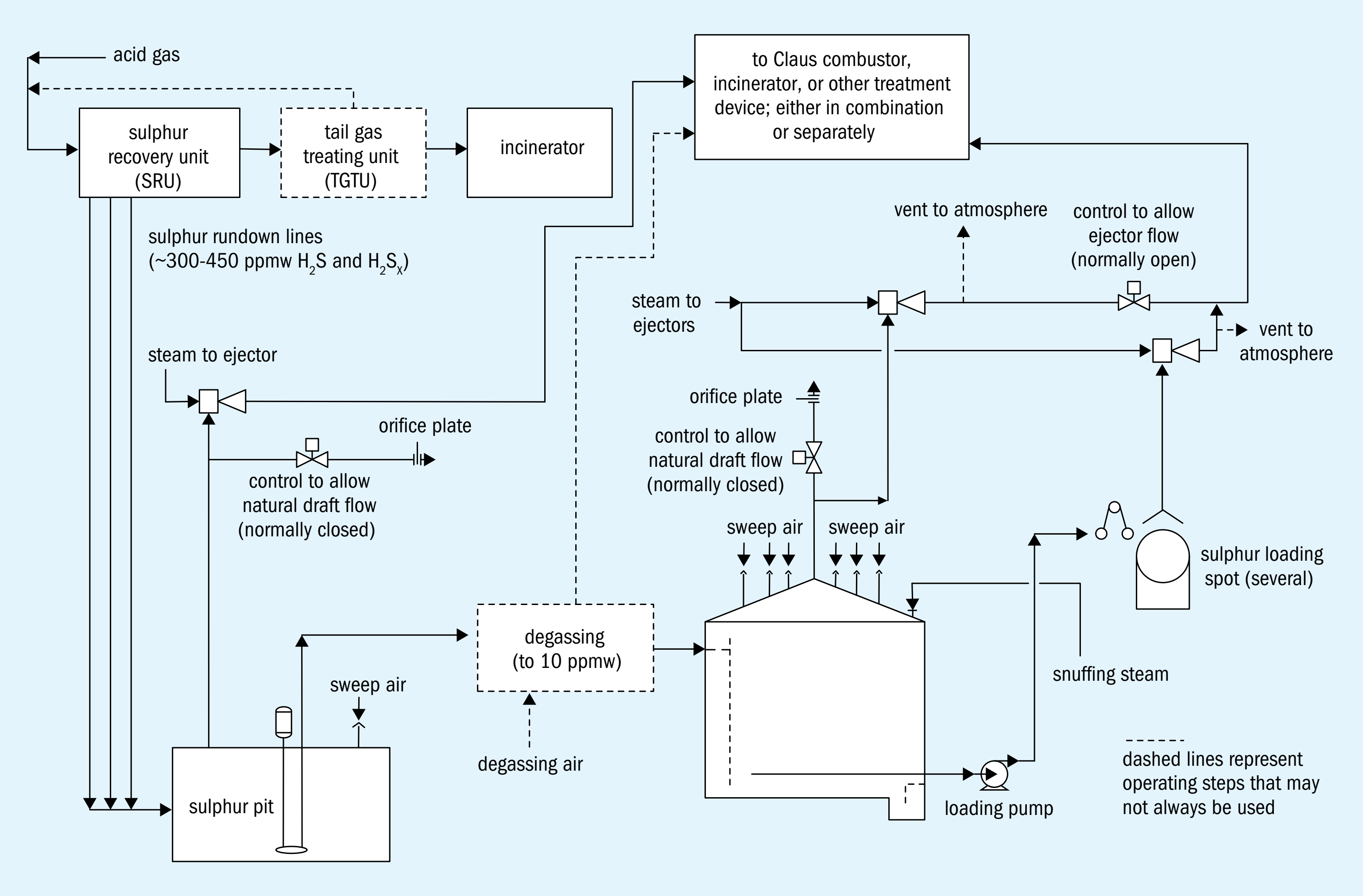
Preventing explosions in molten sulphur tanks

Undegassed molten sulphur can contain several hundred ppmw H_2S. If the headspace in the storage tank is stagnant, the H_2S can accumulate in the vapour space above undegassed liquid sulphur to dangerous levels. Sweeping and blanketing systems are commonly applied to manage the explosion risk in the headspace of molten sulphur storage tanks. **D. J. Sachde**, **C. M. Beitler**, **K. E. McIntush**, and **K. S. Fisher** of Trimeric Corporation review these approaches, outlining the benefits and limitations, design considerations, and industry experience/guidance for each approach. Calculation methods for natural draft flow of sweep air are also presented.

Molten sulphur is commonly stored in tanks in petroleum refineries, other oil and gas facilities, and at locations involved in sulphur processing, handling, storage, and loading. Hydrogen sulphide (H_2S) is a byproduct of processing natural gas and refining crude oils. Environmental regulations often require that the H_2S be treated before emitting gases to the atmosphere. A modified Claus sulphur recovery unit (Claus SRU) is one common treatment method and involves converting the H_2S to elemental sulphur. The molten sulphur produced in a Claus SRU is stored and handled in a number of steps as depicted in the example in Fig. 1.

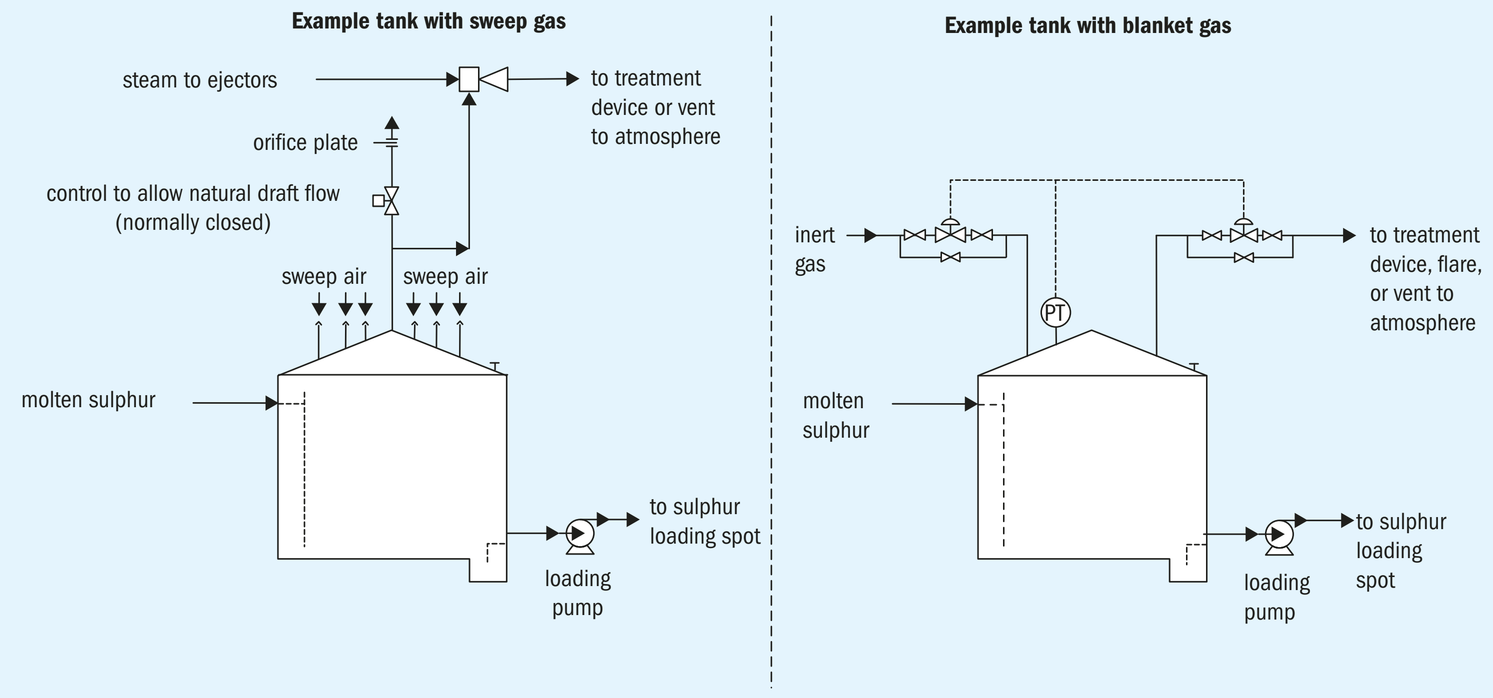
The molten sulphur produced in the Claus SRU contains soluble H_2S and hydrogen polysulphides (H_2S_x). During the storage of the sulphur, the H_2S_x compounds decompose to elemental

Fig. 1: **Molten suphur storage and handling system with tank sweep gas at suphur production site**



Source: Trimeric

Fig. 2: **Example molten sulphur tank configurations with sweep air and inert gas blanket**



Source: Trimeric

sulphur and H_2S as the sulphur cools and is agitated. This results in the formation of dissolved H_2S in the liquid sulphur that will desorb into the gas phase. The molten sulphur flowing into the pit from a Claus SRU is often assumed to contain 300 ppmw[1,2,3] H_2S and H_2S_X, although oxygen enrichment and subdewpoint operation can produce higher levels, e.g. 450 ppmw[4].

Sulphur degassing technology can reduce the H_2S in the sulphur to 10 ppmw or lower. Even if the molten sulphur is not purposefully degassed, some H_2S will evolve (50% has been reported[2]) from the pit depending on the operating conditions. The molten sulphur flows to a tank where it is stored until it can be loaded for transport. The H_2S concentrations in the tank headspace above undegassed sulphur could reach the tens of volume percent levels[2], posing an explosion and/or significant exposure hazard to personnel. (The OSHA permissible exposure limits[5] for H_2S in the atmosphere are: 10 ppmv, 8-hr TWA, for construction and maritime industries). Even with degassed sulphur (e.g., to 10 ppmw H_2S), dangerous concentrations of H_2S can accumulate in stagnant tank vapour space (hundreds of ppmv to low volume percent levels)[2].

Because of the explosion hazard presented by H_2S, the molten sulphur tank design often includes a method to manage this risk. This article presents an overview of two broad approaches used to prevent molten sulphur tank explosions: sweeping and blanketing. Benefits and limitations of each approach are discussed, along with a review of the types of gases commonly used. Within tank sweeping methods, natural draft ventilation of tanks with air will be considered in detail. Natural draft ventilation utilises the temperature difference between the inside of the tank and ambient conditions outside of the tank to generate flow by natural convection and requires unique considerations for tank design and operation.

Preventing molten sulphur tank explosions

Safe handling of molten sulphur and the associated hydrogen sulphide is critical to prevent explosions in storage tanks. H_2S concentrations can reach or exceed the lower explosive limit (LEL), at which point an explosive gas mixture is present. Explosions appear to have happened with relative frequency, as can be assessed via Internet research and industry publications[18]. To prevent an explosion, two general methods are to add gas to the tank vapour space either as a sweep gas or a blanket gas. Fig. 2 shows a simple schematic of the molten sulphur tank configurations with each method.

Sweep Gas

Sweep gas is often used to dilute the H_2S concentration in the vapour space to a safe margin below the LEL. Different sweep gases have been used including: air, nitrogen, fuel gas, steam, and others (e.g., CO_2). Many molten sulphur storage tanks are swept with air. Ejectors, blowers, or natural draft effects pull air through inlets on the tank roof and out of a vent. The vent gas is emitted to the atmosphere or sent to another process downstream (H_2S removal, recycle to Claus reaction furnace, etc.). Sweeping produces a continuous flow of vent gas, and the tank operates under a slight vacuum. Air is a common sweep gas because:

- Air is readily available and inexpensive to use.
- The presence of oxygen keeps the atmosphere in the tank in an oxidising state, which helps prevent the formation of pyrophoric iron sulphides (FeS) on carbon steel surfaces. Iron sulphide forms in significant amounts under the reducing (without oxygen) conditions found in unvented tanks or tanks swept/blanketed with an inert gas (e.g., nitrogen). Under reducing conditions, iron sulphide is not a hazard and can even serve as a protective layer to prevent corrosion on carbon steel surfaces. However, once formed, iron sulphide poses a safety risk if it is

subsequently exposed to air – for maintenance or cleaning – because the iron sulphide could spontaneously combust in the presence of oxygen, resulting in a sulphur fire or explosion.

- Flammability concerns with air (oxygen) can be mitigated by maintaining a safe margin below LEL and installing monitoring equipment.
- Sweep air can be handled by a number of downstream technologies that treat the H_2S in the vent gas.

Considerations for other sweep gases (e.g., nitrogen, fuel gas, steam) include:

- increased risk of pyrophoric iron sulphide formation;
- if the gas is not available on site, it may need to be produced or purchased, which may not be cost effective for the quantities required in "sweep" mode;
- fuel gas introduces additional combustible material into the tank vapour space;
- downstream treatment technology sensitivity to oxygen (e.g., poisoning of hydrogenation reactor catalyst with tail gas recycle) may favour sweep gases other than air (e.g., nitrogen)[17].

A few sites use steam to sweep molten sulphur tanks. As with inert gas-swept tanks, the tank usually operates at a small positive pressure. Using steam introduces water into the vessel, which with the exclusion of air (oxygen), can lead to the buildup of pyrophoric iron sulphide and potentially severe corrosion. However, if the walls of the tank are kept warm enough, it might be possible to prevent liquid water formation and perhaps reduce corrosion rates. The steam is sometimes vented to the atmosphere, but one variant of this approach condenses the steam exiting the tank. A venturi eductor with liquid water as the motive fluid can be used to condense steam/absorb volatiles including H_2S. The combined effluent from the eductor can be sent to a sour water system, waste water treatment plant, or other waste water system. This provides an alternative disposition route that is not available with the other sweep gases.

Blanket gas

Another method to prevent explosions in sulphur tanks is to blanket the tank with inert gas to limit the oxygen content in the vapour space by preventing air ingress. As shown in Fig. 2, the blanket gas (e.g., nitrogen) is fed to or removed from the tank to maintain a constant pressure as inbreathing or outbreathing occur (primarily via liquid movement). As such, the flow of N_2 in "blanket" mode is intermittent and typically less than the gas requirement in "sweep" mode. The blanketing method may be used if a site does not have the means to handle and/or treat the large continuous sweep gas flow. However, inert gas blanketing can result in a significant amount of H_2S accumulating in the vapour space. This represents an explosion hazard if oxygen were to be subsequently unintentionally introduced to the tank. Inert gas blanketing also results in the formation of pyrophoric iron sulphide, and special procedures for maintenance would be required to prevent auto-ignition when tanks are opened to air. A source of the inert gas is also required. For these reasons, the use of inert gas blanketing to prevent molten sulphur tank explosions is less common.

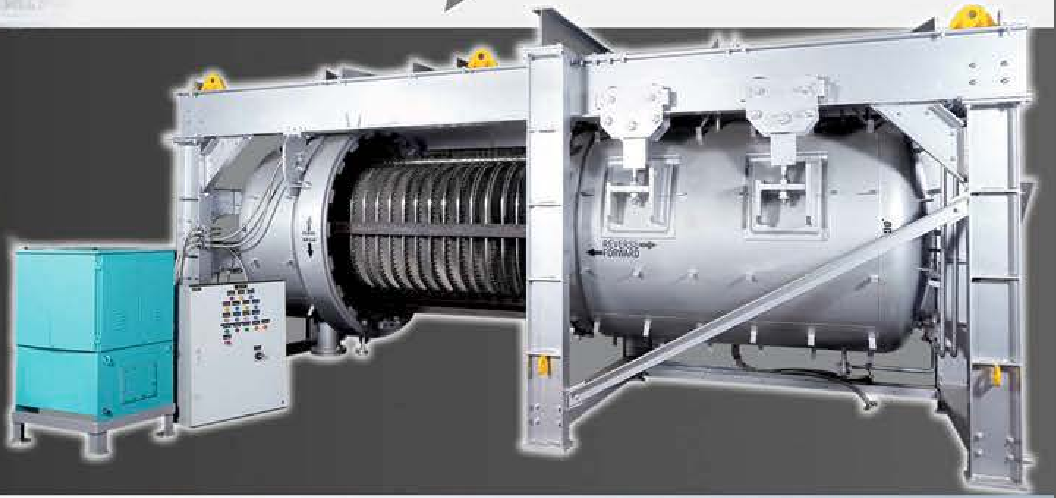
An alternative to inert gas blanketing is to utilise an inert gas with some oxygen in it, such as post-combustion (e.g., exhaust or flue) gas. The gas would need to have sufficient oxygen to prevent pyrophoric iron sulphide formation but not enough oxygen to exceed the limiting oxygen concentration (LOC) for combustion of sulphur. The appropriate oxygen range would need to be determined with a safe margin applied. Instrumentation and gas-phase analytical measurements may be required to ensure proper oxygen levels. Exhaust gas, however, has been reported privately to Trimeric to have been successfully implemented in a molten sulphur tank. Blanketing with exhaust gas is also documented to have been practiced in the transportation industry for various cargos[19,20]. Further, other cases have been identified where inert gas with some oxygen has been used for similar purposes in sulphur recovery units and other equipment where pyrophoric iron sulphide is a risk[8,23].

A summary table comparing the sweep and blanket gas options is presented in Table 1. The selection of sweeping or blanketing and the type of gas used is site specific. Many factors need to be considered including: i) the sulphur load and associated volume of gas needed; ii) whether the downstream H_2S treatment technology can handle sweep gas and H_2S levels, iii) the availability/cost of the gas; and iv) the site risk tolerance and degree of safety measurements in place to control issues with pyrophoric iron

Table 1: **Molten sulphur tank sweep and blanket gas summary**

	Air	**Inert**	**Inert with oxygen**
Tank use	Sweep	Sweep and blanket	Sweep and blanket
Flammability	Introduces oxygen, creates risk for ignition.	No air present.	Introduces oxygen at low level (below the LOC).
Explosion risk	Maintaining adequate sweep air (H_2S < 25% of LEL) mitigates risk.	FeS formation in reducing environment. **Pyrophoric material increases risk if air enters vessel.**	Maintaining adequate oxygen concentration can limit or eliminate FeS/pyrophoric accumulation.
Tank pressure	Operates at slight vacuum. Limit H_2S venting.	Cannot be exposed to ambient air, thus operates under slight positive pressure.	Operates under slight positive pressure, if appropriate, to prevent oxygen from approaching the LOC.
Cost	Readily available. Some cost may be required for heating.	Tie into existing system or add new source of inert gas.	Tie into existing system (e.g., flue/exhaust gas) or add new source of inert gas, both with appropriate oxygen content.

Source: Trimeric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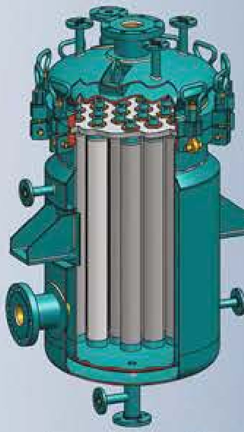

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sulphide and hazardous tank vapour space environments.

Sweep gas and blanket gas are used to prevent explosions in molten sulphur tanks. Both approaches can be designed successfully, but sweeping with air appears to currently be considered best practice in some industries, such as petroleum refining. Given the common use of sweep air with molten sulphur tanks, the remainder of this article focuses on design considerations for sweep air systems. Additional details are available in the literature[21].

Designing for sweep air flow

Designing for sweep air flow requires estimation of the tank headspace composition to:

- define the sweep air requirement;
- determine impact/risks of vent gas properties on sweep air system design (e.g., plugging via sulphur vapour); and
- Identify risks to personnel or impacts on downstream treatment/disposition options.

The following discussion covers methods to estimate vent gas composition and sweep air flow and applies regardless of the sweep air motive method (natural draft or blower/ejector).

Typical sulphur species and estimation methods

The amount of H_2S that evolves from the molten sulphur into the tank vapour space can be estimated from i) measured H_2S and H_2S_X concentration in the molten sulphur and ii) the liquid sulphur flow rate. There are different locations in the molten sulphur storage and handling process where these measurements can be taken. For example, the molten sulphur may be sampled for H_2S and H_2S_X in the rundown lines to the pit, in the pit, in the tank, and/or at the loading stations. These measurements can be used to estimate the H_2S that evolves from the molten sulphur into the storage tank headspace. It may be possible to use only the pit molten sulphur H_2S measurement and assume some conservative percentage (e.g., 100% or other) evolves in the storage tank. An even more conservative approach is to assume all the H_2S present in the initial rundown (e.g., 300+ ppmw) sulphur evolves at each point in the process[2].

Different values for the molten sulphur flow rate can also be used. The nominal/nameplate capacity of the SRU can be used, or the pump design rate or actual flow rate can be used, depending on the operating conditions of the specific facility and level of conservatism desired.

When making estimates of H_2S evolution, all layers of conservatism should be considered together to understand the impact on the design including:

- H_2S_X compounds: Reported total H_2S in the liquid phase consists of both dissolved H_2S and H_2S_X. H_2S_X is relatively slow to convert to H_2S, so assuming that the total concentration of both compounds will evolve as H_2S is a conservative overestimation;
- Total H_2S evolution: It is unlikely that all of the H_2S entering the tank will evolve in the tank;
- Rate of H_2S evolution: The sulphur entering the tank does not degas instantaneously, in part because the sulphur in many tank designs enters through a down-pipe near the bottom of the tank and mixes with the rest of the sulphur in the tank, which limits the rate at which the sulphur can degas; and
- LEL values: The LEL for H_2S is often estimated at conservative temperatures that result in conservatively high amounts of sweep gas being used in the tank.

Since a variety of approaches have been reported in the literature for estimating H_2S evolution, the appropriate assumptions need to be rationalised for each storage tank design.

Various literature sources provide vapour-phase analytical data that can be used to estimate the SO_2, COS, and CS_2 in the molten sulphur vapour vent streams[3,6,7,10]. The literature data show significant variability, and their suitability for estimating the vent gas composition should be reviewed for the particular conditions of the tank design.

The amount of elemental sulphur vapour in the vent gas can be estimated by assuming the gas is saturated with elemental sulphur at the temperature of the molten sulphur and pressure of the vent stream. Vapour pressure information is available in the literature for elemental sulphur[11].

Finally, sulphur mist may be present in the vent gas. There is limited data available on the levels of expected sulphur mist in these systems[10]. The amount of sulphur mist in the vent stream may vary significantly and is impacted by the air sweep rate, molten sulphur temperature, presence of any sources of agitation, steam coil leaks, etc. Care and experience is necessary to arrive at a reasonable value for sulphur mist.

Sweep gas flow requirement

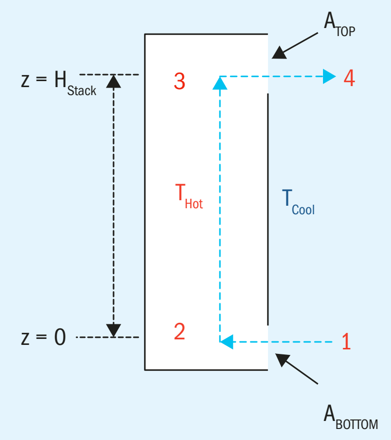
Using 25% of the LEL is a common industry practice for calculating the sweep air flow rate and is recommended in various literature sources; values as low as 15%[8] and as high as 35%[9] as an upper limit to stop operation have also been reported. The LEL for H_2S is sometimes assumed for a conservatively high temperature, because a conservatively high temperature gives a conservatively lower LEL for H_2S and thus a higher sweep rate. A temperature of 330°F (166°C) is a conservative design choice when determining the required air rate and it is warmer than a tank would normally be operated, due to concerns with increasing sulphur viscosity at high temperature and increased fire risks. At this temperature, the LEL is 3 vol-%[22], so 25% of the LEL for H_2S is 0.75 vol-%. It should be noted that there is a chemical reaction in the elemental sulphur which consumes the H_2S and forms H_2S_X that is favoured at higher temperatures (within a range), and this reaction would limit the mass transfer of H_2S into the gas[12]; however, higher temperature is more conservative for LEL and sweep air estimation.

The remainder of the article focuses on the natural draft ventilation design as this approach requires several unique design considerations not common to other motive methods.

Fundamentals of natural draft flow for tank ventilation

The air sweep rate needed to maintain no more than 25% of LEL for H_2S serves as the basis to design a tank for natural draft air flow. Natural draft flow utilises the inherent temperature difference between i) the vapours in the molten sulphur tank headspace and ii) the ambient conditions outside of the tank to create a natural air flow pattern to sweep the headspace of the tank. Since natural draft flow does not rely on a blower/ejector to move the air, it is considered the most reliable source of sweep air. However, the sweep air rate will vary with ambient conditions and operating conditions of the tank, so it is critical to design the tank to ensure that sufficient natural draft flow occurs at all relevant conditions the tank will experience. The following sections describe the

Fig. 3: **Natural draft flow or stack effect**



Source: Trimeric

fundamentals of natural draft air flow and the important design and operating parameters that impact the air sweep rate.

Theory of natural draft flow

Natural draft air flow is sometimes described as the "stack effect" or "chimney effect" referring to the buoyancy-driven flow that occurs in a flue gas stack or chimney. The principles governing flow in these systems are the same as those in the natural draft flow in a tank and can serve as the basis to develop a simplified model and equations used to calculate draft flow in a tank. A "stack" model is depicted in Fig. 3.

Fig. 3 includes a proposed path for air flow – the air flow path is depicted as flowing from station 1 where ambient air enters the stack, warms up and rises in the stack, exits the stack to station 4. In addition, a mechanical energy or pressure balance (i.e., Bernoulli equation) can be written for the path from station 1 to station 4.

Point 1 and 2

The pressure difference across the air inlet at the bottom of the stack represents the frictional losses due to gas entry and should represent the specific inlet device (e.g., orifice, nozzle, etc.). Equation 1 represents the pressure difference across the entry (after simplification) and uses a discharge coefficient to account for frictional losses. Alternatively, fitting or loss coefficients could be used to evaluate frictional losses. The use of a single discharge coefficient for the inlet (and the outlet in the following equations) implies that the discharge coefficient is accounting for all frictional losses at these points (e.g., orifice at the inlet). If a unique design includes additional fittings or a unique design, the discharge coefficient may need to be modified accordingly.

$$P_1 - P_2 = \frac{1}{C^2_{D,BOTTOM}} \frac{\dot{m}_{BOTTOM}^{\;2}}{2\rho_{Cold} A^2_{D,BOTTOM}} \qquad (1)$$

Where:

C_D = Discharge Coefficient;

$\dot{m}_{BOTTOM}$ = Mass flow rate through the bottom stack opening;

ρ_{Cold} = Mass density of "cold" or ambient air;

A_{BOTTOM} = Cross-sectional area of bottom stack opening.

Point 2 and 3

The pressure difference between points 2 and 3 represents the weight of the column of hot air in the stack between the points (hydrostatic head). Equation 2 is a simple hydrostatic equation that is used to estimate the pressure difference based on the hydrostatic head between these points:

$$P_2 - P_3 = \rho_{Hot} g H_{Stack} \qquad (2)$$

Where:

H_{Stack} = Stack height = (Height of the top stack gas opening) – (Height of the bottom stack gas opening) (reference height).

g = Gravitational acceleration (in appropriate units).

Point 3 and 4

The pressure difference from points 3 to 4 represents frictional losses at the exit of the stack and can be represented by Equation 3 (analogous to Equation 1 at the entry):

$$P_3 - P_4 = \frac{1}{C^2_{D,TOP}} \frac{\dot{m}_{TOP}^{\;2}}{2\rho_{Hot} A^2_{TOP}} \qquad (3)$$

Where:

$\dot{m}_{TOP}$ = Mass flow rate through the top stack opening;

ρ_{Hot} = Mass density of "hot" exiting air;

A_{TOP} = Cross-sectional area of top stack opening.

Point 4 and 1

The pressure difference between points 4 and 1 represents the weight of the column of cold air outside of the stack between the points. Equation 4 is a simple hydrostatic equation that is used to estimate the pressure difference based on the hydrostatic head between these points:

$$P_1 - P_4 = \rho_{Cold} g H_{Stack} \qquad (4)$$

Deriving the mass flow rate of natural draft circulation

The driving force for the circulation of the air is the difference in the hydrostatic head inside of the stack versus outside of the stack (Equations 2 and 4). The weight of the column of hot air in the stack is less than that of the equivalent height of cold air outside of the stack due to the difference in density of the two columns of air. Therefore, a new expression can be written to quantify this driving force for flow by subtracting Equation 2 from Equation 4:

$$(P_1 - P_4) - (P_2 - P_3) = \rho_{Cold} g H_{Stack} - \rho_{Hot} g H_{Stack} \qquad (5)$$

Equation 5 relates the pressure driving force for the flow to the density difference of the two columns of air. Equation 5 can be re-arranged to a more convenient form:

$$(P_1 - P_2) + (P_3 - P_4) = (\rho_{Cold} - \rho_{Hot}) g H_{Stack} \qquad (6)$$

The left hand side of Equation 6 now represents the pressure difference across the openings where the gas flows into and out of the stack. Equations 1 and 3, respectively, can be substituted into this equation to relate the mass flow rate of the air to the hydrostatic pressure difference. After substitution and rearrangement (with $\dot{m}_{BOTTOM} = \dot{m}_{TOP}$ for simplicity), the natural draft mass flow rate can be determined from Equation 7:

$$\dot{m} = \sqrt{\frac{2(\rho_{Cold} - \rho_{Hot}) g H_{Stack}}{\left(\frac{1}{\rho_{Hot} C^2_{D.TOP} A^2_{TOP}} + \frac{1}{\rho_{Hot} C^2_{D.BOTTOM} A^2_{BOTTOM}}\right)}} \qquad (7)$$

The mass flow rate of natural draft circulation is related to the height of the stack, density difference between the gas inside and outside of the column, and the size/frictional losses of the opening of the stack (ignoring skin friction losses). This simplified model (and associated derivation) will serve as the basis for natural draft flow in a molten sulphur tank.

Stack model for molten sulphur tank vent

As the discussion of the stack effect illustrates, if a height difference is provided between the point of air ingress (cooler air) and the point of air egress (warmer air) for a molten sulphur tank, a density-based pressure difference (or buoyant force) will exist and will move air through the "stack". In this case, the headspace of the tank and a central stack vent on the tank (described in the following sections) represent the "stack"

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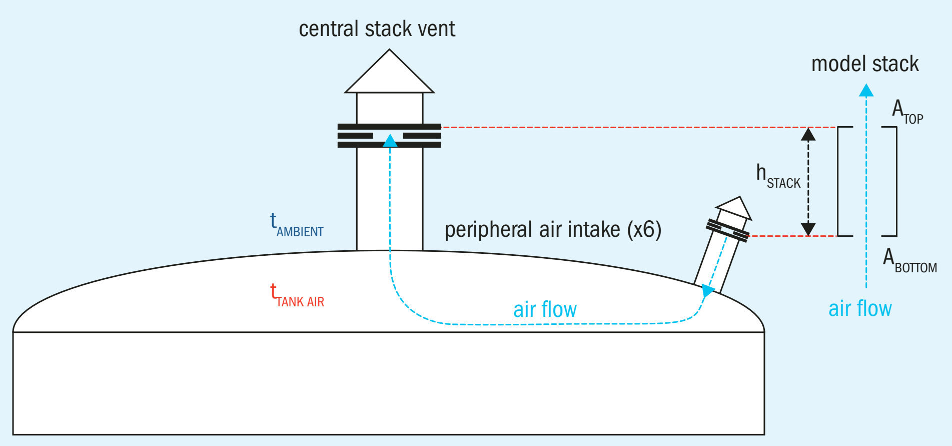
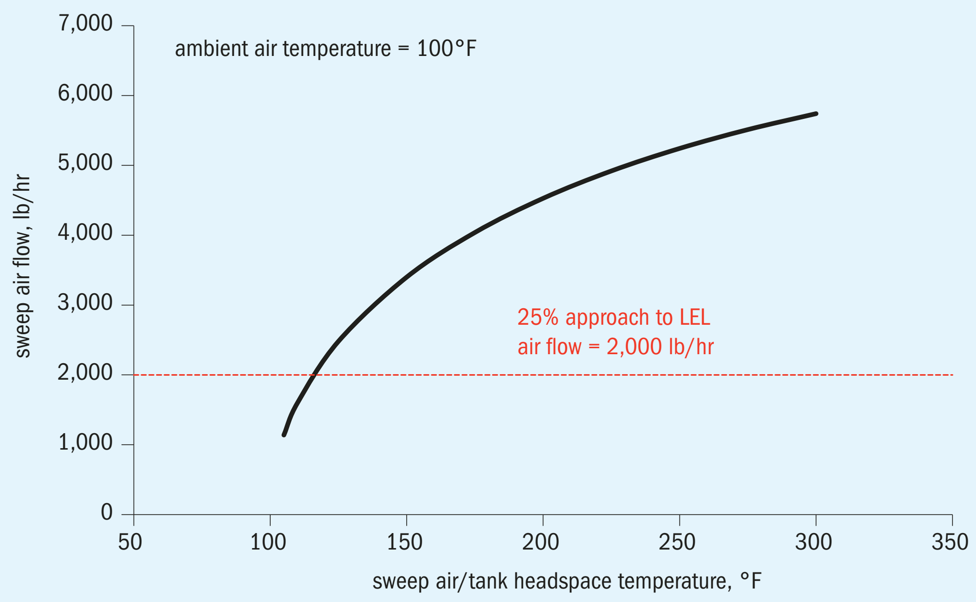
Fig. 4: **Modelling natural draft air flow in a molten sulphur tank headspace**



Source: Trimeric

Fig. 5: **Impact of tank headspace temperature on sweep air flow rate**



Source: Trimeric

for the air flow. Based on this description, a simplified model can be developed to represent the tank stack-effect flow, as represented by Fig. 4.

The total height of the stack includes the vertical distance from the inlets of the peripheral air intakes to the top of the central stack.

For design calculations, the air sweep flow rate required to maintain the tank headspace H_2S concentration below 25% of LEL (or other safe level) can be used to size the air intake and central stack vent via Equation 7. Some key assumptions and information for the calculation include:

- the temperature of the molten sulphur tank;
- the temperature distribution of the air in the headspace above the molten sulphur;
- pressure losses (frictional losses) into and out of the tank and losses to be considered along the flow path;
- the molecular weight of the air coming into the tank and the vapour leaving the tank;
- the atmospheric temperature and pressure for relevant design conditions.

The density of the ambient air and tank vapour are a function of the respective temperature and molecular weight of each gas, so accurate representation of the temperature and composition of the gas is critical to the design of a tank with natural draft circulation.

Equation 1 can be used to evaluate the pressure drop across the air inlets. This is an important aspect of the design of the molten sulphur tank as it should operate at a slight vacuum condition at the air inlet to prevent reverse flow through the air inlets[13]. The vacuum requirement provides a further constraint to limit the variables that must be considered when designing the tank ventilation.

Sensitivity analyses and other considerations

It is critical to understand the impact of the operating conditions and assumptions on the natural draft flow performance of the tank. Fig. 5 illustrates the impact of the tank headspace temperature on the sweep air flow rate.

The sweep air flow varies strongly with the tank headspace temperature. The tank headspace temperature, in turn, may be impacted by many other variables: the molten sulphur temperature in the tank, heat transfer rates to/from the vapour in the headspace, the turbulence/mixing in the tank headspace, conditions of the ambient air sweeping the headspace, etc. The problem may be further complicated by the fact that the air sweep rate itself may impact the tank headspace temperature, leading to a complex relationship between the temperature in the tank and the headspace temperature that provides the driving force for natural draft flow.

Also, the ambient conditions for a molten sulphur tank may vary widely across the seasons. As Equation 7 indicates, the density of the ambient air impacts the natural draft flow through the tank. The limiting condition for natural draft flow (lowest natural draft flow) is the highest ambient temperature experienced by the tank (e.g., maximum summertime temperature). This will produce the lowest driving force for natural draft flow (all other conditions fixed). The minimum ambient temperature condition leads to the largest natural draft flow rate that the tank will experience and is important for the design of the tank heating system (e.g., steam coils, external tank heating system, etc.). This condition sets the maximum heat loss for the tank and is the basis for sizing tank heating elements. Therefore, both scenarios must be evaluated during the design of the tank. Table 2 illustrates the 99.6% high and 0.4% low dry bulb temperatures for a generic site and the corresponding sweep air rates for a specific molten sulphur tank.

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Table 2: Impact of seasonal ambient temperature variation on sweep air rate under natural draft flow conditions (all other conditions identical)

	Temperature (°F)	Sweep air flow (lb/hr)
99.6% Annual high (dry bulb)[14]	100.4	1,960
0.4% Annual low (dry bulb)[14]	19.9	3,600

Source: Trimeric

As Table 2 illustrates, the air sweep rate increases by more than 80% going from high to low ambient temperature. The natural draft system is designed to provide adequate air flow at summer conditions to meet LEL requirements and, as a result, the tank heating vendor is constrained by the large winter flow generated by the same vent system.

Other parameters and conditions may impact the natural draft design or operation. Examples include the following:

- composition of the vent gas (impacts molecular weight and density);
- wind effects (flow reversal through inlets);
- short-circuiting of air flow (flow leaves via an adjacent inlet);
- plugging risks for inlet and vent nozzles; and
- sizing of inlets and vents for tank overpressure/vacuum considerations[9,15,16,21] (e.g., snuffing or sealing steam venting).

Systems with ejectors or blowers will have their own special considerations during the design process.

Summary

This article summarised approaches for preventing explosions in molten sulphur tanks through use of sweep gas or blanket gas. Air-based tank sweep systems that manage the H_2S concentration in the headspace (as opposed to excluding air/oxygen) are often favoured over inert-blanketed tanks from a safety standpoint, although both approaches can be successful with a careful design. The principles of natural draft air flow in molten sulphur storage tanks were reviewed. Natural draft flow through the tank is based on the temperature-induced density differences between the cold ambient air and the hot tank vapours, creating a natural circulation through the tank headspace. Design of the air intake and outlet stack vents can be achieved by a mechanical energy balance around this system. The natural draft design is sensitive to seasonal/daily variations in ambient conditions, vent gas composition, wind effects, tank-inbreathing and outbreathing, and other tank design choices and operating conditions which necessitate careful consideration for each tank design. ■

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