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Indonesia's smelter boom Sulphur market trends SRU start-up and shutdown Acid plant design challenges

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### **BCInsight**

May | June 2020



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Cover: Maintenance worker at a sulphuric acid plant, Kazakhstan. Image: Alexey Rezvykh/ Shutterstock.com



#### **Indonesian acid**

More production and consumption from domestic metals processing.



#### Acid plant design Challenges in building the highest

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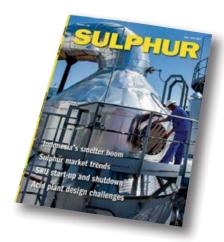
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# New realities

rdinarily I try to choose a different subject each issue for an editorial, but as April lengthens towards May, and here in the northern hemisphere we start to see the first signs of summer, there unfortunately remains only one subject that is obsessing every industry, and that is the Covid-19 pandemic and its impact upon every aspect of our lives. Since our last issue we have all had to come to terms with 'lockdown' and 'social distancing', as the grim toll of deaths climbs in all regions. Here at BCInsight we are working without an office as best we can, and issues of Sulphur will continue to land in your email inboxes, but paper copies of the magazines may take longer to arrive, if at all, as shipping and customs procedures are tightened all around the world, and I can only apologise and ask that you bear with us.

In the meantime, industry conferences are a thing of the past; regular meets such as SOGAT and TSI's World Sulphur Symposium are postponed to 2021, and it is anyone's guess when we will be able to see each other face to face again rather than via a webcam. However, in the two months since our last issue, there are at last some encouraging signs. China's draconian response to the virus seems to have worked, and restrictions are gradually being lifted there. There is a similar story in New Zealand and some parts of Europe. Other parts of the world, however, including the UK where I am writing, and especially the US, remain deeply in the grip of the pandemic. But without a vaccine, which we are told remains 12-18 months away, the potential for more flare-ups and secondary outbreaks remains a very real one, as Singapore discovered only recently. Some measure of social and economic restriction looks set to be with us for months to come.

In the sulphur industry, the main impact so far seems to have been on the refining sector. Air travel is at a virtual standstill, cruise liners are berthed, the mileage being driven by people in lockdown is greatly reduced, and oil tankers are being used to store excess crude. Even though Russia and Saudi Arabia have patched up their dispute, and the US has agreed to coordinate production cuts, oil



demand is down by about 30% compared to 2019. WTI forward prices caused headlines by going negative in April for the first time ever. But looking further forward, investment decisions on large sour gas projects are also being reconsidered. ADNOC's cancellation of its \$1.65 billion Dalma Gas Development Project contracts just two months after awarding them is a sign of where things may go. There could be a large overhang of projects whose timescales are pushed a couple of years further down the line.

Conversely, fertilizer demand seems to be holding up, at least for now, as most countries delineate agriculture as a key industry. Some producers have shut down, especially in India, and supply and labour availability issues will also cause disruption, but a recent report from Fertilizers Canada suggested that 90% of its members had sufficient supply in hand and expected that this season will be normal, if not above average, in terms of fertilizer demand and crop production. This suggests that the forecast sulphur surplus may not materialise after all this year, and we may even see a pick up in sulphur prices this year from their historic lows - there are signs that this is already happening. On the other hand, with copper and other smelters also still producing, acid availability is abundant and prices have fallen into negative territory in some supplier nations, no doubt leading to some substitution for sulphur where possible.

For now, the only certainty is for more volatility going forward, and a difficult working environment for all of us. But as the old adage says: "this, too, shall pass". Let's hope it is soon.



Richard Hands. Editor

Some measure of social and economic restriction looks set to be with us for months to come."

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### **Price Trends**

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#### **MARKET INSIGHT**

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

#### **SULPHUR**

Uncertainty continues to confound the global sulphur market due to the Covid-19 pandemic, with the potential for further downward pressure during this unprecedented and challenging time. The macroeconomic picture is bleak with the exogeneous shock of the global pandemic causing unprecedented shifts in the global commodity markets.

Middle East producers all increased monthly prices for April, on the back of tighter availability and the firmer footing seen in the market since February. The trend is not expected to continue however, with the wider market fundamentals expected to weigh on the short term outlook. In Kuwait, KPC set its April price at \$61/t f.o.b. Shuaiba, a \$14/t increase on a month earlier. State owned Muntajat announced its April Qatar Sulphur Price (QSP) at \$64/t f.o.b., representing a \$21/t increase. The marketer is not expected to have any spot availability for the month of May due to ongoing tightness, following several months of tight supply, with the last offer of spot from Muntajat not since September 2019 Over in the UAE ADNOC does not expect to have spot volumes for the remainder of the quarter, with volumes allocated to contractual customers.

Projects in the Middle East are expected to increase capacity and availability in 2020-2021, although the global pandemic does raise significant questions around new project start up timelines. Some of the most imminent and significant projects in the short term include KNPC's Clean Fuels Project (CFP), the Barzan project in Qatar and Saudi Arabia's Al Fadhili gas project. Combined these three projects will add 4.5 million tonnes of sulphur capacity but uncertainty remains around whether there will be any potential delays to planned start dates. However, KNPC's CFP has seen progress, with three sulphur related units starting up at the Al-Ahmadi refinery. No delays to start up have been announced thus far with estimates of a 04 2020 start up.

Before the coronavirus situation unfolded, total global capacity was expected to rise by close to 4 million t/a in 2020, but how much of this volume will materialise remains

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unclear. The recent crash in oil prices has led to downward revisions in expected oil production, with the potential to lead to drops in sulphur supply in those regions dominated by sulphur recovery from this sector. Projects further out in the timeline that are considered speculative are expected to remain delayed - with several projects at just under 1 million t/a of capacity in this category.

Over in Jordan, JPMC completed a maintenance which had been extended through to the middle of April on the back of the coronavirus outbreak. The end user was in the spot market but is now expected to return to the market when it requires volumes for the second half of 2020. The buyer's demand for the first half of the year was covered via a long term tender at the end of 2019. A 45,000 tonne cargo is due to arrive at the start of May from Qatar.

Canadian oil operations are vulnerable however due to the some of the highest breakeven prices. There has yet to be any major impact reported at Canadian sulphur operations on the back of the low oil prices, with Vancouver sulphur exports continuing. The five major Canadian oil producers announced cuts to 2020 capex budgets. Suncor is to reduce output at its 194,000 bbl/day Fort Hills bitumen venture. In total, Canadian production is estimated to drop by 500,000 bbl/day in 2020. Sulphur production in Canada is forecast to drop in the outlook regardless of any short term changes at oil sands and the refining sector. Production was estimated at over 6 million tonnes in 2010 and is estimated to have dropped below 5 million tonnes in 2019 due to the overwhelming decline of gas-based supply. This trend is set to continue, with the potential to influence export potential in the outlook.

The US market is expected to remain tight during this period on the back of falling refinery run cuts as demand for refined products is low. Some unconfirmed estimates put sulphur losses at 15-20% but this remains to be seen. Sulphur output was already low throughout 2019 versus 2018 as the crude slate changed, on the back of Venezuelan sanctions and the IMO 2020 specifications. Planned turnarounds at refineries in the US that were to take place over the second quarter have been cancelled, potentially aiding in tempering the tightness.

Any shortages in supply in the local market may be met by increased imports - assuming demand remains stable. Another factor may be sulphuric acid pricing, with attractive prices versus sulphur leading to interest in acid procurement.

The Chinese market has become increasingly bearish following the lifting of lockdowns in the country. Sulphur prices have dropped down from the mid-\$80s/t c.fr at the end of March by around \$10/t to the mid-\$70s/c.fr at the start of April. High sulphur inventories at the major ports in China had started to see some erosion but levels have climbed once again, edging up back towards the 3 million tonne mark. Many buyers remain covered for the short term with stocks at plants also healthy, potentially stemming short term demand for additional volumes. Prices in the local market have been softening, driven by ample inventories and weak domestic demand. In January-February 2020 Chinese sulphur imports totalled 1.58 million tonnes, down 22% on a year earlier. This decrease had been expected due to high inventories, reduced demand from processed phosphates operations and plant closures during the coronavirus outbreak.

Indian market sentiment has also suffered against the backdrop of its lockdown, with an extension until 3rd May at the time of writing adding to the pressure. At the start of the initial lockdown, fertilizer producers shut down, considerably reducing sulphur demand. Subsequently the government announced some restriction relaxations from 20th April including for the agricultural sector, adding a glimmer of hope for the market. End user IFFCO made enquiries for a first half May shipment. In the month of January, sulphur imports totalled 144,000 tonnes, around 8% up on the same month a year earlier.

#### SULPHURIC ACID

Global sulphuric acid export prices have dropped into negative territory - NW European f.o.b. levels have tracked below zero following several weeks of negative netbacks from Asia. Delivered prices for spot volumes in Asia dropped below zero in mid-April, a level not previously breached on a c.fr basis - reflecting the unprecedented shock of the global Covid-19 pandemic. Uncertainty prevails throughout the market over how long price weakness will remain, with little clarity on how and when lockdowns across the globe will be lifted. Contract business appears to be continuing as

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normal for the most part, despite the current situation. The attractive sulphuric acid pricing in relation to much higher relative sulphur prices has led to increased interest in merchant acid purchases. However, ongoing question marks over end user demand rates are expected to weigh on the potential for price stability or recovery.

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In key market Chile, spot prices softened in mid-April down to \$20-30/t c.fr, from the mid-\$30s-low-\$40s/t c.fr. High tank inventories were deemed the pressure point for the reductions. Miner BHP anticipates its Chilean copper facilities to see a 30% reduction in its workforce during the quarter to June. Copper output guidance for Escondida and Pampa Norte remained unchanged. Chile imported around 450,000 tonnes of acid from sources outside of Peru in the first guarter of the year. This is dramatically below the 860,000 tonnes imported a year earlier. However 2019 saw a spate of domestic smelter maintenances in the country leading to exceptionally high import demand. Peruvian supply to Chile is estimated at around 100,000 tonnes/month on average.

Brazilian spot prices for acid have also deteriorated down to \$23-29/t c.fr in mid-April with demand remaining slow. Planned fertilizer plant turnarounds put further downward pressure on import demand with reduced consumption estimated from the chemicals sector. The leading domestic producer in Brazil was heard operating smelters at regular rates in mid/end April.

In NW Europe, export prices fell down to minus 18/t f.o.b. in mid-April on the back

of sales to the Americas. There has been a divide between West and East pricing in the market with European levels maintaining higher levels versus Northeast Asian trade from China, Japan and South Korea. However the extreme level of the negative netbacks in Asia led to opportunities for end users typically supplied by European sources. Muted demand also led to the reductions in European export prices. On the contract front, second quarter European business settled down on the first quarter, with €2-3/t reductions confirmed by suppliers. Italian producer Nuova Solmine pushed back its planned maintenance at its Scarlino facility by a month to early June, due to run for around a month. The producer was heard operating at reduced rates, with some industrial users under lockdown orders in the country, impacting end user demand.

South Korean and Japanese export price levels dropped down as low as minus \$45/t f.o.b. in mid-April on the back of market weakness. Some slight easing was heard towards the end of April, with some confidence as May shipments had been booked, and cargoes for the June-July period under consideration. Some demand from Indian buyers also aided in the sentiment. Chinese spot prices have faced significant pressure and producers started to show less acceptance of the dramatic negative netbacks at the end of April. Some improvement was seen in the domestic market, providing hope at the end of the lockdowns in the country. with prices within the country ticking up in Hunan, Guaangxi and Guizhou. Chinese output from smelters is forecast to rise in the outlook with significant investment in the smelting sector. However the recent turn of events does put some project timelines in question or at risk.

Japanese sulphuric acid exports totalled 536,000 tonnes in Jan-Feb 2020, up from 484,000 tonnes a year earlier. The leading market was the Philippines at 192,000 tonnes. South Korean trade during the period totalled 533,000 tonnes, up from 469,000 tonnes the year below. Chile was the leading market followed by India, with China ranking third.

North African sulphuric acid prices were assessed at \$5-8/t c.fr in mid/end April. Major importer OCP in Morocco is due to receive several Asian cargoes in May-June comprising both sulphur-based and smelter acid. Lockdown measures in India led to a reduction in OCP's phosphoric acid shipments to the country as a result of reduced operations at processed phosphates plants.

While there is expected to be some delays to new projects in the sulphuric acid sector as a result of the shock to markets of the coronavirus with its impact still unfolding, there has been some project news in the US. Miner Freeport-McMoRan (FCX) is to complete its remaining \$100 million investment in its Lone Star, Arizona copper leaching project with the status of progress at 90% completion. Initial production is expected during the second half of the year, which would support sulphuric acid demand, due to largely be sourced from the company's own output.

### **Price Indications**

	Table 1: Recent sulphur prices, major markets
	Table 1. Necent Sulphur prices, major markets

Cash equivalent	November	December	January	February	March			
Sulphur, bulk (\$/t)								
Adnoc monthly contract	42	42	44	42	42			
China c.fr spot	72	64	64	64	71			
Liquid sulphur (\$/t)								
Tampa f.o.b. contract	46	41	36	36	54			
NW Europe c.fr	80	70	70	70	84			
Sulphuric acid (\$/t)								
US Gulf spot	75	75	74	60	45			
Source: various								

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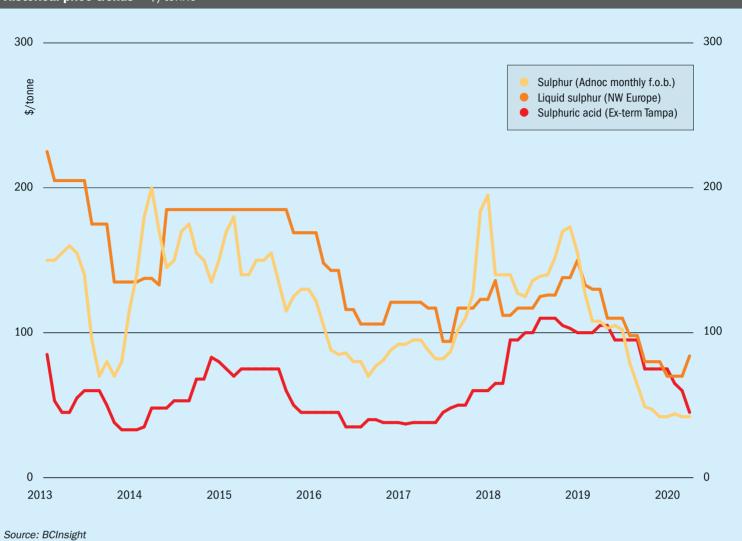
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### **Market Outlook**

Historical price trends \$/tonne



#### SULPHUR

- How the macro market responds to the coronavirus pandemic over the months ahead and governmental response in different parts of the globe will likely have a lasting impact on the outlook for the sulphur market.
- The start-up of any new projects in the refining or gas sector may prove critical during a potentially tight period in the market. All eyes will be on developments in the Middle East as large scale projects may start up towards the end of the year in Kuwait and Qatar.
- Freight rates has provided some limited relief to the market due to the flat to soft trend – bunker fuel prices and length in availability for dry bulk vessels has contributed to this shift. The view is for delivered sulphur prices to ease and soften in the short term – but the falling freight rates are slowing the equivalent drops in f.o.b. ranges.
- Second quarter prices in North Africa settled at increases, covering significant

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portions of end user requirements. Tunisian consumer GCT has reduced operating rates owing to reduced workforce.

Outlook: Weaker prices are expected in the short term following the recent uptick on the back of regional tightness. Sentiment is bearish due to coronavirus and the uncertainty surrounding end user markets. The oil price will give producers pause as we enter unchartered territory in many commodity markets. Potential tightness from the refining sector hit by the price collapse and high oil inventories may be partly neutralized by increased supply from new projects and reduced sulphur demand from end users. The weakness in the sulphuric acid market means continued opportunities for some buyers to substitute higher priced sulphur for merchant acid.

#### **SULPHURIC ACID**

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 Indian fertilizer production has restarted, supporting demand. Meanwhile the industrial sector is experiencing disruption due to the ongoing shutdowns of plants in industries including detergents and surfactants.

- Australian mining operations are facing disruption as a result of the current situation. BHP has reported lower volumes from its Olympic Dam facility in the nine month period to March due to unplanned downtime at its smelter.
- Rio Tinto has cut its 2020 production guidance for mined and refined copper on the back of expected reduced output from its Escondida mine in Chile and repairs to its Kennecott mine in the US in the aftermath of an earthquake.
- Outlook: While uncertainty prevails market sentiment remains overwhelmingly bearish, despite the slight uplift in prices towards the end of April. Support has come as end users are increasingly seeking merchant acid cargoes during a time when elemental sulphur prices have been rising. However, the bleak macroeconomic picture is weighing on various end user operations and the outlook for acid, at least in the short term, is to potentially see the downward, softer trend remain.

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#### WORLD

### **Oil prices forced negative in spite of OPEC deal**

West Texas Intermediate (WTI) forward oil prices for May dropped into negative territory during mid-April, on fears of lack of storage capacity to deal with the excess production. Forward prices for June were also nosing to equally unprecedentedly low levels. Elsewhere, Brent Crude spot prices dropped to \$20/bbl, a fall of \$50/bbl from the start of 2020.

The price falls came in spite of a deal brokered by president Trump between major oil producers, most notably Russia and Saudi Arabia, to reduce oil production. Russia's refusal to abide by an earlier OPEC quote had led to Saudi Arabia also increasing production, precipitating a price war and the current glut of supply over and above the rapid fall in demand caused by the Covid-19 outbreak. The deal, combined with expected production declines and shut-ins for producers in the US and Canada, aimed to remove up to 14 million bbl/d of oil production during May and June, including 5 million bbl/d in Russia, 5 million bbl/d in Saudi Arabia, and 3.7 million bbl/d in the US, Canada and other countries.

Even so, IHS Markit is forecasting that global oil demand for 2Q 2020 will be down 16.4 million bbl/d on the figure for the same

period of 2019, six times the reduction in 2009 caused by the financial crisis, and that the surplus will soon fill storage capacity around the world. Around 1.2 billion barrels of oil storage capacity was available as of 1Q 2020. Producers have been looking to secure empty oil tankers as emergency floating storage capacity as the crisis continues.

IHS also notes that the US may find it harder to return to full production once the crisis is past, as compared to Saudi Arabia and Russia. It projects that by 4Q 2021 US production will be 8.8 million bbl/d: 4.1 million bbl/d down from 10 2020, while Saudi Arabia is forecast to be 1.8 million bbl/d up at that time, and Russian production only slightly lower than 1Q 2020.

By the end of March, oil companies had announced \$50 billion of capital expenditure cuts. Around \$10 billion of this alone came from Saudi Aramco, with other oil majors like BP and Total cutting spending by 20-25%. Merger and acquisition activity in the US oil and gas industry was down 86% for February compared to the average of the previous 12 months.

#### Virus leads to bunker fuel turmoil

All petrochemical markets have been in turmoil because of the Covid-19 pandemic, but none more so than the market for bunker fuels, already in a transition to the new IMO regulations on low sulphur fuels, which came into force just a few months ago on January 1st. During March the prie spread between 0.5% sulphur very low-sulphur fuel oil (VLSFO) and 3.5% sulphur high-sulphur fuel oil (HSFO) fell from \$150/t to \$75/t. Bunker fuel prices had spiked over December and January to levels around 45% higher than normal because of concerns over availability of VLSFO, but this has been followed by a crash in prices as global shipping shuts down. The tightening in the price spread between HSFO and VLSFO will extend the payback period for exhaust scrubbing systems which have been the main competitor to lower sulphur bunker fuels and is likely to dramatically slow the take-up of such systems, which have also seen delays in manufacture and installation caused by virus-related lockdowns. On the other hand, enforcement of the new MARPOL regulations has also been affected – the UK's Maritime and Coastguard Agency (MCA) was reported as saying: "we have suspended port state control inspections, this also means that the checking of compliant fuel has been suspended.'

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#### **UNITED ARAB EMIRATES**

#### Eni announces review of Middle East projects

Eni says that it is reviewing its projects in the Middle East because of the Covid-19 pandemic and the low prices in the oil market. "We are taking these actions in order to defend our robust balance sheet and the dividend while maintaining the highest standards of safety at work," said Eni CEO Claudio Descalzi. The company is looking to cut capital expenditure in 2020 by \$2.2 billion and in 2021 by \$2.8 billion, the latter representing a cut of 35%." The projects involved are related mainly to upstream activities, particularly production optimisation and new projects developments scheduled to start in the short term," Eni said in a press statement. "In both cases, activities will be restarted as soon as appropriate market conditions appear, and related production will be recovered accordingly.'

Under particular scrutiny are its partnership with the Abu Dhabi National Oil Co (ADNOC), including the massive \$12 billion Hail and Ghasha sour gas field development in Abu Dhabi, where the company has announced a joint review with ADNOC. Eni was awarded a 25% stake in the concession, operated by ADNOC, in 2018. Germany's Wintershall, a subsidiary of chemicals company BASF, has 10% while Austria's OMV has 5%. The Ghasha project is aiming at producing 1 bcf/d of highly sour gas.

However, unlike neighbouring Saudi Aramco, ADNOC has not indicated any reduction in planned capital expenditure for 2020, ADNOC CEO, Sultan Ahmed al-Jaber said: "Our focus on driving performance, profitability and efficiency has made us more resilient, agile and responsive to market dynamics. These guiding principles remain unchanged as we move forward with projects across our value chain."

#### IRAN

#### Work begins on gas sweetening plant

The first phase of a gas sweetening project has been launched at the Maroon Oil and Gas Production Company's (MOGPC) Number 3 complex. The unit is aimed at sweetening sour gas produced at Maroon's Asmari oil and gas field and is being developed by a private local company, according to reports by Iranian news agency SHANA.

Mansour Torkaman Asadi, director of technical affairs at MOGPC, told the agency that the hydrogen sulphide content of the Asmari reservoir meant that collection and processing of gas from the field was not possible due to the corrosion that it caused at the gas plant, and this meant that the gas needed to be flared. The new plant will collect

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and sweeten Asmari gas, as well as gas from the Khami field, in order to prevent environmental pollution and reduce waste.

The first phase of the plant has been designed for the production of 12 million scf/d of sweet gas and its output can be used as a petrochemical feedstock, he said. The second phase of the plant will be launched for production of 3 million scf/d output.

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#### **OMV** agrees spending cuts

Austria's OMV said on Thursday it would cut spending by about 20% this year and had reached a deal to pay for its stake in plastics maker Borealis in stages to free up cash, as the company tries to deal with the Covid-19 outbreak and the associated slump in oil and gas prices. OMV said it will cut its €2.4 billion (\$2.6 billion) spending plan for 2020 by €500 million and reduce costs by €200 million. In addition, investments and acquisitions of €1.5 billion will be postponed to 2022, including the already delayed €1 billion purchase of Siberian gas assets from Gazprom.

#### IRAQ

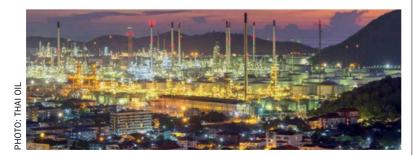
#### **CPECC** wins Iraq sour gas plant contract

According to a statement issued by the company, the China Petroleum Engineering and Construction Corp. (CPECC) has won a \$203.5 million engineering contract to treat sour gas at Majnoon oilfield in Iraq. The project, due to be completed within 29 months, aims to build sour gas treatment facility with daily capacity of 4.39 million cubic metres. Iraq's Majnoon oilfield, operated by state-run Basra Oil Co, is now producing around 240,000 bbl/d and plans to boost output to 450,000 bpd in 2021.

#### THAILAND

#### Thai Oil selects Topsoe sulphur oxide removal technology

Thai Oil has signed an agreement with Haldor Topsoe to license the latter's SNOX<sup>™</sup> sulphur and nitrogen oxides and dust emissions removal technology for Sriracha Refinery in Chonburi province in the east of Thailand. The installation will form part of Thai Oil's \$5 billion Clean Fuel Project, which will boost capacity from 275,000 bbl/d to 400 000 bbl/d as well as improving energy efficiency and environmental performance. The agreement comprises the supply of proprietary equipment and catalyst for the SNOX unit, in order to comply with air emission regulations for a new energy recovery unit at the refinery. This will use three parallel SNOX lines to remove sulphur oxides, nitrogen oxides and dust from the new circulating fluidised bed boilers. Sulphur is recovered as commercial grade concentrated sulfuric acid and the nitrogen oxides are reduced to free nitrogen. The SNOX process includes energy recovery by recycling of surplus heat to reduce energy consumption in the boilers.



The Sriracha refinery, Thailand.







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- Claus unit and tail gas treatment (HCR)
- Oxygen enriched air Claus
- Advanced ammonia Claus
- Sulphur degassing
- Thermal and catalytic oxidisers
- Major Claus equipment

(main burners, thermal reactors, WHB, condensers)



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**BCInsight** 

### Sulphuric Acid News

#### **INDONESIA**

### **Worley wins acid plant contracts**

Shell Global Solutions International BV (Shell) has awarded Worley two contracts for PT Pertamina EP Cepu's (PEPC) new sulphuric acid plant in Indonesia. This plant is part of the Jambaran-Tiung Biru utilised gas field project for PEPC, which is a subsidiary of PT Pertamina-Indonesia's state-owned energy company. Under the contracts, Worley will supply be supplying Chemetics' cooled oxidation reactor (CORE) technology. This is the first time that CORE will be paired with Shell's Cansolv SO<sub>2</sub> capture technology. Worley gained the Chemetics technology as part of its Jacobs Energy, Chemicals and Resources acquisition last year. Cansolv controls the emissions and captures additional by-product value from the sulphur dioxide emitted from various refinery flue gas streams (such as cracking units, process heaters and boilers), sulphur plants and spent acid regeneration units. Sulphur dioxide can be recycled to the sulphur recovery unit to be produced as marketable sulphur or converted to sulphuric acid.

Worley has also been contracted directly by PT Environmate Technology International (ETI) for the design of the acid plant, as well as detailed engineering and the supply of key equipment and materials. The company will also provide technical services for building the plant, operator training, commissioning and testing.

"We are pleased to work with ETI and PEPC on this exciting project and look forward to supporting Indonesia as it continues to grow into the natural gas sector," said Chris Ashton, Chief Executive Officer of Worley.

#### Work on alternative nickel leaching technique

An alternative method for processing mixed nickel-cobalt hydroxide is being developed by a team from the Bandung Institute of Technology, the Indonesian Institute of Sciences and the University of Queensland. Most existing process plants for nickel laterite ores use intermediate precipitation processes to recover the nickel and cobalt from the leach solution. The precipitation produces an intermediate product of nickel and cobalt, either as mixed sulphide precipitate (MSP) or mixed hydroxide precipitate (MHP), while largely separating nickel and cobalt from impurities such as manganese, calcium and magnesium. Mixed sulphite processes have a higher selectivity for nickel and cobalt over manganese and magnesium, resulting in a lower level of impurities compared with mixed hydroxide precipitation. However, the process is relatively expensive and complex because it requires the use of hydrogen sulphide gas at high temperatures and pressures.

The new method comprises a leaching step using sulphuric acid to dissolve the nickel and cobalt from mixed hydroxide precipitates, and subsequently, an oxidative precipitation step to separate the dissolved nickel from cobalt and manganese using ozone as the oxidant. Leaching experiments showed that 97% of the nickel and 96% of the cobalt can be dissolved,

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leaving 92% of the manganese in the residue, using 1 mol/l sulphuric acid solution at 25°C, a slurry density of 100 g/l and leaching duration of 2.5 hours.

#### EGYPT

#### Saipem to lead rail project for phosphate site

The El Wady for Phosphate Industries and Fertilizers Company (WAPHCO) says that it has selected a consortium led by Italian energy contractor Saipem as EPC contractor to build a cargo and passenger railway line to connect a phosphoric acid production site run by WAPHCO at Abu Tartour to the port of Safaga on the Red Sea. Other members of the consortium are Italian engineering group Salcef and Egyptian energy company El Sewedy Electric. The contract was agreed for an undisclosed sum, believed to be in the region of \$500 million. The consortium will now agree a development plan with WAPHCO and the Egyptian National Railway company.

The rail line forms part of the Egyptian government's wider Abu Tartour Plateau Development Plan, to tap into the region's natural resources, and includes a railway line connecting the phosphate site in the New Valley Governorate to Safaga port on the Red Sea, as well as the development of tourism in the region more generally. In April the Egypian government approved the establishment of a free zone in the Abu Tartour Plateau to include the new sulphuric and phosphoric acid plants. The China State Construction Engineering Corporation (CSCEC) won the \$850 million contract to build and operate the plants earlier this year, including a 500,000 t/a phosphoric acid plant and a 1.6 million t/a sulphuric acid unit. Abu Tartour holds up to 5 billion tonnes of phosphate rock reserves, according to WAPHCO.

#### CHINA

#### Acid prices continue to fall as smelters maintain operations

Although some sulphur and pyrite-based acid capacity has idled, China's lead, copper and zinc smelters, expansions of which led to China becoming a net sulphuric acid exporter in 2019 to the tune of 2 million t/a, are continuing to operate, aiming to avoid costly shutdowns and stockpile metal for when restrictions are lifted. China's refined copper cathode output rose 2.6% monthon-month to 665,000 tonnes in March, according to Antaike, with demand from downstream users recovering and higher treatment charges lifting operating rates. Although this is down 5.9% year on year, it is still leading to problems with selling of byproduct acid, storage capacity for which is becoming very limited. Antaike said that it forecast April cathode production would rise to around 680,000 tonnes on recovering acid sales but said that virus-related disruption to concentrate shipments from overseas. was expected to have an impact in May.

Jiangxi Copper, China's biggest producer, says that it will actually produce 6% more refined metal in 2020 (1.65 million t/a) compared to 2019, although it did caution that if the Covid-19 outbreak was not controlled "quickly and effectively" in the rest of the world, then a global financial crisis and economic recession would greatly impact upon copper demand.

#### UNITED STATES

#### **Chemtrade suspends earnings** guidance due to pandemic

Chemtrade Logistics Income Fund has announced that its operations have not been significantly impacted by Covid-19 in the first quarter, but due to the prevailing general economic uncertainty resulting from the Covid-19 pandemic, the company has suspended its 2020 earnings guidance. Chemtrade runs a diversified business, offering industrial chemicals and services in North America and around the world. It

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is also one of the largest suppliers of sulphuric acid, spent acid processing services, inorganic coagulants for water treatment, sodium chlorate, sodium nitrite, sodium hydrosulphite and phosphorus pentasulphide in North America. The company says that it has postponed its major plant turnarounds such as the planned second-quarter turnaround at its North Vancouver chloralkali facility until later in the year.

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Chemtrade Logistics Income Fund president and CEO Mark Davis said: "The global economy has become increasingly uncertain with reduced visibility into the future. It has become apparent that this uncertainty will continue for some time. Accordingly, it is now prudent to suspend our previously issued 2020 Guidance. As noted, our first quarter operations were not materially affected by Covid-19. While we expect demand for many of our products to be unaffected by the virus, for example, our water treatment chemicals sold to municipalities, other segments are likely to experience decreased demand at least in the second quarter, for example, the regen services we provide to oil refineries. The recent decline in the value of the Canadian dollar relative to the US dollar is, however, materially beneficial to our guidance assumption."

#### SOUTH AFRICA

### Foskor says it will continue with operations during lockdown

Phosphates and phosphoric acid producer Foskor says that, contrary to previous press reports indicating that it would not be operating during South Africa's Covid-19 lockdown period, it will continue with mining activities in Phalaborwa and its processing operations in Richards Bay, as it is considered by the government as an "essential service" in providing products to the agriculture and food sectors in South Africa.

#### AUSTRALIA

### Rare earth leach project completing pre-FEED stage

Arafura Resources Ltd says that it is progressing towards commercialising its Nolans Neodymium-Praseodymium (NdPr) Project in Australia's Northern Territory. Although Covid-19 restrictions have postponed the signing off on an agreement with indigenous groups who hold native title rights over the project area, the company says that progress has continued with Hatch on the pre-front end engineering and design (FEED) activities aimed at finalising overall project requirements in preparation for the early contractor involvement phase. Pre-FEED activities are expected to be completed in 2Q 2020, and the project will progress to the tendering of key contracts, including for the beneficiation plant, hydrometallurgical plant and sulphuric acid plant. The company says that it also continues to liaise with partners over securing offtake agreements.

### Nyrstar to be prosecuted over alleged acid leak

South Australia's Environment Protection Authority (EPA) says that it will prosecute Belgian-based Nyrstar Port Pirie Pty Ltd in the Environment, Resources and Development (ERD) Court for "discharging, or failing to prevent the discharge of, about 700 litres of sulphuric acid" from Nyrstar's Port Pirie smelter near Adelaide in South Australia. The acid was allegedly discharged in early 2019. Nyrstar did not comment on the case except to confirm that it had received a summons in relation to it. Following the incident in 2019 it told Australia's ABV News that it had occurred following the failure of a valve and ultimately resulted in a discharge into the water course, but that no persisting environmental impact was observed. The company also said that it has subsequently implemented new processes and alarms.

#### DEMOCRATIC REPUBLIC OF CONGO

### Katanga postpones acid plant commissioning

Katanga Mining says that owing to the Covid-19 pandemic, the commissioning of its new sulphuric acid plant at its 75%owned subsidiary Kamoto Copper Company (KCC) will be postponed from 2Q 2020 into the second half of the year, as a result of being unable to get the necessary commissioning experts to the site. However, the company says it has secured an agreement with state-owned Gecamines, which owns the remaining 25% holding in KCC for the purchase of \$250 million of land adjacent to existing mining concessions for construction of a new long-term tailings facility and the possible exploitation of additional resources that would enhance KCC's ability to more efficiently operate its mines and facilities and fulfil other key infrastructure requirements, although final payments are being held up by a government investigation into certain Gecamines executives.

The acid plant is designed to produce 1,900 t/d of sulphuric acid for copper leaching at the site, 200 t/d of sulphur dioxide and a net 17 MW of co-generated power.



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Siroj Loikov has been appointed First Deputy CEO of PhosAgro. Loikov, who was previously Deputy CEO in charge of international projects and personnel policy, will coordinate the work of the company's headquarters in Moscow, its management company in Cherepovets and the company's production sites. He will also oversee the implementation of the PhosAgro's priority development projects and will be responsible for the appointment, development and assessment of the work of the company's top management.

Evgeny Novitsky, also First Deputy CEO at PhosAgro, will continue working to improve the system for interaction between the Company and government agencies, and he will also continue to oversee PhosAgro's GR communications at the federal and regional levels.

Mikhail Rybnikov, who has been appointed as an executive director, will focus on the integration of production, logistics and sales, further improvement of the economic efficiency of production and supply processes and cost management. He will also oversee the implementation of key IT projects and integrated planning, as well as improvement of industrial safety standards and the occupational health system at PhosAgro enterprises.

PhosAgro CEO Andrey Guryev said, "Today, the company is facing external challenges that require a prompt response and serious international expertise. We have a great deal of work ahead of us to build new partnerships, to implement major international projects, including in terms

of expanding the use of environmentally friendly fertilizers, research and international trade, and to support the creation of a Green Standard for agricultural products in Russia and for its recognition as a global quality standard. Also on the agenda is the implementation of in-house projects to digitalise production and to restructure our occupational health and industrial safety functions. Meeting these challenges will require a great deal of commitment and attention. With this in mind, I decided to make some changes to the organisational structure of the Company's management and delegate some of my duties as CEO. These changes will ensure that equal attention is paid to finding solutions to challenges both within the Company and in interaction with our partners, and they will enable us to develop in new areas and achieve the key performance indicators outlined in our Strategy 2025. I am confident that Siroj Loikov's previous work experience in the Company - managing international projects and personnel policies - will help him succeed with the challenges before him.'

Worley has announced the appointment of Chris Ashton as Chief Executive Officer (CEO) and Managing Director of Worley, following the retirement of Andrew Wood. Worley's Chairman, John Grill said "Andrew Wood has had a distinguished career with Worley spanning 26 years, with the last seven as our CEO. Andrew's contribution has been fundamental to creating the global company we are today. Under Andrew's strong leadership, we successfully restructured Worley to realign our operations through a period of rapid change in the markets we serve, and then doubled the size of the business through the acquisition of the Energy, Chemicals and Resources (ECR) division of Jacobs to create the global leader across Worley's core market segments. The Board and management thank Andrew for his significant and valuable contribution to Worley and wish him well in his retirement."

Ashton has been at Worley since 1998 and has held many leadership roles in the company. Prior to his appointment as CEO, he was Chief Operating Officer (COO) responsible for the integration of ECR and strategy for the transformed Worley business. Previously he was accountable for the Major Projects and Integrated Solutions portfolio. He has also held executive roles with responsibility for Europe, Middle East and African operations, and the Power sector globally. He holds a degree in Electrical and Electronic Engineering from the University of Sunderland, an MBA from Cranfield School of Management and has completed the Executive Management Program at Harvard Business School as well as the AICD Company Directors Course.

Commenting on his appointment Ashton said: "It is a great privilege to assume the leadership of this great company. The next decade will see unprecedented change in the energy, chemicals and resources industries which we serve. Our customers are being driven by having to address two fundamental structural disruptions; the Energy Transition and changes resulting from the adoption of digital processes."

### Calendar 2020

#### JUNE

CANCELLED 3-4 European Sulphuric Acid Association General Assembly, VIENNA, Austria Contact: Francesca Ortolan, Cefic Tel: +32 2 436 95 09 Email: for@cefic.be

44th Annual International Phosphate Fertilizer and Sulphuric Acid Technology Conference, CLEARWATER, Florida, USA Contact: Miguel Bravo, AIChE Central Florida Section Email: vicechair@aiche-cf.org Web: aiche-cf.org/Clearwater\_Conference

#### JULY 13-17

Brimstone Amine Treating and Sour Water Stripping Course, HOUSTON, Texas, USA Contact: Mike Anderson, Brimstone STS Tel: +1 909 597 3249 Email: mike.anderson@brimstone-sts.com Web: www.brimstone-sts.com

#### **SEPTEMBER**

21-25

Brimstone Sulfur Recovery Fundamentals Course, HOUSTON, Texas, USA Contact: Mike Anderson, Brimstone STS Tel: +1 909 597 3249 Email: mike.anderson@brimstone-sts.com Web: www.brimstone-sts.com

#### **OCTOBER**

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.

7-8

TiO<sub>2</sub> World Summit, CLEVELAND, Ohio, USA Contact: Shannon Siegferth, Smithers Tel: +1 330 762 7441 Email: ssiegferth@smithers.com

#### **NOVEMBER**

2-4

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

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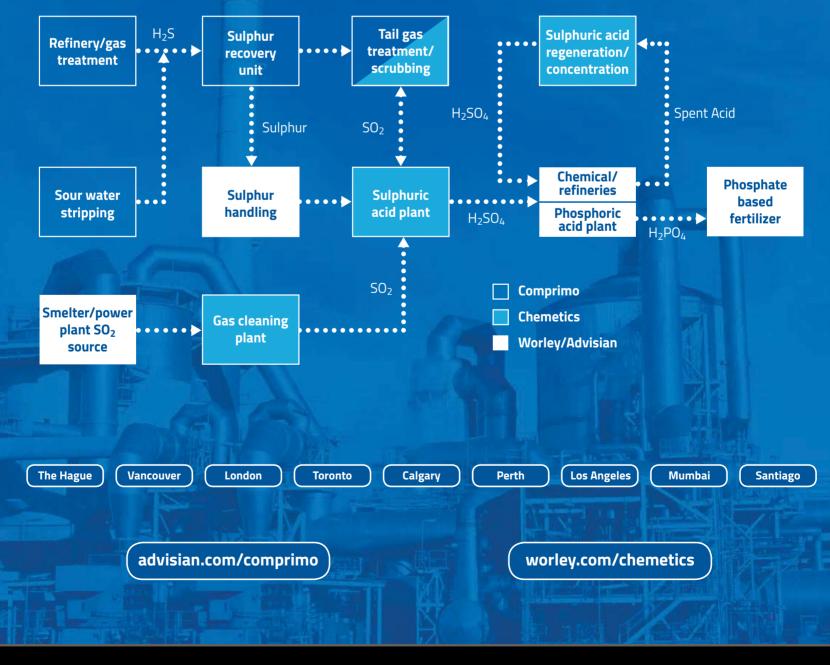
CHEMETICS

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DTO: ALAMY

### A look at the major factors influencing the sulphur market around the world.

orld production of elemental sulphur reached 66 million tonnes in 2019, and continues to come almost exclusively from recovered sulphur from refineries and sour gas plants, with mined sulphur less than 1% of production. Additions to sulphur capacity are coming from new refinery projects, especially in the Middle East and Asia, and large sour gas projects, again dominated by new production in the Middle East.

ends

markets

sulphur

#### Supply – refineries

Sulphur supply from refineries has been rising steadily for decades as regulations on sulphur content of fuels continue to tighten and overall use of vehicles fuels increases, especially in Asia. In the short term this is likely to increase – with the exception of the period of the Covid-19 crisis of course – as the effects of the latest global reduction in sulphur content; the new International Maritime Organisation (IMO) regulations on shipping fuels, continue to work their way through the market for bunker fuels.

However, in the longer term this boost to sulphur production may begin to level off

and even decline due to changing patterns of use of refined products.

Increases in global oil consumption have been slowing noticeably, and in 2019 consumption rose by only 0.8%. About 40% of demand is accounted for by road vehicle fuel consumption, and this is likely to peak in the next few years due to a variety of factors. One major one is the increasing fuel efficiency of vehicles, but ageing global populations (who drive less), the approaching saturation of vehicle ownership in formerly industrialising economies, and the increasing use of ride sharing apps and other shared mobility services will all play a part. One factor expected to become increasingly important as the decade progresses will be the increase in market penetration of alternate drive trains, especially electric vehicles.

Consequently there will be a peak in demand for vehicle fuels which may come sooner than expected. A consultancy paper by Bloomberg puts the peak at 2030, with consumption slowing markedly in the run up to that date, and Wood Mackenzie has picked a similar date. This part of a wider pattern of a peak in overall global oil demand, where the spread in predictions runs from 2030 to 2040, with forecasts clustering to the lower end of that range, and forecasts for demand becoming essentially static by around that time. The International Energy Agency last year said that global oil demand would be roughly flat from 2025 onwards. In April this year, the UK's *Financial Times* even ventured to suggest that, with the lingering effects of Covid-19 on the world, the collapse of demand from aviation and cruise lines, and perhaps a post-Covid push towards greater home working and teleconferencing, we may even have already seen peak oil demand in 2019.

Sulphur stockpile at a terminal in Vancouver.

Another factor which has driven increasing sulphur output from refineries has been that tightening emissions regulations have called for steadily increasing percentages of sulphur to be removed from refined products. However, the potential for additional recovery, at least in raw tonnage terms, is also starting to fall. Most sulphur is now already recovered from oil before the products leave the refinery. North America, Europe, Russia and most of industrial Asia (China, Japan, Korea, etc) have already moved to 15 ppm or lower standards for sulphur content of

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vehicle fuels, and India is moving to that level this year. Some of the major holdouts on high sulphur fuel standards used to be in the Middle East, but even here, Saudi Arabia has also moved to a 50 ppm sulphur standard, and many African countries which also used to permit large sulphur content in fuels have followed suit. It follows that further reductions from vehicle fuels will be incremental only. Aviation and maritime fuels used to still permit high sulphur levels, but with the world's shipping fleet moving to a 0.1% sulphur standard in Emission Control Areas - the number and scope of which continues to increase - and 0.5% outside of these, most of the sulphur is now removed from bunker fuels as well. Exhaust scrubbing systems have not caught on to the extent that was hoped, and the current rock bottom fuel prices make the economics of that even less enticing for now. Aviation fuels have managed to fend off global sulphur standards for now, but both the shipping and aviation industries are facing increasing pressure to lower carbon dioxide emissions, which may mean moving to more efficient engines and alternative fuels. At the same time, new liquids production is coming particularly from the US, from fracked 'tight oil' and natural gas liquids, which are generally lower in sulphur content.

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Once again this is a longer term development. For the moment, many refineries are still expanding their sulphur recovery capacity to meet existing regulations, especially in Asia - much of this has been in response to the IMO 2020 regulations. The Middle East is also seeing new refining capacity - Kuwait's new refineries, discussed in our previous issue, will increase sulphur recovery capacity there by up to 1.8 million t/a over the next two years, and there will ramp ups of new refinery capacity in India, China, Malaysia, Indonesia, adding perhaps another 2.7 million t/a of sulphur recovery capacity over the next few years. Beyond 2025, however, additional sulphur volumes from refineries may be incremental at best. Conversely, US refinery sulphur output fell in 2019 by 500,000 t/a as refineries switched to sweeter crudes to produce low sulphur shipping fuels, and some places, like Europe and Japan, may see more refinery closures due to competition from larger, more efficient Asian refiners.

Processing of heavy oil sands crude was supposed to have driven a significant increase in sulphur supply, but the implosion of the Venezuelan economy has destroyed the prospects for the Faja de Orinoco oil sands belt for now, and Canadian oil sands processing has faced difficulties from low oil prices, shortage of export routes and environmental opposition in the US. Additional sulphur recovery from Canadian oil sands looks to be more modest in prospect now – perhaps a couple of hundred thousand tonnes per year over the next five years from expansions at existing projects, with few new projects on the cards until export pipeline routes become available.

#### Supply – sour gas

The other main source of sulphur is from processing of sour gas, and here the situation is somewhat different. Use of natural gas is also rising steadily around the globe, mainly for power production, increasing 5.2% in 2018, although this was an exceptional year. Overall, global gas consumption has risen from 3.03 trillion cubic metres in 2008 to 3.87 trillion cubic metres in 2018, according to BP figures, an average annual growth rate of 2.3% worldwide. Demand growth has been strong in North America and Asia, but it has been fastest over the past decade in the Middle East, where rapidly rising populations and demand for electricity in fast-growing cities like Dubai and Abu Dhabi have pushed growth in power generation. In North America, gas has steadily replaced coal as a power generation fuel, partly for environmental reasons, but mainly because of the boom in production in shale gas which has made gas much more price competitive with coal as a feedstock for power and chemical production. Conversely, Europe has seen gas consumption fall because of falling domestic production and the higher cost of importing from Russia and the international LNG market.

Global gas consumption continues to increase, but as with oil the rate of growth is slowing markedly. McKinsey puts the rate of demand growth at 1.3% year on year over the next five years, and then 0.7% thereafter out to 2035. As well as an increasing focus on carbon emissions in places such as Europe, Canada and even China, there is rapidly increasing availability of renewable electricity. Meanwhile, supply from new conventional gas fields is becoming harder to source, and there has consequently been considerable growth in 'unconventional' gas – from shales, coalbed methane, or 'tight gas', as well as biogas and other sources. Lack of availability of sweet gas in some regions, especially the Middle East, but also including China and Central Asia, has led to an increasing focus on sour gas resources to meet demand. This in turn continues to generate large new volumes of sulphur.

In China, production comes from three gas plants, at Chuangdongbei, Puguang and Yuanba. Production reached about 2.3 million t/a in 2019, and is continuing to increase slowly, perhaps by 500,000 t/a over the next five years. Central Asia has seen the start-up of the South Yolotan/ Galkynysh sour gas plant in Turkmenistan, and the re-start of the huge Kashagan sour associated gas project, as well as additional production at Tengiz and the Kadym project in Uzbekistan. However, most new sulphur from sour gas is coming from the Middle East, where Saudi Arabia is adding 1.3 million t/a of sulphur production capacity via the Fadhili gas plant, due to be commissioned this year. Qatar's Barzan LNG project will generate an additional 800,000 t/a sulphur, and Abu Dhabi is expanding the already huge Shah sour gas project to add a potential 1.7 million t/a of sulphur from around 2023, as well as looking longer term to production from the Hail and Ghasha sour gas fields. Production from Iran's South Pars and other sour gas projects is also adding incremental capacity.

Set against this, sour gas production is in long term decline in Europe and North America. US sulphur production from sour gas fell by 300,000 t/a last year and Canadian production is on a long, slow decline. Falling production in Germany could remove another 200,000 t/a of sulphur from the market over the next 5 years. Nevertheless, in spite of these reductions, sour gas is going to be the main new source of sulphur supply over the medium term, mainly from the new Middle Eastern gas projects.

#### **Demand – sulphuric acid**

Most sulphur – around 90% – is consumed as sulphuric acid. Sulphuric acid is the most widely used industrial chemical, but burning elemental sulphur is not the only source of sulphuric acid – around 8% comes from roasting of iron pyrites, mainly in China, and another 30% from capture of sulphur dioxide emissions at metallurgical smelters. The smelter acid

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segment is involuntary production and tends to be relatively independent of sulphur prices, but instead determined by the markets for base metals, especially copper. There is however some interchangeability between sulphuric acid and sulphur for some producers, like OCP in Morocco, who can to a limited extent turn from buying sulphur on the international market to importing sulphuric acid directly instead. This complicates the market for elemental sulphur slightly, as it must to an extent compete with pyrites and smelter acid production, especially in countries like China. As smelter acid, as a waste product, can often be relatively inexpensive, it can often be preferred where there is a source of supply locally. But the difficulties of storing and transporting large volumes of acid have conversely also meant that some consumers have installed sulphur burning capacity in order to gain greater control over feedstock supply, as has happened in Cuba and Chile in recent years.

Nevertheless, because most sulphuric acid is used in phosphate fertilizer production, and fertilizer production centres do not often coincide with metal smelting or pyrite roasting regions, demand for elemental sulphur to be burnt for acid production remains dominated by producers of single superphosphate (SSP), ammonium sulphate and especially phosphoric acid for phosphate fertilizer production - mainly mono- and di-ammonium phosphate (MAP/ DAP), accounting for around 60% of all sulphuric acid consumption.

#### **Phosphates**

Fertilizers of various types account for 90% of phosphate demand, with the rest used for a variety of industrial uses, from food and animal feed to detergent and metal treatment. Some 63.3 million t/a  $P_2O_5$  of phosphate rock was mined in 2018. Some of this was combined directly with sulphuric acid to make single superphosphate (SSP) fertilizer, and most of the rest was used to make phosphoric acid. Global phosphoric acid production stood at 47.0 million t/a  $P_2O_5$  in 2018, about 85% of which was used for fertilizer production, mostly monoand di-ammonium phosphate (MAP/DAP) or triple superphosphate (TSP). The main centres of phosphate fertilizer production are China, the US and North Africa, with other significant producers including India, Russia, Brazil and Saudi Arabia.

Growth in demand for fertilizer is tied to increasing global populations and more intensive agriculture in some parts of the world, especially South America and Africa. However, in other parts of the world such as Europe, demand is mature, while China has been over-applying fertilizer and is

Acid demand for

other industrial

to increase at a

fertilizer use"

processes continues

higher rate than for

attempting to make its application more efficient and environmentally friendly by restricting the application of nutrients. This has led to a gradual slowing in the rate of demand increase for fertilizer. Overall demand for phosphate fertilizer is projected by IFA to increase by 1.4% year on year over the next four years, a total increase of 3.3 million  $t/a P_2O_5$ , but this can be sub-

iect to considerable annual variation due to weather and other issues. Last year, for example, phosphate fertilizer application was down considerably in the US due to widespread flooding in the main agricultural region of the mid-West.

New phosphate fertilizer plants are being built, mainly in Morocco and Saudi Arabia, but there has also been considerable industry overcapacity, much of it in China, where tightening environmental emissions legislation and low product prices are leading to a shake-out in the phosphate sector and the closure of numerous production sites. The once dominant US phosphate industry also continues to rationalise due to falling mine outputs and higher costs. The upshot is that most new sulphuric acid demand for phosphate production in the medium term will come from places such as Morocco, Algeria and Egypt as well as Saudi Arabia, which will add 5.2 million t/a  $P_2O_5$  of phosphoric acid capacity between them out to 2024. There are also capacity additions projected in Kazakhstan, Russia and Turkey, and possibly Brazil. North Africa and Saudi Arabia are not large scale producers of metallurgical acid, so the resulting acid consumption will mainly come from sulphur burning acid plants and hence represent several million tonnes of additional sulphur demand.

#### Industrial uses

On the industrial side, sulphuric acid is used in the leaching of rocks for metal extraction - primarily copper, but also nickel, uranium, rare earths and gold. It is also consumed by a wide range of industrial uses, including titanium dioxide pigment production, especially in China and Europe, caprolactam manufacture, and many others. Metal leaching operations are strong in Chile, Peru, the USA and southern Africa's copper belt, and likewise Kazakhstan uses large volumes of acid for

uranium extraction. A number of large scale plants were built for nickel laterite processing in places such as Madagascar, Australia, Cuba, New Caledonia and the Philippines which consumed large volumes of acid. However, costs and technical difficulties and changes in nickel markets led to more of a focus on other processes

such as nickel pig iron and ferronickel manufacture. But Indonesia's decision to halt exports of nickel ore and the rise in demand for high quality nickel sulphate for battery manufacture for electric vehicles is leading to a resurgence in interest in high pressure acid leach (HPAL) plants, as detailed elsewhere in this issue. This in turn could lead to demand for another 2.5 million t/a of sulphuric acid in Indonesia for new HPAL plants. Whether this could be met by increases in smelter acid production or sulphur burning remains an open question.

Elsewhere, acid demand for other industrial processes continues to increase at a higher rate than for fertilizer use. This has been particularly true in China. New Chinese acid demand is however being met mainly from new copper smelting capacity, and sulphur consumption is expected to remain relatively constant.

#### **Pandemic disruption**

The spread of the Covid-19 virus has been the most disruptive event to global markets in living memory, and the effects are at present hard to gauge. Much depends upon the length and intensity of so-called 'lockdowns' of populations across the world, beginning in China's Hubei province, but now spread to most of Europe and North America, India, Australasia and beyond. The entire global economy has to an extent been placed on 'pause'. Refiners are lowering operating rates as tanks fill up, with demand for refined products badly affected. Argus calculate that US and European sulphur production may be down

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10-20% in March, and lower still in April. Gas-based producers are continuing to operate however, as the gas is needed to keep power plants running. ADNOC's sulphur output is reported to be unaffected, at least for now.

On the demand side there are shutdowns too. China's phosphate fertilizer industry is heavily based in the worst affected regions, where many plants have been closed since January, although as the lockdown is lifting, there are indications that demand has rebounded as producers try to fulfil orders before the spring application season. In India, major fertilizer producers took maintenance turnarounds in March that have extended into full shutdowns. The nickel plant at Ambatovy in Madagascar is likewise idled, although most African fertilizer producers continue to operate, especially OCP in Morocco. Elsewhere, the closures or increased checks at many borders, even within Europe's notionally border-free Schengen Area, has slowed the passage of products of all kinds. Ironically, the resulting difficulties in securing supply have actually pushed sulphur prices up as a result.

#### Supply/demand balance

Leaving aside the unforeseeable, where does this leave the overall supply/demand balance for sulphur over the next five years? New supply from refining and sour gas, taken together, adds about 9 million t/a of capacity, provided that there are no further project delays, while new demand may only reach 5.5 million t/a over the same period. The market is and continues to be in surplus, although a lot of the new supply is concentrated towards the start of the period, while demand is more spread out.

On a regional basis, the Middle East continues to be the largest exporting region, as new refineries and sour gas projects push additional output much higher than projected demand increases from Saudi Arabia's phosphate processing. North America may run a slight surplus while European supply is looking increasingly tight due to sour gas and refinery closures and run downs. There is additional sulphur available from Central Asia, but how much of that will find a market may depend upon pricing, and those prices are likely to become increasingly set by Middle Eastern producers. On the demand side, China will continue to be the largest importer of sulphur. Additional acid production in China due to new smelter capacity may reduce the demand for sulphur burnt acid, at the same time that additional sulphur comes from refineries and sour gas production, while demand from phosphate producers remains stable or falls. But how far Chinese imports fall also depends upon closures in the pyriteroasting acid sector. This has contracted, yet it has also proved remarkably resilient to previous forecasts of closure. Elsewhere, Morocco and other North African countries will be major consumers due to phosphate expansions, and Brazilian and Indian demand should increase slightly for the same reason.

The effects upon this forecast of the Covid-19 pandemic continue to be unpredictable – we are certainly in for a period of volatile prices. However, while, longer term, the return to some semblance of 'normality' is unlikely to affect demand for fertilizer or natural gas, industrial closures and potential delays to relaxing travel restrictions may continue to weigh heavily upon refinery producers.



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# Indonesia: the rise of domestic smelting

The Grasberg copper mine, Papua, Indonesia.



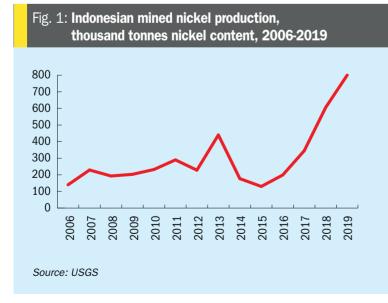
The Indonesian government's decision to enforce the processing of more copper and nickel ores domestically rather than export them to China has led to the rapid development of domestic smelter capacity as well as nickel acid leaching projects. ndonesia is now far and away the largest producer of nickel in the world, and production is growing rapidly. Indonesia produced 30% of the world's nickel ore in 2019 (Figure 1), with a larger proportion than ever being processed locally to nickel pig iron (NPI). Global nickel mine output increased by over 10% for the third straight year in 2019, according to the International Nickel Study Group (INSG), and two thirds of this growth came from Indonesia, where mined production increased by 25%. Indonesia exported 32 million t/a of nickel ore

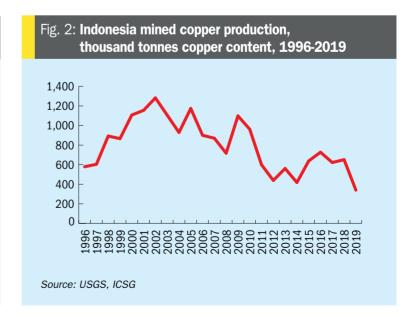
and ferronickel in 2019, 96% of which was destined for China. The country holds 25% of the world's estimated nickel resources, most of it as lower grade laterite ores.

On the copper side, Indonesia's share of global copper production is much smaller, at about 3.5%. However, until about 10 years ago it was a bigger producer than China, and it is still the second largest copper producer in Asia. As Figure 2 shows, though, this production has been extremely variable over the past two decades.

#### Added value

Thanks to its export restrictions, Indonesia is also processing more nickel and copper domestically. During the 2000s, Indonesia had become mainly a supplier of nickel and copper ores to China's rapidly industrialising economy. However, as Indonesia's mining boom gathered pace, the government became concerned that much of the value of the ore was leaving the country, and it determined that it would try to capture more of that value within Indonesia. This began with a new mining law in 2009 which aimed to force mining companies to build downstream minerals processing capacity in Indonesia rather than shipping raw ore to China to be smelted. The government set a five year deadline to build smelting capacity in Indonesia or face a





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ban on the export of raw mineral ores and concentrates.

Initially there was an attempt by some miners to call the Indonesian government's bluff on this, and this led to a ban on exports of nickel and aluminium ores in January 2014. This had the side effect of reversing what had been overcapacity in the nickel market due to a slowdown in the Chinese economy and leading to a price spike, which in turn was able to fund building new capacity within Indonesia. It also demonstrated the government's seriousness and belatedly led to the development of nickel and copper processing capacity in the country. The government also relented on exports of nickel and copper ores in the interim, with a quota system for nickel ores, in order to improve the country's much worsened balance of trade. The quotas were to last until 2022 provided that minimum requirements for processing and refining are met; companies are required to build or are in the process of building smelters for relevant mining minerals in Indonesia.

#### Nickel

The nickel market has been changing considerably over the past two decades. For most of that time it has been trying to keep up with Chinese demand for stainless steel production. About 70% of nickel goes to make stainless steel. Historically it has been supplied primarily from higher grade sulphide ores, but the number of suitable sulphide deposits was insufficient to supply the market (sulphide deposits are only about 30% of overall nickel resources), and attention has turned instead to lower grade laterite ores, primarily found in tropical regions. The expansion in laterite processing means that currently just under 60% of nickel comes from laterite deposits and 40% from sulphide - while the tonnage of nickel coming from sulphide processing has been relatively stagnant over the past decade; virtually all new nickel mining has been of laterites.

Processing of laterites requires more energy than sulphides, and can take a variety of forms. Of most interest to the sulphuric acid market was the development during the 1990s and 2000s of high pressure acid leaching (HPAL), which produces high grade nickel, albeit at great capital and process cost (and huge volumes of sulphuric acid). Several large plants were developed in Australia, New Caledonia, Cuba, the Philippines and Madagascar, although the complexity of the process led to slow ramp-ups and



Amamapare Port, exporting copper concentrate from Freeport's mines.

many technical hitches. Moreover, HPAL's development was undercut by the growth in so-called nickel pig iron (NPI). NPI is a nickeliron agglomerate produced by a low grade and far cheaper pyrometallurgical process. As nickel was primarily needed for the Chinese stainless steel industry, the presence of iron in the nickel was not problematic, and so China developed large-scale NPI processing and hoovered up large tonnages of laterite ore from the Philippines and especially Indonesia to feed it.

China's boom in NPI processing undercut much of the nickel market, in spite of the shortage caused by Indonesia's export ban and production cutbacks in the Philippines, although Indonesia's export ban has moved a lot of NPI processing back into the domestic economy, with the NPI itself then being exported on to China.

But over the past few years the nickel market has seen another major change the growing use of nickel in rechargeable batteries for electric vehicles. This currently absorbs 4% of the nickel market, but that figure is - or at least was, before the current pandemic - rising very rapidly, and was projected to reach 10% of the nickel market by 2022 and 20% by 2028. Battery manufacture requires high grade (so-called Class 1) nickel sulphate, and this is beginning to create a two-tier market for nickel, with premium prices being paid for plating/battery chemicals. This in turn is leading to a new look at acid-based processing and the development of new HPAL plants in major nickel producing countries such as Indonesia and the Philippines. At present, HPAL is the only way of producing Class 1 nickel sulphate for battery use from laterite ores. The pace of this development has been accelerated by Indonesia's nickel ore restrictions, which tightened again in August 2019, when the Indonesian Ministry of Energy and Mineral Resources (MEMR) brought forward the export ban on low grade nickel ore (<1.7% nickel) to January 1st 2020, two years ahead of schedule, with a waiver provided that 90% of smelter construction was complete.

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#### Copper

Copper is used in a variety of uses, including wiring, piping, construction, machinery and electronics, and increasingly these days is electric vehicles. As such its demand is often used as a proxy for industrial output, and over the past two decades growth in copper demand has essentially come from China and its increase in industrial output. For the same reason, the slowdown in the Chinese economy in the past few years has seen mined copper output overshoot projected demand, and copper output has been cut back as prices fall. Recent figures from the International Copper Study Group (ICSG) show that global copper mine production fell by 0.7% in 2019 compared to 2018, copper concentrate production fell by 0.6%, and acid leaching of copper (solvent extraction/electrowinning or SX/EW) fell by 1%. Chinese imports of copper fell by 7%, although apparent usage rose by 2%.

HOTO: PT FREEPORT INDONESIA

Globally, Chile remains the top producer, at 5.6 million t/a. Unlike with nickel, Indonesia's share of copper production is much smaller, at around 340,000 t/a, and Indonesia's output fell 45% in 2019 to this figure from the previous as a result of a fall in output at the huge Grasberg mine, where output was down 85% due to a move from surface mining where ore bodies are depleted to new underground mining zones. Grasberg is expected to ramp up production from the new ore body out to 2022.

The major copper producer in the region is PT Freeport Indonesia, the local subsidiary of Freeport-McMoRan which owns the Grasberg mine. Smelting is carried out by PT Smelting at Gresik, Indonesia's first copper smelter, established in 1997 and jointly operated by PT Freeport Indonesia and Mitsubishi. PT Smelting processed 1.1 million t/a of copper concentrate in 2019 to produce 290,000 t/a of copper cathode. It also produced 1.04 million t/a of sulphuric acid as a by-product.

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#### **New smelters**

Indonesia's change to the mining law, which banned low grade nickel ore imports from the start of this year, and which is expected to ban higher grade nickel and copper ore imports from 2022, has spurred a major slew of new project developments to process copper and nickel ores domestically, which will increase both sulphuric acid production and consumption.

On the copper front, PT Freeport Indonesia is spending a reported \$3 billion on building a new copper smelter at Gresik, East Java. Capex planned for 2020 will total \$600 million according to the company. The smelter will have capacity to process 2.0 million t/a of copper concentrate to produce 550,000 t/a of copper cathodes and 40 t/a of gold (and 1.6 million t/a of acid). The development comes after extensive negotiations between the company and the government to be allowed to continue operations which have seen Indonesia's government take a 51% stake in Freeport Indonesia based on a new mine licence replacing existing contracts which will allow Freeport to continue operating its huge Grasberg copper mine until 2041. Freeport has been reluctant to build the smelter, which it says will only operate on a break even basis, but this will be offset by profits from the continued operation of Grasberg. The smelter is due on stream by 2023, by which time underground mining at Grasberg should have reached capacity.

State gold and copper mine Amman Mineral Nusa Tenggara has also started developing its own copper smelter with a capacity of 1.3 million t/a of copper concentrate in Sumbawa. This would produce 300,000 t/a of copper cathode and 900,000 t/a of sulphuric acid. Amman is also targeting 2023 as a completion date for the smelter.

On the nickel side, in addition to a slew of ferronickel and nickel pig iron (NPI) smelters, mainly geared at stainless steel production, there are three high pressure acid leach (HPAL) projects, all of them funded by Chinese investments to produce high grade nickel sulphate for electric vehicle use. The most advanced in terms of timescale is now thought to be the \$1.5 billion project being developed by PT Halmahera Persada Lygend, a joint venture between Indonesia's Harita Group and China's mining firm Ningbo Lygend. The project is aiming at a total production capacity of 240,000 t/a of nickel sulphate (37,000 t/a nickel metal equivalent) and 30,000 t/a of cobalt sulphate by 2023 following two-phase construction.

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Autoclaves were reportedly installed at the site last year and construction work for the downstream sulphate plant began in early 2020. First production of mixed nickelcobalt hydroxide precipitate is targeted for late 2020, with production of nickel sulphate beginning in Q1 2021. Sulphuric acid requirements are projected to be approximately 1.4 million t/a at capacity.

It seems to have leapfrogged the project being developed by Chinese battery firm GEM Co Ltd in conjunction with stainless steel giant Tsingshan, which had been looking to begin operations in 2020, but which has been delayed by seeking an environmental permit for tailings disposal at sea - this approval was finally granted in January this year. The plant at Morowali is looking to produce 150,000 t/a of nickel sulphate, and expenditure was originally put at just \$700 million, and although Tsignshan argues that the Morowali plant would cost less than previous HPAL plants because infrastructure such as port facilities, roads, and power plants are already present, this seems likely to be a significant underestimate. The startup date has been pushed back to late 2021 because of the permitting delay.

Finally, Tsingshan has a 10% stake in another HPAL project with Chinese cobalt producer Zhejiang Huayou and China Moly. This is looking to 60,000 t/a of mixed nickel hydroxide cobalt production at a cost of \$1.3 billion, and according to Zhejiang Huayou is also looking to a 2021 start-up.

Sumitomo Metal Mining (SMM) said in November last year that it was on track to finish a definitive feasibility study and make a final investment decision on the Pomalaa nickel project in Indonesia by the end of March 2020. This would be a partnership with PT Vale Indonesia to build a 40,000 t/a mixed nickel sulphide HPAL plant by about 2025.

#### Coronoavirus

Of course this year has seen a major new unforeseen development in the Covid-19 pandemic. In Indonesia the government has admitted that it expects the timescales of many of its ferronickel smelter projects to be put back. Of the 68 ferronickel/NPI smelters that it is targeting the completion of by 2022, only 17 have been built and are in operation, and the government has talked about reducing the final target to 52. Another four smelters with a total processing capacity of 2.07 million t/a of ore and nickel output of 200,000 t/a (a mixture of nickel pig iron, ferronickel, lead bullion and ferromanganese) are due to begin operations this year. The largest is PT Aneka Tambang's (Antam) \$1.6 billion nickel smelter in East Halmahera, North Maluku, which will produce 64,655 t/a of ferronickel. A fifth smelter, belonging to PT Elit Kharisma Utama's (EKU) at Banten, will operate at half of its 100,000 t/a NPI capacity when it comes onstream in June. While there has been no official statement on them, the development of the HPAL projects are closely tied to China and the guarantine of staff involved in the projects is likely to have also delayed construction.

#### Acid balance

Assuming that the copper smelter construction goes to plan, an additional 2.5 million t/a of sulphuric acid could be produced from the new smelters when they reach capacity, sometime in 2024. Freeport had been aiming to begin construction of its smelter in August, although how delayed this will be due to the Covid-19 pandemic remains an open question.

Likewise, if all of the HPAL plants start up as planned in 2021, this will eventually lead to a surge in acid requirements for the leaching plants. Acid consumption per tonne of nickel ore processed is generally around 260-400 kg/t at existing HPAL producers, implying around 3.2 million t/a of sulphuric acid consumption if all three plants operated at capacity. However, historically it has required an average of four years to achieve 80% capacity for existing HPAL producers, and although some (eg Coral Bay) have been considerably faster, Murrin Murrin in Australia took seven years to achieve more than 50% capacity. This would imply on average an extra 2.5 million t/a of acid consumption by 2025, neatly balancing the projected additional acid coming from the copper smelters. In the interim, however, Indonesia could find itself in acid deficit as the HPAL plants ramp up prior to the copper smelters coming on-stream.

Indonesia typically imports around 400-500,000 t/a of sulphuric acid (491,000 tonnes in 2018), mainly from Korea, as well as operating some sulphur burning acid capacity, most of it aimed at phosphate production, which leads to another 80-100,000 t/a or so of sulphur imports. It is not clear at present whether any of the HPAL producers are considering sulphur burning acid plants, or whether they are relying on smelter acid.

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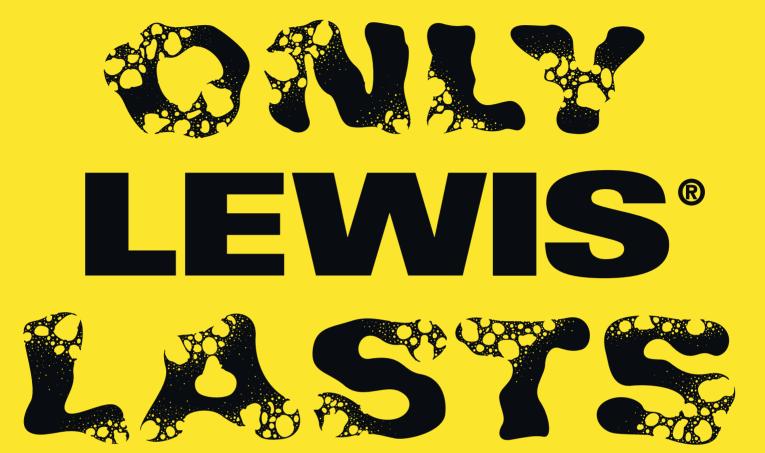
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## Sulphur recovery projects 2020



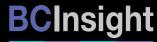
The Fadhili gas plant.

Operating company	Operating site	Process type	Total new capacity	Licensor(s)	Lead contractor	Project type st	Planned artup date
ALGERIA							
Sonatrach	Hassi Messaoud	Claus, TGT, amine, SWS	14 t/d	n.a.	Wood Group	New	2024
AZERBAIJAN							
SOCAR	Baku HAOR	Claus, TGT, amine,	2 x 30 t/d	Tecnimont, UOP,	Wood Group,	New	2021
		$H_2S$ , $CO_2$		Wood Group	KT-Kinetics Tech.		
BAHRAIN							
Варсо	Sitra Refinery	Claus, NH <sub>3</sub> , amine,	3 x 250 t/d	Comprimo	n.a.	New	2022
		SWS, AGRU					
BRAZIL							
Petrobras	Belo Horizonte	SuperClaus	2 x 62 t/d	Comprimo	n.a.	Revamp	2020
CANADA							
Pembina-Veresen	Hythe	SuperClaus	2 x 310 t/d	Comprimo	n.a.	New	2021
Pembina-Veresen	Two Lakes	SuperClaus	2 x 62 t/d	Comprimo	n.a.	Revamp	2020
PetroCanada	Fort Hills Upgrader	Claus, NH <sub>3</sub> , amine	2 x 700 t/d	Comprimo	n.a.	New	On hold
IOL	Nanticoke Refinery	EuroClaus	127 t/d	Comprimo	n.a	Revamp	2022
Encana	Pipestone Gas Plant	Sulfinol M	n.a.	Comprimo	n.a	New	2021
Veresen Midstream	Hythe Gas Plant	Claus, SuperClaus, degas	265 t/d	Comprimo	n.a.	Revamp	2021
CHINA							
Jiutai Energy	Linyi, Shangdong	EuroClaus	32 t/d	Comprimo	n.a.	New	2019
Sinopec	Fujian	SuperClaus	513 t/d	Comprimo	n.a.	New	2019
Shaanxi Yancheng	Yulin, Shaanxi	EuroClaus	41 t/d	Comprimo	n.a.	New	2019
Unocal East China Sea	n.a.	Sulfinol X	n.a.	Comprimo	n.a.	Revamp	2019

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Operating company	Operating site	Process type	Total new capacity	Licensor(s)	Lead contractor	Project type sta	Planne artup dat
COLOMBIA							
EcoPetrol	Barrancabermeja	Claus, NH <sub>3</sub> , amine	2 x 130 t/d	Comprimo	n.a.	New	On ho
EcoPetrol	n.a.	Claus, NH <sub>3</sub> , annie	90 t/d	Siirtec Nigi	n.a.	Revamp	201
	11.a.	Claus	90 Y U		II.a.	Revailip	201
CROATIA			05.1/1				
INA	Rijeka	Claus	95 t/d	Comprimo	n.a.	New	202
EGYPT							
ASORC	Asyut	Claus, HCR, TGT	2 x 130 t/d	Siirtec Nigi	TechnipFMC, Petrojet	New	202
Eni	Zohr	Claus, acid gas enrich, TGT, degas	4 x 12 t/d	KT-Kinetics Tech.	Petrobel	New	203
FRANCE							
Total	Donges	SWS	n.a.	Wood Group	Wood Group	New	202
Total	Normandy	SuperClaus	96 t/d	Comprimo	n.a.	Revamp	201
GREECE							
Hellenic Petroleum	Thessaloniki	Claus, TGT, degas	40 t/d	Siirtec Nigi	n.a.	New	20
INDIA							
HPCL	Vishakhapatnam	Claus, SCOT	2 x 450 t/d	Comprimo	Petrofac	New	20
IOCL	Panipat	Claus, LT-SCOT	465 t/d	Comprimo	n.a.	New	202
IOCL	Panipat	Claus, TGT	225 t/d	PROSERNAT	n.a.	New	20
IOCL	Mathura	Claus, TGT	2 x 425 t/d	PROSERNAT	n.a.	New	20
IOCL	Bongaigon	Claus, TGT	20 t/d	PROSERNAT	n.a.	New	202
IOCL	Bathinda	Claus, TGT	750 t/d	PROSERNAT	n.a.	New	20
INDONESIA							
Pertamina	Balongan	Claus, NH <sub>3</sub> , H <sub>2</sub> , amine, TGT	1,100 t/d	Wood Group	n.a.	New	n
IRAQ							
Turkish Pet Int	Mansuriyah	Claus, amine	230 t/d	Comprimo	n.a.	New	20
JAPAN							
JXTG	Mizushima	SuperClaus	2 x 175 t/d	Comprimo	n.a.	Revamp	202
JXTG	Kawasaki	SuperClaus	2 x 146 t/d	Comprimo	n.a.	Revamp	20
JORDAN							
JPRC	Zarqa	Claus, SCOT	2 x 250 t/d	Comprimo	n.a.	New	202
KUWAIT							
KNPC	Al Zour Refinery	Claus	1,500 t/d	Wood Group	Comprimo	New	202
KOC	JPF	Claus, TGT	2 x 100 t/d	Siirtec Nigi	Schlumberger	New	20.
KOC	JPF	SmartSulf	2 x 100 t/d	PROSERNAT	PROSERNAT	New	20
KNPC	Mina al Ahmadi	Claus, amine, TGT	2 x 100 t/d	Comprimo	n.a.	New	202
MALAYSIA							20
MRC	Melaka	SuperClaus	220 t/d	Comprimo	n.a.	New	202
Petronas	Johor	SuperClaus	3 x 470 t/d	Comprimo	n.a.	New	202
MEXICO							
PEMEX	Cadareyta	SmartSulf, NH <sub>3</sub>	132 t/d	Comprimo	na	New	On ho
PEMEX	Tula, Hidalgo	EuroClaus	3 x 640 t/d	Comprimo	n.a.	New	20
		LUIUGIAUS	J X 040 L/U	COMDITINO	11. <b>a</b> .	INC W	20.

#### KEY

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AGRU = Acid gas removal unit BTX = BTX destruction Fuel = Fuel gas supplemental burning  $H_2$  = Hydrogenation  $O_2$  = Oxygen enrichment  $NH_3$  = Ammonia destruction

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SRU = Sulphur recovery unit SWS = Sour water strip TGT = Tail gas treatment unit n.a = Information not available

Note: From April 2019, ComprimoParsons acquired Comprimo' Energy, Chemicals and Resources line of business. Since then all sulphur technologies from both ComprimoParsons Sulphur Group and Comprimo Comprimo Sulfur Solutions are marketed as Comprimo.

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**BCInsight** 

Operating company	Operating site	Process type	Total new capacity	Licensor(s)	Lead contractor	Project type st	Planne artup dat
NETHERLANDS							
Total/Lukoil	Zeeland	SWS	n.a.	Wood Group	Wood Group	Revamp	202
BP Raffinaderij	Rotterdam	Claus, LT-SCOT, SWS	2 x 100 t/d	Comprimo	n.a.	New	202
NIGERIA							
Dangote Oil	Lekki Refinery	SuperClaus	2 x 115 t/d	Comprimo	n.a.	New	201
OMAN	2010.0.100.000		2 / 110 / 4	compilito			
0000	Duqm Refinery	Claus H SW/S amina	2 x 255 +/d	Comprime	Taaniaaa Daunidaa	Now	202
		Claus, H <sub>2</sub> , SWS, amine	3 x 355 t/d	Comprimo	Tecnicas Reunidas	New	202
PERU							
Repsol	La Pampilla	2 x Claus, NH <sub>3</sub> , O <sub>2</sub> , H <sub>2</sub> , amine, TGT	37 t/d	Wood Group	n.a.	New	n.
QATAR							
Qatar Petroleum	Mesaieed	AGE, Claus, TGT	310 t/d	Comprimo	n.a.	Revamp	201
RUSSIA							
Bashneft	Ufa	Amine, SWS	n.a.	Wood Group	n.a.	New	202
Gazpromneft	Moscow	LPG treat, amine	n.a.	Wood Group	Wood Group	New	201
Lukoil	Volgograd	NH <sub>3</sub> , H <sub>2</sub> , amine, TGT, D'GAASS	2 x 76 t/d	Fluor	n.a.	New	201
Lukoil	Kstovo	Claus	240 t/d	KT-Kinetics Tech	KT-Kinetics Tech.	New	202
Rosneft	Novokuibyshev	Claus, NH <sub>3</sub> , amine	2 x 192 t/d	Comprimo	n.a.	New	201
Rosneft	Saratov	EuroClaus	283 t/d	Comprimo	UOP	New	202
Taneco	Nizhnekamsk	Claus, TGT	3 x 410 t/d	Comprimo	n.a.	Revamp	202
SAUDI ARABIA			7				
PetroRabigh	Rabigh	EuroClaus	3 x 292 t/d	Comprimo	KT-Kinetics Tech.	New	202
Saudi Aramco	Tanajib Gas Plant	Claus, $O_2$ enrich, amine	3 x 1,000 t/d	Comprimo	Tecnicas Reunidas	New	202
Saudi Aramco	Jafurah Gas Plant	Claus, $0_2$ enrich, amine	3 x 350 t/d	Comprimo	Samsung	New	202
Saudi Aramco	Fadhili Gas Plant	n.a.	6 x 667 t/d	Wood Group	Petrofac	New	202
Saudi Aramco	Khursaniyah Gas Plant	O <sub>2</sub> enrich	5 x 1037 t/d	Comprimo	n.a.	Revamp	202
SAMREF	Yanbu Al Sinaiyah	Claus, Flexsorb	2 x 480 t/d	Comprimo	n.a.	New	202
SERBIA							
NIS	Pancevo Refinery	Claus, NH <sub>3</sub> , amine	170 t/d	Comprimo	n.a.	Revamp	202
SINGAPORE	,	, 3,	,	•		· · ·	
SRC	Jurong Island	Claus, $O_2$ enrich, $NH_3$	145 t/d	Comprimo	n.a.	Revamp	On Ho
SRC	Jurong Island	SuperClaus	2 x 65 t/d	Comprimo	n.a.	Revamp	201
ExxonMobil	Pulau Ayer	SuperClaus	400 t/d	Comprimo	n.a.	New	201
Linde Gases	Jurong Island	Claus, amine	undisclosed	Comprimo	n.a.	New	202
SOUTH AFRICA							202
Chevron	Cape Town	Claus, SCOT	2 x 45 t/d	Comprimo	Fluor	Revamp	2019-2
SOUTH KOREA				Somplino		torump	2010 2
Hyundai	Daesan	$O_2$ enrich	410 t/d	Comprimo	n.a.	Revamp	201
	Succur		110 y u	Somplino		Revenip	201
THAILAND	Srirooho Dofinera			Comprime	Wood Crown	Now	000
Thai Oil	Sriracha Refinery	Claus, NH <sub>3</sub> , Flexsorb	2 x 837 t/d	Comprimo	Wood Group	New	202
TURKEY							
STRAS	Aliaga/Izmir	SRU, TGT, amine, SWS	463 t/d	KT-Kinetics Tech.	•	New	201
Tupras	Izmir	Degas	240 t/d	Comprimo	n.a.	New	202
Tupras	Izmit	EuroClaus	240 t/d	Comprimo	n.a.	New	202
Tupras	Kirikale	EuroClaus	135 t/d	Comprimo	n.a.	New	202
TURKMENISTAN							
Turkmenbashi Oil	Turkmenbashi City	SuperClaus	25 t/d	Comprimo	Hyundai	New	Delaye
UGANDA							
	n.a.	Claus, HCR	7 t/d	Siirtec Nigi	n.a.	New	201

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Operating company	Operating site	Process type	Total new capacity	Licensor(s)	Lead contractor	Project type sta	Planned rtup date
UNITED ARAB EN	MIRATES						
Al Hosn Gas	Shah	n.a.	4 x 1,250 t/d	Fluor	Wood Group	New	2023
Takreer	Ruwais	n.a.	n.a.	n.a.	Wison Engineering	Revamp	2021
UNITED KINGDO	M						
Eni	Point of Ayr	Claus, amine, TGT	n.a.	Comprimo	n.a.	Revamp	2019
UNITED STATES	VIRGIN ISLANDS						
Limetree Bay Terminals	St. Croix	Degas	2 x 200 t/d	Comprimo	n.a.	Revamp	2020
UZBEKISTAN							
Mubarek	Mubarek Gas Plant	Claus, amine	1,000 t/d	Comprimo	n.a.	New	2020
VENEZUELA							
PDVSA	Puerto La Cruz	Claus, amine	2 x 225 t/d	Comprimo	Hyundai, Wison	New	2019
VIETNAM							
Bin Son Refinery	Dung Quat	Claus, SCOT, TGT, SWS	2 x 105 t/d	Comprimo	Wood Group	New	2019

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AGRU = Acid gas removal unit BTX = BTX destruction Fuel = Fuel gas supplemental burning  $H_2$  = Hydrogenation  $O_2$  = Oxygen enrichment NH<sub>3</sub> = Ammonia destruction SRU = Sulphur recovery unit SWS = Sour water strip TGT = Tail gas treatment unit n.a = Information not available

Note: From April 2019, ComprimoParsons acquired Comprimo' Energy, Chemicals and Resources line of business. Since then all sulphur technologies from both ComprimoParsons Sulphur Group and Comprimo Comprimo Sulfur Solutions are marketed as Comprimo.



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# Degradation of chemical additives under downhole conditions

When producing from shale reservoirs, technologies such as horizontal drilling and hydraulic fracturing have been used successfully to access hydrocarbons that otherwise could not be. A less publicised issue in producing from certain hot shale gas reservoirs (T > 100°C) is the presence of  $H_2S$  and organo-sulphur compounds in the production fluids. In trying to understand the non-biogenic sources of  $H_2S$ , Alberta Sulphur Research Ltd has been involved in studying the decomposition of chemicals used in hydraulic fracturing when exposed to high temperature and high pressure. **R.A. Marriott, J.J. Marrugo-Hernandez** and **R. Prinsloo** of ASRL discuss the findings of the study.

ossil fuels, at present, provide around 85% of the world's energy need<sup>1</sup>. At the same time, energy demand is expected to grow worldwide by an average of 1.2%. As such,  $CO_2$  emissions could increase by 30% by 2030, even if the increases in energy efficiency and the intensification in renewable and nuclear energy is accounted for. Consequently, to sustain the energy demand, industry is continuously exploring alternative fuels which can help drive down the carbon footprint. Among the multiple alternatives, natural gas appears to meet the short term requirements in helping to lower  $CO_2$  emissions.

Natural gas can be found in conventional and unconventional reserves<sup>2</sup>. While conventional plays have been extensively explored, drilled and produced successfully in the last century, the more challenging unconventional plays have only emerged in the last 20 years<sup>3</sup>. The late exploration and production of shale plays have coincided with the advancement in combined technologies of horizontal drilling and hydraulic fracturing, leading to economically feasible extraction of natural gas.

Hydraulic fracturing fluid is a combination of water, proppant (approximately 10%) and chemical additives (0.5-3%). Each additive is incorporated into the fracturing fluid to achieve a desired result, be it corrosion inhibition, anti-foaming, lubrication, among others and it is specifically formulated for a selected well. Two wells within the same reservoir

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could be fractured with different additives (different fracture packages), as physical and chemical conditions are known to vary within wells producing from the same reserves. Many of the chemicals used for fracturing applications in the US and Canada have been disclosed to the public via online databases such as Fracfocus. While the list of chemicals is quite extensive and many of them have been widely applied in multiple processes, the degradation and possible reactivity under downhole conditions is still unknown.

Although native shale gas is often regarded to be sweet (low  $H_2S$ ); in reality, shale gas can contain tens to several hundred parts per million of native hydrogen sulphide ( $H_2S$ ). However, when producing from hot shale reservoirs (T > 100°C), the  $H_2S$  levels have been reported to increase once production is ongoing for a few months. This is particularly challenging for producers who are required to treat gases with variable concentration of  $H_2S$ .

Anecdotal field evidence shared with the authors suggests that shale gas can show an increase in total sulphur concentration in the gas phase, from undetectable levels to percent levels over the course of several months.

ASRL's research group has been studying the degradation of chemical additives under downhole conditions for several years<sup>4,5,6,7,8</sup>. Initially, the decomposition of sulphurcontaining surfactants, corrosion inhibitors and biocides were investigated. Under high temperature and high pressure, several of these additives were capable of producing hydrogen sulphide and organo-sulphur compounds through various mechanisms<sup>9</sup>.

In trying to better link the degradation of sulphur-containing additives with the delayed souring of shale gas, ASRL has come to realise that the water used for hydraulic fracturing is not degassed and is saturated with oxygen at field conditions. Consequently, during fracturing, the oxygen present in the fluid can rapidly react with native  $H_2S$  producing elemental sulphur at downhole conditions (reaction 1). Once the elemental sulphur is generated, it can react with geogenic or anthropogenic hydrocarbons present in the reservoir (reaction 2).

#### **Chemistry occurring at downhole conditions**

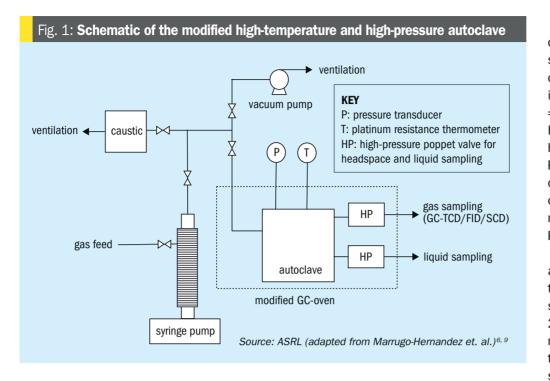
- $0_2 + 2H_2S \rightarrow 2S^\circ + 2H_2O \tag{1}$
- $2S^{\circ} + C_{X+2}H_{2X+6} + H_20 \rightarrow 2H_2S + 2CO_2 + C_XH_{2X+2}$ (2)
- $O_{2} (aq) + \frac{1}{3}C_{X+2}H_{2X+6} \rightarrow \frac{2}{3}H_{2}O + \frac{2}{3}CO_{2} + \frac{1}{3}C_{X}H_{2X+2}$ (3)

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When combining both reactions 1 and 2 (reaction 3), it can be seen that the oxygen present in the fracturing fluid can temporarily scavenge the native  $H_2S$ and regenerate it later when reacting with hydrocarbons. As such, by studying the H<sub>2</sub>S formation kinetics of sulphuroxidation reactions involving chemical additives, the understanding of the chemistry occurring at downhole conditions can be enhanced to explain better the shale gas souring observed on the fields. In the study presented here, six commonly used chemical additives were selected (due to their higher disclosure rate and variable organic functional groups) and reacted with elemental sulphur at various

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downhole conditions. The  $H_2S$  concentration was measured over time, and kinetic parameters of each additive were determined. All six additives were used individually and later combined as a mixture when reacting with elemental sulphur.

#### **Materials and methods**

All the additives and phosphoric acid (85 wt-%) were purchased from Sigma-Aldrich. The water was polished to a resistivity of 18.2 M $\Omega$ ·cm (EMD Millipore model Milli-Q type 1) and then degassed under vacuum for a minimum of 12 hours. Control of pH was achieved by the addition of 25 mM phosphate buffers.

Experiments were completed in an overhead-stirred 50 mL autoclave (316 stainless steel, fully protected with a corrosion-resistant tantalum film) with operating conditions up to p = 24.1 MPa and T = 300°C, previously described by Marrugo-Hernandez et al (Fig. 1)<sup>10</sup>. The system was held isothermally by a modified Hewlett-Packard 5890 GC oven. The temperature of the system was measured by two 100 ohm, four-wire platinum resistance thermometers connected to a Pico Technology PT-104 data logger.

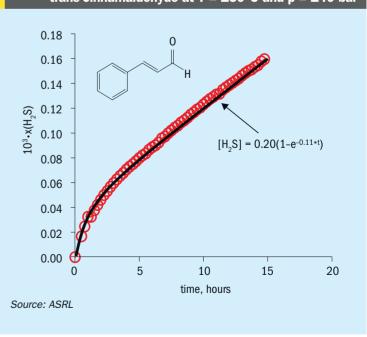
The high purity  $N_2$  gas was delivered and used to maintain constant pressure throughout the experiment via a high-pressure syringe pump (Teledyne ISCO Model 260D). The pressure in the system was monitored by a Keller PA-33X pressure transducer. The sampling of the headspace gas was automatically controlled by a high-pressure poppet valve (HP). When sampling, the HP valve was opened for 100 milliseconds, permitting the release of an aliquot of the high-pressure gas from the headspace to flow into the online gas chromatograph.

Before running the experiments, each additive was prepared to a concentration of 500 ppmw. The reactor was loaded with 50 mL of the mixture (water + additive + buffer) and the required amount of elemental sulphur.

The reactor was then pressurised and heated up to the target pressure and temperature. During the reaction high-pressure and high-temperature gas aliquots were withdrawn, and gases concentration were

hemical additive	Chemical structure	k'H₂S
innamaldehyde	O H	0.11 ± 0.01
Benzoic acid	ОН	0.12 ± 0.01
ropargyl alcohol	<i>М</i> ОН	$1.22 \pm 0.02$
thyl acetate		0.34 ± 0.02
ropylene carbonate		1.25 ± 0.01
-butoxyethanol	ОН	$1.15 \pm 0.01$

Fig. 2: **H<sub>2</sub>S evolution for the sulphur oxidation of** trans-cinnamaldehyde at T = 150°C and p = 140 bar



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quantified on regular time intervals via the online GC coupled with thermal conductivity detector (TCD), flame ionisation detector (FID) and a sulphur chemiluminescence detector (SCD).

#### **Results and discussion**

The six common chemical additives are highlighted in Table 1 with their respective chemical structures and corresponding rates. These chemicals were selected based on the study of Sumner and Plata, in which a spatial statistical analysis was performed on all the publicly available databases, and a list of the most frequently used additives was constructed<sup>11</sup>. Note that the compounds selected for this study did not contain any halogen atoms, to avoid possible formation of corrosive chlorine or bromide.

When reacting the chemical additives with elemental sulphur at high-temperature  $(125^{\circ}C \le T \le 175^{\circ}C)$  and high-pressure (p = 140 bar), the only species observed in the gas phase were  $H_2S$  and  $CO_2$ . Note that no organo-sulphur species were detected as by-products for the additives used in this study.

As the reaction progressed, the change in the concentration of these species (H<sub>2</sub>S and  $CO_2$ ) over time was monitored. Once finalised, one can obtain the H<sub>2</sub>S evolution graphs for each compound (Table 1). With the data obtained from the evolution plots one can fit a first-order product generation equation ([H<sub>2</sub>S] =  $\alpha$ (1-e<sup>-kH<sub>2</sub>St</sup>)) and therefore, obtain various kinetic parameters such as the  $H_2S$  formation rate constant (k $H_2S$ ).

In Fig. 2, the  $H_2S$  evolution plot is shown for the sulphur dehydrogenation reaction of trans-cinnamaldehyde.

The solid line corresponds to a firstorder product formation. Each chemical additive was reacted individually with elemental sulphur at T = 150°C and p = 140bar and the H<sub>2</sub>S kinetic parameters are listed in Table 1.

Note that Fig. 2 shows a pseudo rate up to 15 hours, where the reaction has a constant concentration of soluble sulphur (sulphur is in excess of saturation). Once the sulphur is no longer in excess, the rate decreases with decreasing sulphur concentration. The kinetic parameters in Table 1 are reported for the early portion of the plot, where they are considered pseudo first order (k' =  $kK_{satn}[S_8]$ )

These additives can be arranged in decreasing order as follows: propylene carbonate > propargyl alcohol > 2-butoxyethanol >

benzoic acid > cinnamaldehyde. This trend follows the water solubility of these compounds, and it could be inferred that the higher the solubility (more hydrophilic), the faster the dehydrogenation reaction with elemental sulphur was at downhole conditions. Note that it is possible that the chemical additives first undergo hydrolysis and the hydrolysis products are dehydrogenated by elemental sulphur at downhole conditions.  $H_2S$  formation is unlikely to occur in a single step. This could explain why the higher the solubility, the faster it generates  $H_2S$ .

The sulphur mass balance of these experiments was found to be lower (50% to 65%) when compared to previously studied systems. When accounting for the carbon mass balance it was found that the numbers were less than 10% of the loading for all the chemical additives studied. However, CarSul (carbon-sulphur polymers) formation was evident once the reactor was cooled to room temperature and cleaned for subsequent experiments. CarSul formation could impact production as it could damage the reservoir and limit future production.

Finally, the results illustrate that certain chemical additives used for hydraulic fracturing can react with elemental sulphur at downhole conditions and generate H<sub>2</sub>S. It is essential to highlight that shale plays have variable bottom-well temperatures (variability in well depth), therefore changing the kinetics of the H<sub>2</sub>S being formed by this mechanism. In lower temperature wells, a slower reaction would be expected in comparison to a hotter well. Consequently, it would take longer for the H<sub>2</sub>S concentrations to reach a significant level in colder wells. Although these results exemplify one of the multiple mechanisms by which a shale well could sour, the overall souring of a shale well could be a combination of multiple mechanisms, due to the complex nature of these chemical processes.

#### Conclusions

The sulphur dehydrogenation reaction with six chemical additives (propylene carbonate, propargyl alcohol, 2-butoxyethanol, benzoic acid, cinnamaldehyde) resulted in variable amounts of H<sub>2</sub>S, CO<sub>2</sub> and CarSul at downhole conditions. The H<sub>2</sub>S formation rate was determined for all six additives and was found to follow the water solubility trend. Finally, it is essential to bear in mind that the fracturing fluids are composed of hundreds of chemical additives, and each chemical can potentially be hydrolysed or dehydrogenated by elemental sulphur. Therefore, one can expect a much more complex mixture, where multiple chemical reactions could contribute to the total H<sub>2</sub>S being generated. Therefore, future research in this area is expected.

#### Acknowledgement

The authors are grateful to the member companies of ASRL and for Discovery Grant support from the Natural Science and Engineering Research Council of Canada (NSERC). Juan J. Marrugo-Hernandez is grateful for support from the Vanier Program.

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# **Upgrade of Claus TGTUs**

BASF has developed a new generation of promoter system compatible with MDEA solutions named OASE® yellow. The new promoter system increases the selectivity and capacity of the amine solvent, resulting in improved performance of tail gas treating units and allowing the processing of more sour crudes. A. Kern and G. Vorberg of BASF discuss two case studies demonstrating the benefits of OASE yellow.

efinery sulphur recovery units (SRUs) are faced with the challenge of processing increasingly sour crudes, while maintaining, or even reducing, the level of sulphur emissions.

Higher sulphur loads need to be treated by the Claus process and its tail gas treatment section. As a first measure, operators are exploring various ways to improve the performance of the SRU without incurring the additional costs required for revamping.

Replacing the common MDEA-based amine solution in the Claus TGTU can provide a very cost-effective option, not only reducing emissions, but also allowing significant opex savings as illustrated in this article.

#### **MDEA-based amine solvent in TGTUs**

Methyl-diethanolamine (MDEA) is a tertiary amine, widely used in SRU TGTUs because of its natural selectivity towards the removal of  $H_2S$ . However, it is reaching its limits for more advanced acid gas removal requirements.

First generations of promoter systems (mainly comprising inorganic acid compounds) have been introduced. This socalled "acidification" of MDEA reduces the pH value of the amine solution, which is beneficial for the regeneration step, but has a negative effect on the absorption capacity of the amine. It allows a lower residual acid gas lean loading of the amine. As a result, lower H<sub>2</sub>S concentrations and therefore sulphur emission reduction is achievable at lower reboiler duties for regeneration.

However, acidified MDEA is lacking with regard to absorption capacity and can lose its benefits when more sour crude is being processed in the refineries leading to much higher sulphur loads to the SRU and the respective tail gas sections. In addition,

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Table 1: <b>Performance gain</b>	by selectiv	/e MDEA-based	l amine form	ulations in TGTUs
	Reboiler duty	Sulphur specification	Amine circulation rate	Operation at high lean amine temperatures
MDEA plain				
Formulated/acidified MDEA	r	r	-	x
OASE yellow (MDEA based)	r	r	t	$\checkmark$

such systems are more prone to corrosion incidents due to the (too) low residual acid gas lean loading of the amine adversely affecting the corrosion protective layers build up during plant operation.

To overcome these constraints, BASF has developed a new generation of promoter system compatible with MDEA solutions, named OASE yellow, providing an amine solvent with high selectivity and high capacity.

An overview of selective MDEA-based amine formulations available and used in tail gas treatment units is shown in Table 1.

Reduction of reboiler duty for the regeneration of the amine solution translates into opex savings. Reduction of the amine circulation rate also translates into opex savings with regard to the power consumption of the amine pumps.

The new generation, high selectivity, high capacity MDEA formulation can offer both.

#### Case studies

The following two case studies demonstrate the benefits of running the TGTU on the new high selectivity and high capacity amine solvent after successful introduction of the innovative OASE yellow promoter to existing MDEA systems.

Both conversions are carried out during 100% plant load, meaning no plant shutdown and no process interruption.

#### Case study 1 – A German refinery

This case study describes a commercial refinery TGTU, previously running on MDEA, which converted to OASE yellow with the aim to reduce sulphur emissions.

The tail gas to the amine absorber has a  $H_2S$  content of 1.2 vol-% and a  $CO_2$  concentration of around 30 vol-%

Within a timeframe of 72 hours the OASE yellow promoter was dosed into the TGTU amine loop by using a small dosing pump. While the unit was running at full capacity, new operational settings were adjusted accordingly, and the process was optimised.

The effect of the amine conversion was visible instantaneously: The H<sub>2</sub>S concentration in the treated gas leaving the amine absorber and passing to the flare decreased from 90 ppmv (start of the OASE yellow promoter addition) down to 15 ppmv (end of the OASE yellow promoter addition).

Overall, the SO<sub>2</sub> emission of the SRU TGTU system was reduced by 80%.

In parallel, the increased specific absorption capacity of the solvent allowed the amine circulation rate to be reduced by >25%. Fig. 1 summarises these findings.

In a later optimisation stage, the lean amine temperature was raised to the feed gas temperature in order to achieve an almost neutral water balance and subsequently no reflux bleed stream. The amine losses were thereby much reduced.

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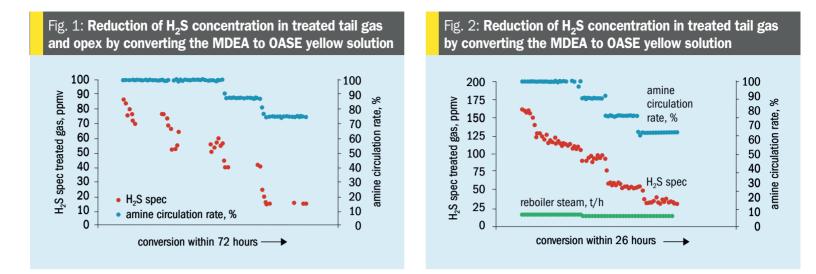
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#### Case study 2 – A Korean refinery

In this case study a commercial refinery TGTU previously running on acidified MDEA solution was converted to OASE yellow with the aim to reduce opex costs.

Due to oxygen enrichment in the burner operation of the sulphur recovery unit, the tail gas to the amine absorber has a high  $H_2S$  content of 6.8 vol-%. The  $CO_2$  concentration is 3.5 vol-%.

When processing more sour crude the sulphur emission can exceed the maximum emission levels allowed. This can happen especially during hot summer months when lean amine temperatures are increasing (e.g. due to limited air cooler duty) leading to violation of the TGTU treated gas  $H_2S$  spec. The OASE yellow system shows little temperature sensitivity providing another advantage compared to MDEA solutions.

Before OASE yellow promoter was introduced to the TGTU amine loop, the treated off gas going to the stack had an  $H_2S$  concentration of 165 ppmv. The flow rate of tail gas to the absorber was 10,030 Nm<sup>3</sup>/h.

The conversion was completed within 26 hours and the  $H_2S$  concentration in the off-gas dropped to 35 ppmv. Meanwhile, the amine circulation rate was reduced by >30%. Fig. 2 is illustrates the conversion process.

In a second step, following the conversion, the optimisation phase started focusing on opex savings. A key driver for lower energy consumption and related cost is the reduction of the low-pressure steam used to regenerate the amine solution.

Without changes in the gas flow rates and its composition, the steam flow to the reboiler was step-wise reduced starting with 9.4 t/h. This in turn increased the  $H_2S$  concentration in the treated tail gas. However, the  $H_2S$  spec of maximum 150 ppmv can still be achieved while significantly reducing steam flow to 5.5 t/h. This translates into an outstanding steam saving of 4 t/h (-40%).

In addition, since the conversion of the amine system the plant has been able to run at 5-10 K higher lean amine temperatures, while still achieving the  $H_2S$  spec. In combination with the reduced amine flow rate, total lean amine cooling duty has been lowered to such an extent that the lean amine air cooler is no longer required and the plant is running a small amine water cooler in its place.

Fig. 3 summarises provides data for the optimisation process following the amine conversion.

#### **Results and discussion**

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The upgrade i.e. conversion of the amine inventory can be carried out at any time while the TGTU system is in full operation and does not require a shutdown.

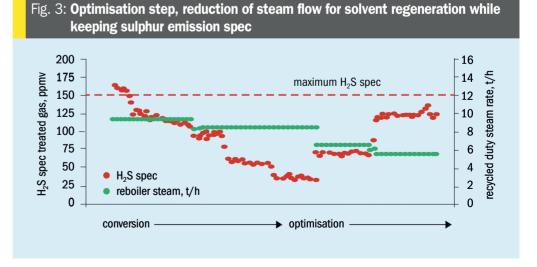
In order to follow more stringent environmental regulations, some TGTU systems have incorporated a caustic wash unit downstream of the tail gas absorber. By doing so, the sulphur emission issue is in effect converted into a wastewater treatment task. Running a caustic wash unit is also an added cost and increases plant complexity. Application of an innovative, highly selective and high capacity solvent, such as OASE yellow, may allow the caustic wash unit to be mothballed.

Both case studies showcase the performance gain of existing TGTUs that have been converted to the new solvent. The same benefits also apply to new TGTUs. In addition, a grassroots design will be smaller in size, therefore resulting in lower capex.

#### Conclusion

OASE yellow solvent can reduce the operational cost and sulphur emissions of Claus TGTUs compared to plain MDEA or formulated (acidified) MDEA solutions. Alternatively, the capacity gain of OASE yellow can also be used to increase the SRU load and TGTU throughput.

Keeping the existing amine inventory of the tail gas unit means no disposal of material is necessary, which is both economic, and very environmental-friendly.



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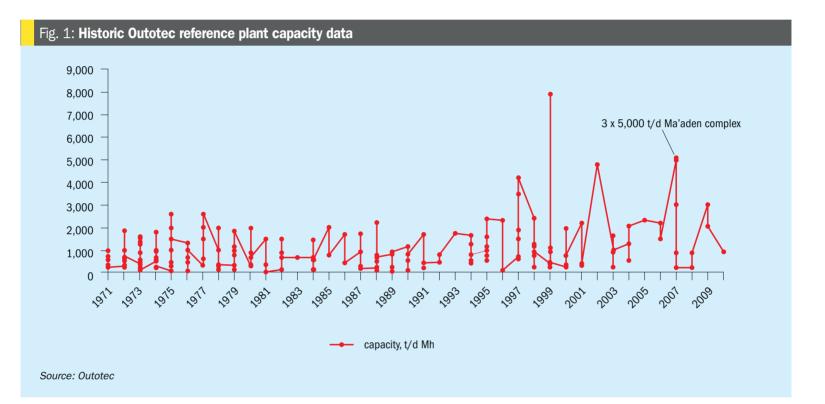
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# Design challenges of mega acid plants

What are the limits for future single stream sulphuric acid plant capacities? **H. Storch**, **C. Bartlett, and S. Mohsler** of Outotec discuss design considerations for large capacity sulphuric acid plants with reference to the world's largest acid plants built to date.



istorical data of the capacity of sulphuric acid plants built by Outotec within the last 40 years reveal a trend to larger capacity plants. Fig. 1 shows the capacity of Outotec designed plants since 1971, displaying an obvious growth in average plant capacity over the years.

Among the reasons for the upward trend are a general growth of project dimensions, e.g. mega fertilizer complexes such as the Ma'aden project, which have a high demand of sulphuric acid as a base component of the final product. Further reasons for the increase in requested plant size can be found in economic requirements based on the economies of scale. The cost impact of plant size cannot be considered to be linear, but rather follows a power function with exponents between 0.6 and 0.85, as shown in Fig. 2. This easily demonstrates why more and more plants are constructed with a larger capacity, as the specific costs are lowered.

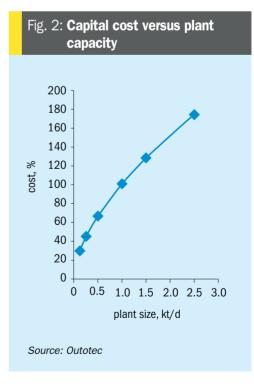
Obviously, one main driver is economy of scale and even this goes in hand with certain operational limitations, the financial benefit of these "mega" plants triggered the industry to install such units. One prominent example for mega-plants is the Ma'aden/Saudi Arabia acid plant complex where three plants of 5,000 t/d capacity each have successfully passed their performance testing in 2012 and since then have been in operation at full capacity. These are the world's largest single train sulphuric acid plants running at consistent capacity and thus can be regarded as state of the art for Outotec technology and the industry benchmark at large.

It has been noted that the industry is now asking for capacities beyond the proven 5,000 t/d capacity and Outotec as designer

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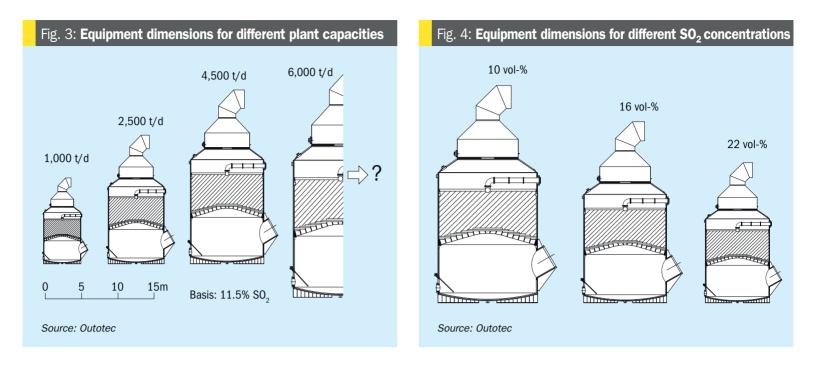
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of such plants is of the firm opinion, that larger single stream capacities are possible. Yes, there will be technical challenges and some new thinking will be required, but some of the solutions for key issues are already invented and some of these aspects are discussed below. The level of digitalisation of such plants will also play a vital part of operational feasibility of this kind of plant.

### Process and mechanical considerations

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The process design, as a first step, is the basis for the subsequent engineering phases and various project execution stages. With the process parameters fixed, it is possible to proceed with equipment sizing and design, which again impacts the following steps of construction, fabrication and transportation. Of course, there are limits to be kept in mind such as size limitations of certain equipment which essentially can be traced back to mechanical stability or gas and liquid distribution challenges. Another valid point is the changing characteristic of flow dynamics which can differ vastly for different equipment sizes. These issues are presenting a connection between process and mechanical design, which has to be in constant information exchange to prevent any of the aforementioned problems.

The initial challenges for even larger capacities are related to key aspects, such as gas distribution, mechanical integrity of equipment and ultimately OEM supply of process equipment, such as blowers, etc. There is however a secondary level of challenges that are not considered as the industry drives towards an ever lower investment cost per tonne of acid produced. These issues relate to the operability, turndown/ fluctuating load conditions, particularly relating to metallurgical acid plants, which historically have proven to be solved.

For the process design of sulphuric acid plants, two of the main parameters available to react to these requirements are gas velocities in the process equipment and ducts, as well as the  $SO_2$  concentration of the process gas. The effect of equipment dimension increase for different plant capacities is shown in Fig. 3.

Based on the trend to larger plants, it is shown how the size of e.g. an absorption tower is expected to evolve for larger capacity plants. It is obvious that there is a limit to equipment size increasing as a reaction to the increasing capacities requested. For further increases in capacity it might be necessary to adjust other process values or refine mechanical designs. As an example for mechanical design customisation, the number of gas inlet nozzles to the towers can be regarded as a variable. With increasing air flows it may be preferential to facilitate the gas distribution in the lower part of the towers by adding a second gas inlet nozzle. Further measures can include a design change to a combi-absorber, with a two-staged absorption, first in a venturi and then in a packed bed.

Fig. 4 shows the effect of changing one of the process design means available. With rising  $SO_2$  concentrations it is again possible to drastically reduce equipment sizes. Of course, not all the equipment in a sulphuric acid plant allow for such high  $SO_2$  concentrations, unless a special process is selected, such as Outotec's

ISSUE 388 SULPHUR MAY-JUNE 2020 LUREC<sup>™</sup> process. Nevertheless, with the "standard" double absorption process it is at least possible to reduce equipment dimensions in certain plant areas.

#### **Future considerations**

When considering larger units, some restrictions must be observed, which potentially constitute major hurdles, but subject to the design, can be overcome. Some examples are discussed below:

There are no restrictions in the wet gas cleaning section, as multiple parallel units are already common practice in the industry.

Two parallel main  $SO_2$  blowers are currently used in large plants. Larger single blowers are available on the market and hence this is not a restriction to design larger capacity acid plants even beyond 8,000 t/d.

As the gas throughput increases with acid output capacity, the vessels, particularly the SO<sub>2</sub> converter, will significantly increase in size. While the impact on the mechanical design of very large vessels can be managed using modern design tools, the uniform distribution of gas to the individual catalyst beds becomes a more challenging issue. Outotec's radial flow converter with integrated heat exchangers is perfectly suitable for such enlargement in capacity. In Fig. 5 an outline of a modern five bed converter for processing of metallurgical off-gas is presented and the radial gas distribution from the centre to each bed is shown. Each of the converter beds is thus fed radially with the gas originating from the converter core. Thus the gas must not "travel" the entire diameter of the converter, as is the case with a conventional

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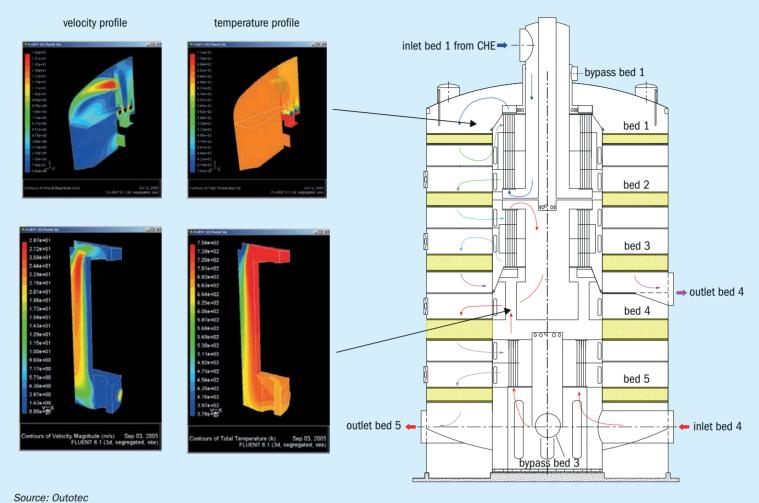
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#### Fig. 5: Radial flow converter and CFD modelling

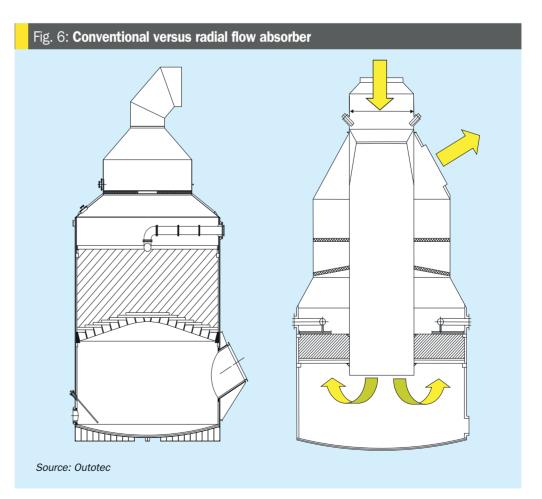


lateral gas inlet, but only the radius and hence the superior distribution quality. Nevertheless, in "mega" plants gas distribution is a challenge and that will become ever greater, requiring additional measures in the converter design.

Large absorption towers of conventional design have been built up to 12 m diameter, which would theoretically be suitable for acid plant capacities around the 6,000 t/d level. However, also here the issue of uniform gas and liquid distribution becomes paramount.

While a variety of liquid distributors designs are available and well proven, the gas distribution has been widely disregarded as a critical issue in the past and was overcome by conservatively designed tower packing. CFD simulations have demonstrated that larger towers with high efficiency internals cannot tolerate the conventional single lateral gas inlet, even when this is split into two nozzles. Since the 1970s, Outotec has built a number of towers using the same principle as applied for the converter, i.e. radial gas distribution. Fig. 6 illustrates the schematic

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Fig. 7: Shop fabrication of absorption tower parts and transportation of the compete upper portion.

design of such a unit (the design can be one or two stage).

### Fabrication, transport and construction

The degree of pre-fabrication of equipment generally has to be considered according to the final equipment size, weight and plant location (including cost/availability of logistics).

Pre-fabrication is often limited by the size of equipment parts, in order to still allow for later transport to site. Fig. 7 shows the shop fabrication of the upper part of absorption towers including the candle filter tube sheet, with transportation to site after being joined with the upper part of the towers.

Another aspect apart from size and weight limitations for transport to be considered when prefabricating equipment, is the decrease of structural integrity with growing equipment dimensions. It is often necessary to include additional reinforcements for the transport and construction phase to maintain the exact equipment dimensions, e.g. the sphericity as shown in the converter construction in Fig. 8.

Generally, it should be considered that fabrication tolerances increase with increasing part dimensions. This fact might lead to a higher workload on site when parts to be joined are at their tolerance extremes and need additional site fitting to allow for the proper erection of the equipment. Further

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aspects of large prefabricated equipment include higher cost for transport due to oversized loads and exceptional convoys, as the equipment is usually not fabricated in the country of destination.

Many plants are situated at locations without a direct connection to freight ports, further adding to the transport/logistical costs. Longer transport durations are therefore to be expected compared to shipment of semi-finished products, which might fit into standard transport containers. This time critical aspect needs special attention, particularly in connection with

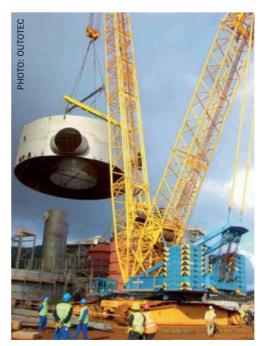


Fig. 8: converter construction at site.

ISSUE 388 SULPHUR MAY-JUNE 2020 lead times of material which is needed for the preceding fabrication step.

All these arguments seem to indicate that on-site fabrication is superior to prefabrication of equipment, but it has to be taken into consideration that often a lack of skilled workers is to be expected on site. Together with missing or inferior production facilities this may lead to quality deficiency or time losses due to e.g. repetition of faulty work. The availability of supervisors and skilled workers for mega projects is often above normal standards due to the impact and importance of such projects for the plant supplier. That said, there is competition between plant suppliers within the complex development for the best resources. Prefabrication and site work must therefore be carefully balanced according to existing experience to maximize the benefits arising from these two approaches.

#### Summary

In summary, Outotec is of the firm opinion that the current largest units with 5,000 t/d capacity do not constitute a limit for future single stream acid plant capacities. Obviously certain design principles will need to be re-introduced into the sulphuric acid industry, but lots of the required elements are already available. If the market demands the next generation of "new mega" plants, plant designers will be ready to offer this next step in technological development.

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# Start-up, shutdown and turndown

With the ongoing changes in gas field and refinery feedstock compositions, many sulphur recovery units around the world are facing turndown scenarios to such an extent that it is difficult to meet stringent environmental regulations. Equipment and instrumentation behave differently under turndown conditions, and not always in ways that are desirable. Start-ups and shutdowns can place demands on the equipment that are more severe than years of normal operation. In this article, Optimized Gas Treating, Sulfur Recovery Engineering and Comprimo share some of their learnings and experiences of these scenarios.

lphur recovery units are designed to meet a specific set of targets given an initial set of premises such as feed flowrates, feed composition, feed temperatures, and pressure. During the design phase, considerations are generally given to different operating scenarios such as varying feed quality, feed rate (turndown), equipment fouling, and catalyst aging to help assess the robustness of the design. However, start-ups and shutdowns arguably cause the most damage to an SRU through thermal cycling of the process equipment, and it is these very conditions that are often overlooked or not given much thought. Thermal cycling affects the reliability of the waste heat boiler (WHB) most notably by degrading the tube sheet system, which includes the refractory, ferrules, the tube sheet itself, the tube-to-tube sheet joints, and the tubes. Through proper design, operating practices, and maintenance procedures, the reaction furnace and WHB system can have life expectancy in excess of 20 years. However, with an inadequate design, poor operating practices, or poor maintenance, it could be as short as two to three years. Being able to model accurately varying feed quality, feed rate, exchanger fouling and catalyst aging can provide better understanding of the effects of these parameters.

#### **Start-up operations**

The initial start-up of a new facility is typically a complicated endeavour with potential risks for problems as all equipment,

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instrumentation and control systems are essentially used for the first time. In addition, very often, the start-up will be done with new operation crews that may or may not have worked together. During the commissioning of the units, a lot of activities will be done to verify the design of the systems, check the equipment, instrumentation, electrical systems and control systems for their readiness for start-up, but there is still the potential for issues to arise during the initial introduction of process and utility streams into the units.

Procedures for starting up an SRU, as it relates to the refractory, vary slightly between bringing an existing unit back online after a shutdown versus a new unit being started up for the first time. In overlysimplistic terms, the following steps are usually taken.

The first step is to light the pilot (if so equipped). Many recent designs feature high energy spark ignition systems that eliminate the need for the pilot. However, this may complicate the heat up procedures. The goal of either a pilot or high energy spark ignitor is to safely establish a main flame on natural gas.

If it is a new unit that has never seen sulphur, or if the refractory is "green", then excess air is typically used to control the rate of refractory heat up per the manufacturer guidelines with regard to the maximum temperature change per hour for the refractory to minimise the potential for refractory thermal shock and consequent damage. Considerations in some jurisdictions for maintaining a tail gas treating unit (TGTU) downstream in operation that is always "coupled" to the SRU may preclude excess air operations to prevent damage to the Co/ Mo catalyst if presulphiding has been previously conducted.

If the unit is being brought back online after processing sulphur previously, then excess air is forbidden in order to prevent sulphur fires. The procedure involves firing natural gas and air at 90% to 95% of stoichiometric at a hydraulic load corresponding to at least 30% of the design operating rate on acid gas. A convenient average hydraulic load for the SRU that is often taken for a basis is the molar flowrate as measured at the outlet of the first condenser. The natural gas will then gradually be replaced with acid gas until the unit is running on only acid gas and air at the 30% design rate.

The third step is to bring in acid gas when the unit is properly heated up and stable.

Most flowmeters start losing accuracy at flows below 25% turndown so setting the limit for start-up at 30% ensures flowrates will be well within the range of most instruments. Having some hydraulic back pressure on the unit also helps to maintain feed gas and air control valves in operable positions. Burner backfiring is a serious issue at turndown because it causes damage to the burner tip which can then lead to an irregular flame pattern, hot spots, and ultimately burning a hole in the reaction furnace wall.

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#### **Shutdown operations**

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Simplistically put, shutdown procedures, can be considered the direct opposite of start-up. The unit is first turned down to approximately 30% of the design rate and the acid gas is replaced with natural gas until the unit is operating on only natural gas, tempering steam and air. This period of operation without acid gas is also referred to as hot standby. The purpose here is to keep the equipment hot and remove the elemental sulphur from the plant equipment, either in preparation for a true shutdown or to keep the system idling.

#### **Turndown operations**

It is normal for an SRU to operate at below design flowrates. More often than not, the initial operating conditions (which include flowrates) change after construction and commissioning, as well as during operation of the unit. Ensuring that the unit will perform adequately under these non-design conditions is crucial to successful operation.

Heat losses from plant equipment also become more significant at turndown, and separations equipment may not perform as advertised either. In a sulphur condenser, for example, fogging has been reported at low mass velocities. Fogging is a phenomenon in which submicron mist is formed in the bulk vapour versus normal film condensation on the condenser tubes This mist is so fine it evades conventional mist elimination devices.

An important part of turndown operations is knowing whether the plant equipment is operating safely and reliably. Here, process simulation can complement plant operations.

#### **Design challenges for turndown** operations

One thing that an SRU is not, is flexible. The fixed design conditions on which the SRU was built fix in turn the maximum and minimum operating rates for the unit. Although there are facilities which have transitioned to operation to as low as 10% of design, most facilities operating below 40% have had significant modifications performed to them in the past. Nonetheless, completing the design modifications can be significantly less costly than the build of a new SRU.

The design challenges associated with an operating, already-designed SRU fall into the following unit operation categories:

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- not meeting environmental regulations, daily/quarterly recovery efficiency guidelines:
- more frequent plugging of the tail gas analyser:
- main burner flame stability is becoming less controlled and burn-back operation is significant.

When faced with turndown, an SRU operator has limited choices, and all options come with an associated financial cost.

From a refinery point of view, many facilities are now switching to low sulphur crudes in order to meet the IMO 2020 bunker fuels rules. This switch will inevitably lead to lower quality acid gases going to the SRU which has already been built for a normal capacity (inclusive of composition and flow rate). When evaluating a variety of crude slates, taking into account all external factors connected to feed decisions, it may still prove to be the economical choice to modify the SRU to handle a sweeter mix of crude grades. In contrast, in the case of a gas plant, the dwindling gas well reserves and variable sour content over time are not a decision to be made, but a factor that must be dealt with.

In all cases, the first step in determining the options is to define the eventual acid gas quality and quantity that is anticipated to be processed by the SRU in the future. From that definition, the study of each individual unit operation can be performed.

When deciding upon the best course of action, it is important to consider not only the current turndown, but also possible or likely changes in future operation and regulation. Any major changes made to a SRU should take into account not only current conditions, but also future conditions that may require further unit changes.

It is likely that regulatory requirements will become more stringent over time, so it is inadvisable to incorporate temporary changes in a SRU that might hinder further improvements that will be required in the near or distant future, resulting in more expensive solutions.

#### Effects of turndown

The primary equipment affected by turndown comprises the:

- reaction furnace:
- converters:
- condensers.

Beyond the effects on these main components, there are multiple ancillary components that must also be considered in order to fully account for the effects of turnover conditions on the SRU as a whole. These include:

- acid gas knock out;
- combustion air blowers;
- air flow control:
- waste heat exchanger: •
- direct fired reheaters;
- incinerator.

#### **Reaction furnace**

The reaction furnace is normally designed for a residence time of 0.8 to 2.0 seconds. This time, in conjunction with temperature. is needed to ensure that all contaminants entering in the SRU with the amine acid gas and the sour water stripper acid gas are destroyed. Under turndown conditions, the reaction furnace temperature becomes an issue. With the large space that exists past the main burner, the combustion gases lose heat very quickly, and at high turndown conditions, an adequate flame temperature, namely 1,050°C for BTX destruction and 1,250°C for ammonia destruction, is difficult to achieve. Furthermore, the lack of acid gas quality, through declining H<sub>2</sub>S content, results in an amine regenerator off-gas that does not possess the necessary Btus to achieve the minimum temperatures for optimal destruction efficiency.

Understanding the flow dynamics during turndown conditions and the changes in formation rates of various compounds are crucial elements in determining the ability of the SRU to meet its environmental license. CFD (computational fluid dynamics) is the use of applied mathematics/physics which allows the user to visualise how gas flows based on the Navier-Stokes equations. Doing such studies is very expensive, and the applied fluid mechanics do not account for the chemical reactions occurring within the reaction furnace. To study formation rates properly, especially when co-firing with natural or refinery fuel gas, onsite sampling and testing of the sulphur-bearing compounds must be conducted.

The main problem arising from turndown conditions is the reduction in inlet flow rates of acid gas. Co-firing with natural gas may prove a viable solution to this temperature issue by increasing the overall volumetric flow, due to the fact that for one part natural gas, ten parts of stoichiometric air is required to achieve complete combustion. The increased volumetric flow would be beneficial during turndown conditions.

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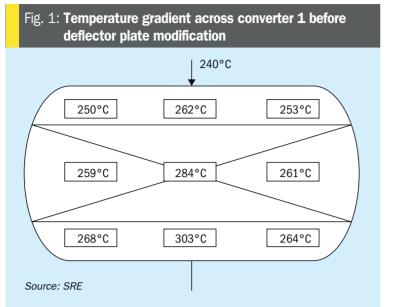
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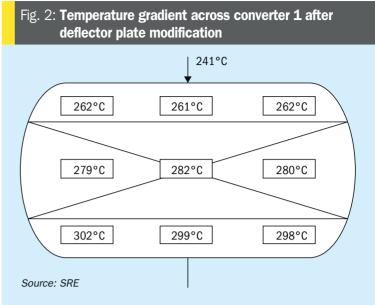
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#### Converters

Converters, whether filled with alumina or full titania catalyst, are designed with a gross hourly space velocity of approximately 1,000h<sup>-1</sup>. Lower flow rates, and consequently lower pressure drops across the catalyst, can result in channelling. Channelling involves the process gas distributing asymmetrically throughout the catalyst bed within the converter and as such may result in a lower expected lifespan from the catalyst. There are multiple options for mitigating this problem:

- deflector plate rearrangement;
- multiple entry points;
- catalyst size reduction;
- reduction of available bed area.

The converter bed illustrated in Fig. 1 showed large variation in spot temperatures throughout the converter bed as well as reduced overall conversion rates across the converter. Both of these signs strongly indicated the occurrence of channelling within the catalyst bed. By modifying the deflector plates to direct the inlet flow more evenly across the bed a much more even temperature gradient throughout the catalyst bed was achieved (Fig. 2).

While rearrangement of inlet deflector plates and an increase in the number of entry points can help create a more turbulent inlet flow, reducing the likelihood of channelling, it does not address the decrease in pressure drop across the bed.

Reducing the catalyst size can create a more densely packed bed, resulting in a higher pressure drop under lower flow conditions, which would decrease the effects of channelling. In addition to this, isolating a portion of the bed from the inlet flow would result in a smaller bed area for the same inlet flow, which would also theoretically increase the pressure drop across the bed, again decreasing the effects of channelling.

#### Condensers

Turndown conditions result in lower volumetric flow rates into the SRU, and this in turn results in lower internal flow velocities inside the condenser tubes, which can result in both liquid sulphur entrainment and sulphur fogging. Both of these circumstances lead to the condenser not operating correctly, and can negatively affect the SRU as a whole. In extreme cases, sulphur entrainment could lead to catalyst bed contamination, and uncontrolled sulphur fires.

Fig. 3 shows the adverse effects on a final condenser caused by the SRU operating at a highly reduced operating capacity.

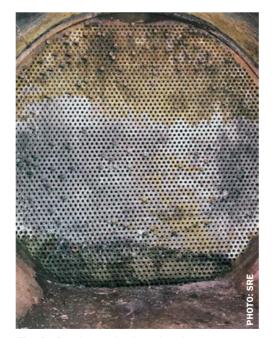


Fig. 3: Condenser bed – tube view.

ISSUE 388 SULPHUR MAY-JUNE 2020 The most effective solution to prevent these problems is the systematic plugging of a number of condenser tubes, to maintain a constant cross-sectional velocity across the tubes.

#### Acid gas knockout drum

In turndown conditions, the instrumentation and piping for the acid gas knock out drum should remain largely unaffected by the changes in volumetric flow rates. However, the mesh pads within the vessel can only be assumed to perform adequately down to 40% of design capacity. Below this, it may be necessary to redesign and/ or replace the pads to better suit the associated downturn flow rates.

This is due to the fact that at lower flow rates into the vessel, the pressure drop at the nozzle decreases, which in turn decreases the rate of flashing upon entry to the vessel.

In order to counteract the loss in pressure drop at the nozzle a larger number of mesh pads could be installed, or the existing mesh pads could be resized to account for the lower pressure drop and higher residence time within the vessel.

#### **Combustion air blowers**

Combustion air blowers are theoretically capable of performing adequately under any level of turndown, assuming proper surge protection is in place, and the blower has undergone mandatory reviews.

Turndown of an SRU could be due to a decrease in overall inlet gas flow rates, with acid gas quality maintained, or the inlet gas flow rates could remain constant, but the overall acid gas quality could drop. The coexistence of both of these factors should also

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be considered. In all of these situations, the result is a drop in overall volumetric flow into the system, which in turn has cascading effects on the entirety of the SRU.

In the case of high turndowns, venting volumes can become quite large, resulting in a drop in operating efficiency, and an increase in operating costs.

Complete blower replacement should be strongly considered at high turndown rates, to offset increases in operating costs associated with high venting losses.

In addition, proper review and comparison with design blower air capacity should be performed in order to evaluate the suitability of the existing air blower to adequately operate under lower inlet flow rate conditions.

#### Air flow control

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In the case of turndown, the reduction in overall volumetric flow into the SRU must be accounted for within existing air flow control methods. The sizing of the main air line is based on the expected design capacity, and therefore is not as effective or efficient if the overall volumetric flow rate decreases. If volumetric flow rates drop below roughly 30% normal operating levels, it is likely necessary to replace existing orifice plates within the SRU with equivalent plates sized to more effectively and accurately handling the lower rates.

The different types of valves used in air flow control react differently to turndown conditions, in terms of efficiency of operation. In this situation, the butterfly valve is poorly suited for large changes in inlet flow rates, while the globe or ball valve is relatively better suited, and the V-ball valve performs best under varied conditions.

It is highly recommended to perform dynamic modelling of the SRU to identify whether making adjustments to the existing air flow control valves will be adequate for handling the reduced flow rates, or whether it is necessary to replace them with more effective valve types.

#### Waste heat exchanger

During turndown, lower inlet flow rates can result in a decrease in the outlet temperature of the reaction furnace/waste heat boiler. It may be necessary to plug a number of the waste heat exchanger tubes in order to maintain or increase the internal velocity and raise the outlet temperature above the process dew point.

This will help maintain a constant outlet temperature from the waste heat

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exchanger, reducing the likelihood of sulphur entrainment within the system, as well as maintain consistent flow in the sulphur condensation rundown lines.

#### **Direct fired reheaters**

Typically, during turndown, burner rates in the reheaters are firing at roughly 35% normal operating capacity. This reheater turndown rate is not directly proportional to the SRU turndown rate, due to heat losses in the system, as well as lower condenser outlet temperatures.

If the burner rate requirements in the SRU reheater(s) drop to below 35% design capacity, replacement of the burner and its associated instrumentation is recommended.

Some advanced burners are capable of handling higher turndowns, as they are adjustable, and it may be worthwhile to initially install an advanced burner to reduce the effects of turndown when they arise.

In addition, alternative reheating methods such as steam are often better suited to handle higher turndown rates, with the exception of gas-gas exchangers.

#### Incinerator

In the case of turndown, the lower expected flow volumes may result in flow measurement and plume dispersion problems. While increasing dilution air may counteract this volume reduction, it in turn results in higher fuel costs, as well as a larger environmental impact in the form of SO<sub>3</sub> and NOx emissions.

Considering the notable variability of all of these phenomena, there is no accurate predictive model which can evaluate these parameters.

In order to increase stack exit velocities, it may be necessary to introduce a stack exit cone or stack liner. Both of these solutions reduce the residence time within the stack and thus reduce the overall formation of SO<sub>3</sub> and NOx emissions.

#### **Case study 1: Reaction furnace** performance

This case study focuses on a southern Alberta gas plant, operating an SRU with an initial design capacity of 100 t/d. The SRU was operating a 3 -stage configuration consisting of a single modified-Claus converter followed by a 2-converter MCRC sub-dewpoint unit (Fig. 4) and then a thermal incinerator for further processing of the tail gas stream from the MCRC bed in adsorption.

Due to turndown conditions, the plant was running at a much lower rate of 10 t/d, using fuel gas co-firing and an acid gas front side split configuration in order to maintain reaction furnace temperature, as well as an adequate  $H_2S$  to  $SO_2$  ratio.

The facility was planning to operate the unit at even lower turndown conditions of roughly 5 t/d. They contacted Sulfur Recovery Engineering (SRE) to perform baseline studies for these expected conditions, however the facility was unsure about the performance of CFD prediction models in regard to the reaction furnace.

In order to avoid a complete replacement of the existing burner, SRE was consulted to conduct performance testing on the unit while operating at 5 t/d. To perform these tests, SRE conducted them while one of the compressors was down. effectively mimicking lower operating conditions expected in the future.

At the lower production rate, the facility's sulphur recovery license requirement was 95.9%. In addition to the lower production rate, a reduction in overall acid gas quality was expected, dropping from their usual value of 60% H<sub>2</sub>S (dry basis) down to 12%. Due to both the lower production rates and quality of inlet acid gas, the reaction furnace main burner was operating with co-firing of natural gas in order to maintain high enough temperatures to adequately remove BTEX components in the reaction furnace. In order to maintain adequate H<sub>2</sub>S:SO<sub>2</sub> ratio, an acid gas split stream was introduced to the second zone of the reaction furnace.

SRE conducted several tests in regard to co-firing and split configuration flow ratios, in order to fine-tune the best possible scenario in which to operate at 5 t/d. The factor of priority was ensuring that the reaction furnace would still be able to effectively destroy contaminants while maintaining a satisfactory H<sub>2</sub>S:SO<sub>2</sub> ratio (Table 1).

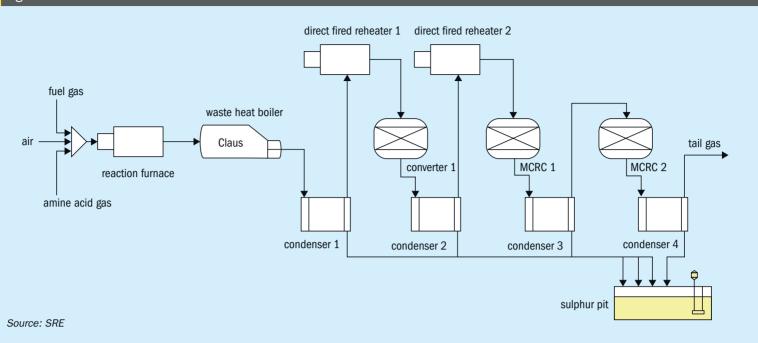
As shown in Fig. 5, toluene breakthrough was entirely eliminated once temperatures reached a minimum of 1,020°C. Benzene breakthrough was present throughout the testing, but was considered to be minimal, and posed a very low risk to the catalyst.

The H<sub>2</sub>S:SO<sub>2</sub> ratio was considerably lower than the optimal ratio of 2:1, at a range of roughly 1.2 to 1.6. This result was anticipated however, as the co-firing required to maintain furnace temperatures resulted in a higher than normal conversion rate of H<sub>2</sub>S

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#### Fig. 4: Modified Claus reaction converter unit PFD



RF temperature, °C	1,000	1,010	1,020	1,035	1,050	1,060	1,070
H <sub>2</sub> , mol-% dry	0.8256	0.848	0.9661	0.8181	0.7913	0.8182	1.0585
CO, mol-% dry	3.7643	3.6844	3.7842	3.7376	3.9127	4.1512	4.4093
CO <sub>2</sub> , mol-% dry	44.8758	45.0308	44.2446	42.8818	43.8733	42.4007	41.4774
H <sub>2</sub> S, mol-% dry	1.9107	1.8275	1.8877	1.6372	1.5143	1.3297	1.4867
COS, mol-% dry	0.4980	0.4887	0.5302	0.4823	0.4991	0.4717	0.5737
SO <sub>2</sub> , mol-% dry	1.3424	1.2921	1.1890	1.3262	1.2301	1.1201	1.0957
CS <sub>2</sub> , mol-% dry	0.0862	0.088	0.0847	0.0785	0.0603	0.0887	0.0683
Benzene, mol-% dry	0.0094	0.0095	0.0082	0.0067	0.0046	0.0063	0.0044
Toluene, mol-% dry	0.0002	0.0001	0.0001	0.0000	0.0000	0.0000	0.0000
H <sub>2</sub> S:SO <sub>2</sub> ratio	1.4233	1.4143	1.5876	1.2345	1.2310	1.1871	1.3568

Source: SRE

in the reaction furnace. This lower  $H_2S:SO_2$  ratio was remedied by introducing the acid gas split stream to the second zone of the reaction furnace. In implementing this stream, we were able to achieve results that met all licensing requirements.

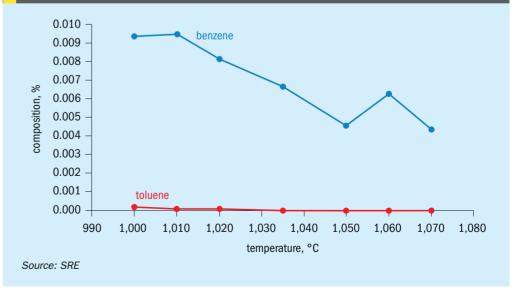
This approach was much better than solely relying on a predictive model, and SRE was able to determine that it was indeed possible to operate the plant at the lower predicted tonnage while still meeting satisfactory regulatory conditions.

The trace amount of benzene breakthrough was a notable concern due to its role in catalyst poisoning.

However, SRE was assured by the catalyst provider that breakthrough quantities below 100 ppm of benzene would not have any serious effects on the catalyst.

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Fig. 5: Benzene and toluene composition (mol %, dry) in reaction furnace outlet/ condenser 1 outlet vs temperature (°C)

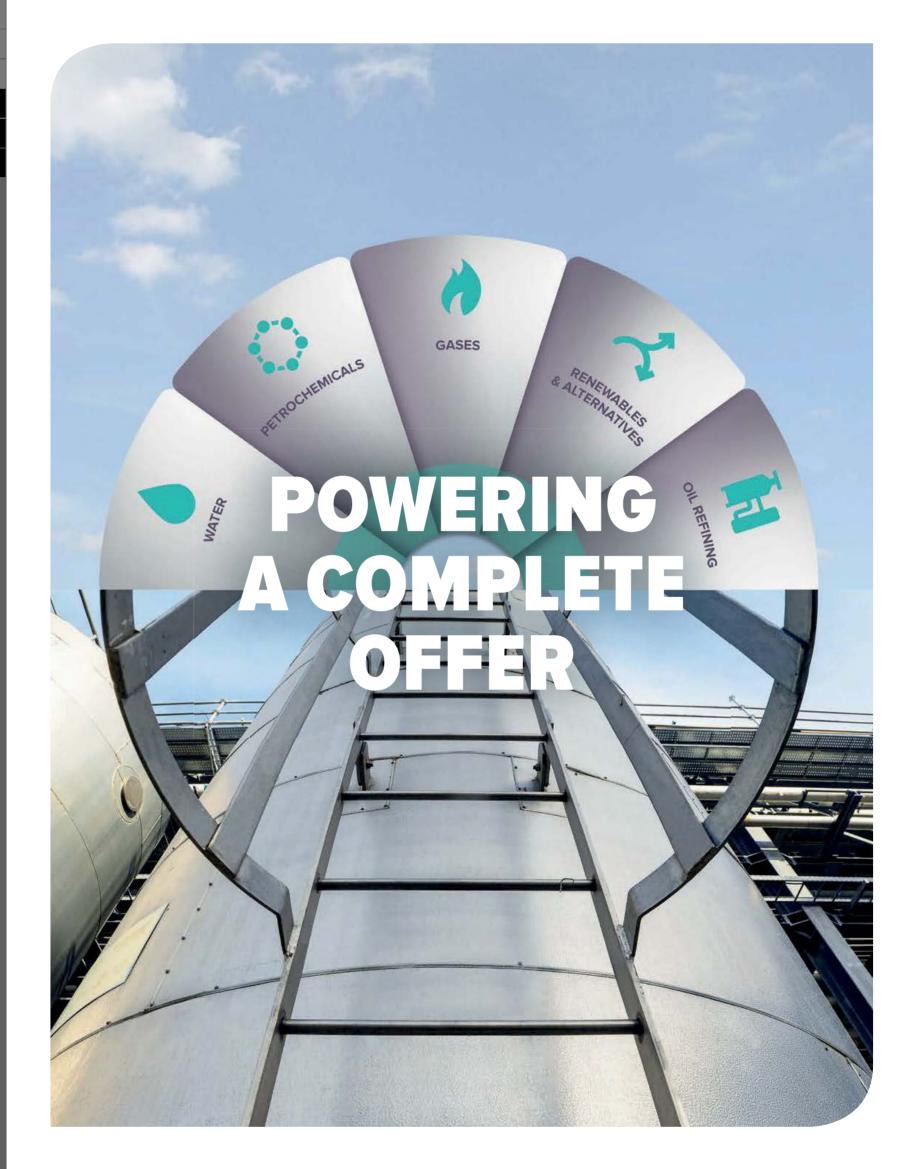


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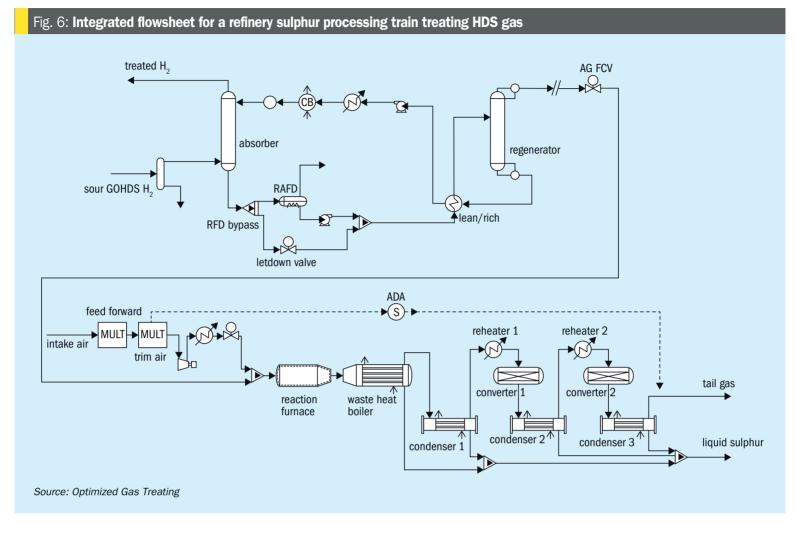
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#### **Case study 2: Repetitive** hydrocarbon upsets to the SRU

In this case study, performed by Optimized Gas Treating (OGT), turndown was found to reduce dewpoint margin inside a refinery HDS contactor and degrade the quality of the acid gas. Amine units without rich amine flash drums have higher consequences in addition to being more susceptible to upsets.

This case study refers to a refinery sulphur processing train treating mainly HDS gas. The system uses 45 wt-% MDEA to treat 200 million std ft3/d of recycle hydrogen containing normally 1.2% H<sub>2</sub>S from a gas oil hydrotreating system (GOHDS). A multidiscipline root cause analysis (RCA) team was commissioned to investigate repetitive hydrocarbon upsets to the SRU. Within this plant, upsets historically occurred every HDS start-up. A sister refinery with no rich amine flash drum (RAFD) installed experienced the same problems with worse consequences. This study assesses the impacts and ramifications of both scenarios for an upstream amine unit with and without a RAFD.

Fig. 6 shows a SulphurPro<sup>®</sup> and Pro-Treat<sup>®</sup> seamlessly integrated flowsheet for a refinery sulphur processing train treating HDS gas.

#### **Case study results**

On start-up, the lighter oil (distillate) feedstock together with the lower HDS operating pressure were found by simulation to produce more heavy hydrocarbons in the feed to the amine contactor. The upstream separation equipment was designed for HDS recycle flow at higher operating pressure (900+ psig vs. 550-600 psig start-up operation). Separator calculations at the lower operating pressure found the system to be inadequate. These factors were the root causes for liquid slugs of hydrocarbon entering the amine system.

On a more subtle note, considerably less H<sub>2</sub>S was present in the amine contactor feed processing start up distillate versus the normal gas oil feed. The RCA team found that the amine contactor could be bypassed for a major portion of the start-up. The systems were modelled postmortem using ProTreat® and SulphurPro® simulation at 30% turndown operation to mimic HDS start-up on a lighter oil.

With 30% of design  $H_2S$  in the feed, ProTreat identified that absorber column internal temperatures are much colder at turndown and closer to the dry gas dew point as seen in Fig. 7. The heat loss from the turndown lowers the dewpoint approach temperature by an additional degree. The 13°F dewpoint approach at design drops to only 3-4°F at turndown. With this dewpoint approach, even minor hydrocarbon inlet liquid entrainment can be expected to result in major problems in the amine and Sulphur recovery units.

In addition to analysing the operations, the economics and a few performance metrics related to lost hydrocarbon product were also evaluated. Table 4 shows that hydrocarbon content in the acid gas increases nearly six-fold for turndown rates compared to design. The ramifications here are:

- Feedforward air ratio control in the SRU will be off 1-5% at turndown versus design. While this is not a huge amount, it is enough to significantly impact the TGU reliability (SO<sub>2</sub> breakthroughs) if the feedback air demand analyser has problems. Here there would be value in having a rich amine flash drum.
- There is an economic penalty to burning hydrocarbon in the SRU versus leaving it in the money-making hydrocarbon units that amounts to the value of

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#### Fig. 7: Absorber column temperature profiles

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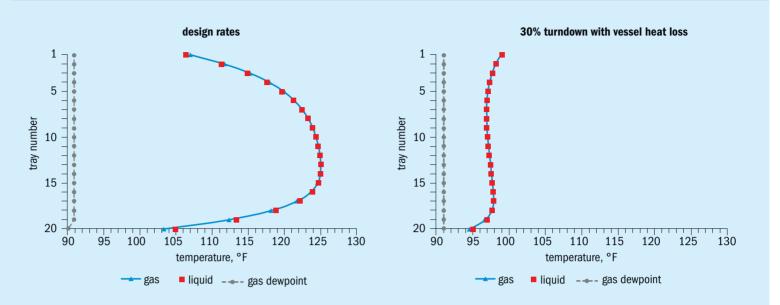
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Source: Optimized Gas Treating

#### Table 2: Economic and performance comparison turndown vs design

Parameter	Design	rates	30% turndown	
	RAFD	No RAFD	RAFD	No RAFD
% Hydrocarbon as $C_1$ in AG	0.12	1.07	0.60	4.60
Air demand, mole/mole AG	2.16	2.18	2.18	2.27
Btu/year of hydrocarbon lost				
Acid gas	7.68E+08	6.18E+09	1.14E+09	8.39E+09
Flash gas	5.41E+09	5.41E+03	7.25E+09	7.25E+09
Total	6.18E+09	6.18E+09	8.39E+09	8.39E+09
\$/year of hydrocarbon lost				
Acid gas	\$2,303	\$18,531	\$3,433	\$25,160
Flash gas	\$16,225	\$0	\$21,735	\$0
Total	\$18,529	\$18,531	\$25,168	\$25,160
SRU recovery, %	94.43	94.28	96.68	96.18
H <sub>2</sub> in tail gas, % dry	1.95	1.98	2.09	2.24
COS in tail gas, ppmv dry	9.5	48.9	2.4	17.1

Source: Optimized Gas Treating

roughly a new pickup truck. The larger penalty that cannot be as easily quantified is the lost SRU capacity from reliability downtime.

Table 2 also shows improved SRU recovery at the turndown conditions. This is due to more residence time in the Claus catalyst at the decreased rate. Looking at the Claus reaction approach to equilibrium in the second converter, the design case is at 59.5% while at turndown the equilibrium approach is 95.5%. As developers of the kinetic rate-based Claus Converter in

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SulphurPro®, OGT questioned whether this was valid data or a bug in the software. After comparing the reactor conditions versus plant performance test data for similar applications, this effect appears to be real. However, the observations are not universal to all situations. The dependence upon rates, temperature, and degree of catalyst aging can be quite touchy. In fact, the second converter in this case operates cooler than many plants in an area where Claus reaction equilibrium is more favourable, but kinetics are slower than at higher operating temperatures.

#### Case study 3: Turndown of the SemCAMS KA gas plant SRU

The SemCAMS Kaybob Amalgamated (KA) gas plant was originally designed with two sulphur recovery units (SRUs), each designed to process 550 t/d of sulphur which were followed by a common Sulfreen unit designed for 1,100 t/d of sulphur. Due to declining sour gas reserves, SemCAMS was predicting that the processing capacity of the one remaining SRU in operation would need to be reduced to 50 t/d of equivalent sulphur in the feed gas. Simultaneously SemCAMS predicted that the acid gas composition would be reduced from 70 mol-%  $H_2S$  to a minimum expected value of 50 mol-% H<sub>2</sub>S. The overall sulphur recovery had to be maintained above 98.6%

Comprimo was contracted to evaluate options for SemCAMS to handle the lower sulphur tonnage and predicted leaner acid gas. During this evaluation, equipment modifications, changes in operating parameters and catalyst replacement were considered to allow the plant to process the new acid gas flow rates and compositions while still maintaining the overall regulatory sulphur recovery efficiencies. In addition, the ability to be able to start up with the lower acid gas flow rates and composition were considered to determine whether additional gas needs to be brought in during start-up to ensure the heating of the converter beds.

The existing sulphur recovery unit was a three stage Claus unit which was

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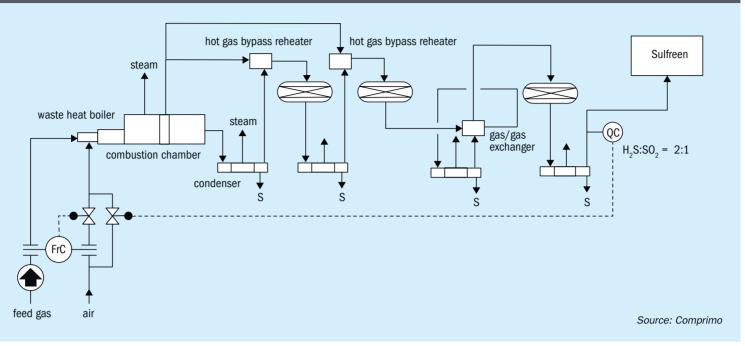
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followed by a Sulfreen unit achieving an overall sulphur recovery efficiency of 99.0%. The configuration of the sulphur recovery unit was provided in Fig. 8.

The plant was made up of a thermal stage, consisting of a high intensity HEC burner followed by a water tube waste heat boiler (WHB), which produced 27.5 barg (400 psig) steam. The waste heat boiler was a two pass design and the gas from the first pass was used to reheat the gas into the No. 1 and No. 2 converters via hot gas bypass valves. The gas from the second pass of the waste heat boiler was routed to the thermal condenser. The No. 1 and No. 2 converters contained alumina catalyst and were operated at higher temperatures than usual due to the hot gas bypasses and gas/gas No. 3 reheater. The inlet gas to the No. 3 converter was reheated in a gas/gas exchanger in which the outlet gas from the No. 2 converter was cross exchanged with the outlet gas from the No. 3 condenser. Each stage was equipped with a condenser that produced 3.5 barg (50 psig) steam. The tail gas from the unit was routed via a long tail gas line to the existing Sulfreen unit. The Sulfreen unit was originally designed as a four bed system, however was operated by SemCAMS as a three bed unit at the time of the study.

Comprimo was requested to determine the minimum possible processing capacity of the plant based on the predicted future acid gas composition. A target capacity for the study was set at 50 t/d of sulphur production. Additionally SemCAMS wanted to determine what the minimum required acid gas supply would need to be to properly start up the unit from cold conditions with the proposed future configuration for the unit.

#### Study parameters and requirements

The study parameters and requirements set by Comprimo and SemCAMS were to determine the modification to the plant required to minimise the turndown of the plant while maintaining:

- Overall sulphur recovery efficiency per the Alberta regulations
- Operation of the unit above sulphur dewpoint
- Capability to start up the unit cold with the low acid gas rates
- Minimum capital investment
- The overall sulphur recovery target for the study was set at 98.6%.

#### Study results

The obvious limitation of the plant to operate at high turndown was the reheater configuration. Based on the plant's operating experience, the minimum processing capacity of the unit at the start of the study corresponded with approximately 120 t/d.

As a first step it was essential to determine the actual turndown limitations of the plant. It was concluded that with the current configuration it was not possible to turn the unit down to 100 t/d.

The following options were therefore considered to allow the plant to process the expected future sulphur processing capacity: • install a new 100 t/d SRU;

 replace the second and third reheater with steam reheaters;  use co-firing with natural gas to increase the mass flow through the unit and use titania catalyst to counteract the higher formation of COS and CS<sub>2</sub>.

#### **New SRU**

The first option to install a new 100 t/d SRU that was able to meet the required 98.6% sulphur recovery was estimated to cost approximately \$25-30 million. As a conventional three-stage Claus unit would not be able to meet the required sulphur recovery efficiency, a new 2+1 SUPER-CLAUS® unit was considered as the basis for the evaluation. The cost of this option was deemed too expensive by SemCAMS so this option was eliminated without much review. This option would also limit the plant preventing a return to higher capacities in the future in case new sour wells would be added to the plant.

#### **Reheater replacement**

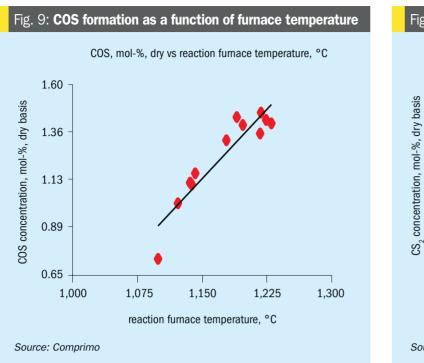
As the key limitation of the plant's turndown capabilities appeared to be its configuration, Comprimo evaluated the option to replace the second and third reheaters with steam reheaters. In addition, two options were considered to increase the thermal reactor temperature to deal with the higher BTEX concentration in the acid gas:

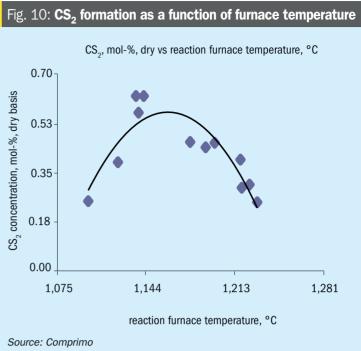
- co-firing natural gas with the current configuration;
- installation of steam heated acid gas and air preheaters.

Based on the available models in the simulators used (Promax and Comprimo

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simulator), it became evident that it would not be possible to meet the required sulphur recovery efficiency with the co-firing option. The option to co-fire to maintain the thermal reactor temperature for proper BTEX destruction was therefore initially discarded.

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The estimated cost for the replacement of the first and second reheaters and the installation of an acid gas and air preheater was \$9 million, which was again in excess of SemCAMS's expectations and Comprimo was requested to further evaluate alternative options.

#### **Co-firing with catalyst replacement**

From the evaluation of the waste heat boiler performance, it became clear that in order to maintain a temperature that was sufficiently high from the first pass of the WHB for the hot gas bypass reheaters, the mass flow would have to be increased through the exchanger. As the waste heat boiler was a water tube boiler it was not possible to plug tubes as would be the case for a fire tube design. It might have been possible to remove tubes from the exchanger, however this option was not further pursued as this action would likely be irreversible. Therefore Comprimo evaluated how a minimum mass flow through the unit could be maintained under all turndown scenarios. By maintaining a minimum mass flow through the unit, the outlet temperature from the No. 2 converter would have been sufficiently high to enable the gas/gas exchanger to maintain the No. 3 converter above the sulphur dewpoint.

In order to increase the mass flow, cofiring with natural gas could be used, as it required additional air for the combustion of the natural gas component.

To understand the impact of natural gas co-firing at the KA gas plant, Comprimo had the most recent performance test report data available, in which the overall sulphur recovery efficiency was evaluated for both normal operation and with the addition of natural gas co-firing. This data proved very useful, as it indicated that the overall sulphur recovery was heavily impacted by the introduction of natural gas co-firing and it was clear that the sulphur recovery efficiency target could not be met with the current configuration with co-firing with natural gas.

Although it is well known that operation with co-firing will result in additional formation of COS and  $CS_2$ , the exact increase of these components is hard to predict and varies widely in commercially available simulators. A test programme was therefore set up for the plant to determine the relationship between the level of co-firing and the formation of COS and  $CS_2$  in the reaction furnace.

A sulphur plant testing company was brought in to sample and analyse the gas streams in the Claus unit while operating the unit in turndown with different levels of co-firing. The results of the testing are provided in Figs 9 and 10. It was determined that COS increases as a function of increased natural gas co-firing, however  $CS_2$  goes to a maximum as a function of temperature.

The test data indicated that when cofiring was considered to increase the mass flow, there was a definite impact on the overall sulphur recovery efficiency of the plant to the point where the regulatory requirements would no longer be met. Therefore it was clear that co-firing alone would not meet the requirement to meet both the capacity and the overall sulphur recovery targets for the SemCAMS KA gas plant. As a result it was decided to evaluate the option to install titania in the Claus unit in order to meet the sulphur recovery requirements.

Comprimo contacted Axens to discuss the potential of using titania catalyst in the No. 1 and No. 2 converters to counteract the effects of the formation of COS and  $CS_2$  in the thermal reactor during cofiring. The information supplied by Axens suggested that a COS hydrolysis of 98% and 96% for No. 1 and No. 2 converters respectively and  $CS_2$  hydrolysis of 92% and 75% for No. 1 and No. 2 converters respectively could be met when the catalyst beds in both converters are replaced with a 25% alumina/75% titania bed.

Comprimo estimated that for the case where sufficient natural gas co-firing was added to maintain the WHB at the minimum turndown mass flow, and replacing the catalyst as described above, a sulphur recovery of 98.7% was expected, i.e. still above the target level of 98.5%.

In discussion with Axens, the decision was made to install a 85/15% split alumina/titania catalyst bed in the No. 1 and No. 2 converters, which would be adequate to ensure high COS and CS<sub>2</sub> hydrolysis.

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The expected values for the hydrolysis were 97% and 88% for COS and 89% and 55% for CS<sub>2</sub> in the first and second bed respectively, which depending on the capacity of the plant would still result in an overall recovery between 98.7% and 98.9% for a capacity of 70 t/d to 120 t/d.

One of the items that was identified as a potential concern with the installation of the new catalyst configuration was the low space velocity in each of the converters due to the large size of the unit. Low space velocity in a catalyst bed can result in channelling of the gas through the bed. In order to overcome this concern, Axens proposed the installation of a smaller bead size for the CR-3S alumina catalyst (2-3 mm), resulting in a higher pressure drop and thereby better distribution of the gas.

The high intensity burner installed on the thermal reactor was also evaluated for operation in co-firing mode. As back burning is typically a concern with burners in turndown operation, the addition of co-firing was found to be beneficial to the operation of the burner. With co-firing the air demand of the burner is increased as well, resulting in a higher pressure drop across the burner. Therefore as long as the control system was able to handle the required natural gas flow rates, the burner was not going to be a concern. Based on Comprimo's evaluation, the limitation of co-firing was not in the sizing of the equipment, but in the limitation of the installed refractory. Co-firing results in higher temperatures in the thermal reactor and although this has benefits for contaminant destruction, the amount of co-firing was limited by the refractory maximum service temperature.

The total estimated cost of the installation of new catalyst in the converters was less than \$1 million.

#### Testing of the selected option

The new catalyst configuration was installed in the converters and the performance of the sulphur plant was tested to determine the impact of the installation of the new catalyst together with co-firing operation.

The data from the September performance test showed promise in the ability to turn the plant down to approximately 80 t/d, so it was decided that a further test needed to be done to truly operate under these turndown conditions. Therefore the plant blocked in several of the sour wells supplying the plant, thereby being able to reduce the capacity of the plant to about 60 t/d equivalent. The intent of the test runs was to determine the limiting parameter when the plant was turned down.

Based on the results from the tests, Comprimo deduced that the possible turndown of the KA gas plant SRU was a function of the acid gas composition. When the acid gas became leaner, it was possible to increase the amount of co-firing until the limitation of overall sulphur recovery was met, whereas with a higher acid gas  $H_2S$  concentration, the first limitation was the refractory temperature. Therefore, Comprimo concluded that the following minimum capacities could be attained with the new catalyst configuration using co-firing to maintain the mass flow through the unit:

- At 65% H<sub>2</sub>S in the acid gas the minimum processing capacity of the unit was 65 t/d
- At 50% H<sub>2</sub>S in the acid gas the minimum processing capacity of the unit was 48 t/d.

#### Three years of studying and testing

Comprimo started with a turndown target from SemCAMS and initial performance data that was based on a much higher capacity than the predicted future capacity. Based on this information the initial recommendations were made, which led to a requirement for further performance testing to determine whether these recommendations were attainable. It was found during the study that the best way to come up with a predictive model for a plant was to tie the simulation results of the model with the data from operating and performance test data. By progressively testing of the facility and simulating the results of these tests, Comprimo was able to narrow down the results to come up with a more accurate prognosis for where the plant could operate in the future and how low the turndown of the plant actually could be. This proved to be substantially different than the originally predicted values.

It was concluded that it should be possible to reduce the capacity of the plant to a capacity of 50 t/d with co-firing at reduced acid gas concentrations. At higher acid gas concentrations, the actual turndown was limited by the maximum limitation on the refractory of the thermal reactor.

By installing Axens titania catalyst and improving the capability of the No.1 and No. 2 converters to hydrolyse the COS and  $CS_2$  formed in the thermal reactor during co-firing, it was possible to consider cofiring for the unit to maintain a minimum mass flow through the unit and thereby overcome the limitations of the installed gas/gas exchanger as the No. 3 reheater. This minimised the cost of the modifications substantially and allowed the plant to remain in operation. In addition the performance test work allowed Comprimo to estimate the required acid gas that was necessary to be able to bring the unit from a maintenance turnaround to steady state operation. This allowed SemCAMS to plan ahead of time the amount of raw gas that needed to be supplied to the gas plant to ensure a smooth and successful start-up, before the capacity can be decreased again to the predicted turndown.

Some additional potential future limitations were discovered that would need SemCAMS' attention before the minimum turndown can be achieved. These mostly related to the Sulfreen unit which was very large compared to the future processing capacity of the unit.

### Case study 4: The burning tail gas line

The plant configuration for this case was a large four-stage EUROCLAUS® unit (also called a 3+1 EUROCLAUS® unit). The plant had been processing acid gas for some time already. After a trip of the unit, the plant was put on hot standby operation. It was during this time that flames were observed to be coming out of the cladding of the tail gas piping to the incinerator. The tail gas line had been installed with ControTrace® to maintain the wall temperature of the piping above the freezing temperature of sulphur (118°C) and was insulated. The tail gas pipe was sprayed with water to extinguish the fires and the plant was returned to acid gas operation. After a subsequent trip, a similar incident occurred, and a second fire was observed. In Fig. 11, small orange flames can be observed coming out of the cladding around the insulation in several locations.

Upon shutdown and removal of the cladding and insulation, it was found that the tail gas piping was deformed and showed indication of a fire on the outside of the piping. No indication was found of a loss of containment of the piping.

As under normal conditions there is no combustible mixture in the tail gas, the initial thought was that the heat transfer cement had caught fire after the transition from acid gas firing to fuel gas firing, however tests done in the Ametek CSI labs (who designed and supplied the ControTrace<sup>®</sup>) indicated

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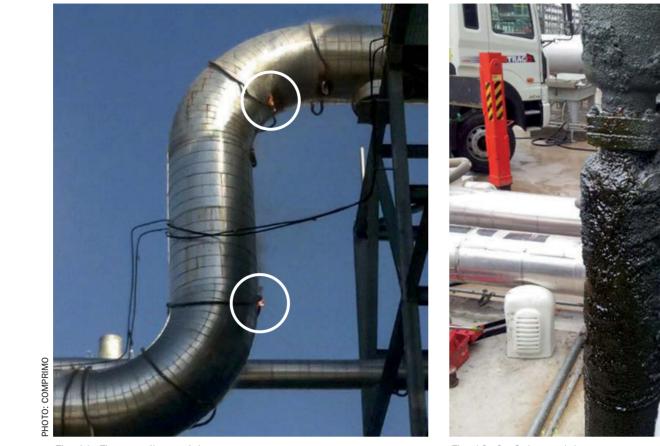


Fig. 11: Fire on tail gas piping.

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that a temperature of 400°C is required to ignite the heat transfer cement. This meant that the tail gas piping needed to have been heated to a temperature of over 400°C in order to be able to ignite the heat transfer cement. Per discussion with CSI, there was some evidence though that the installers of the ControTrace<sup>®</sup> had added a solvent to the heat transfer cement to make the material smoother for easier installation, which very likely decreased the auto-ignition temperature of the heat transfer cement.

As there was no acid gas in the plant at the time of the fire, the main culprit was deemed to be related to the hot standby operation. Based on the available DCS information at the time of the incident, Comprimo determined that during the hot standby operation the plant had been operating with a combustion in the order of 80% stoichiometry without the introduction of steam for moderation. Using this data, Comprimo estimated that the tail gas (that was bypassing the final selective oxidation reactor) contained approximately 5% CO and 4% hydrogen. In addition, due to the normal operation of a EUROCLAUS® unit requiring air addition for the final stage as well as the introduction of vent air from the sulphur pit degassing unit, oxygen would have been present in this gas stream as well. Comprimo believes that due to the very low stoichiometry of the natural gas firing, sufficient combustible material

was available in the tail gas piping to light off the gas by the incinerator (as the ignition source) thereby resulting in a fire in the tail gas piping. With a fire in the tail gas piping during hot standby, when the gas velocities were relatively low (especially with no moderating steam), the temperature of the tail gas piping gradually increased, resulting in the auto-ignition of the heat transfer cement with the diluent material.

The main lesson learned from this experience was that the stoichiometry during hot standby operation can play a substantial role in a SUPERCLAUS®/EUROCLAUS® unit due to the presence of air downstream of the final reactor. This could also be the case for a plant that introduces the vent air from a sulphur pit in the tail gas piping upstream of the incinerator. It is very important to have good measurement of all feed streams flows into the main burner of the SRU, which means pressure and temperature compensation on all streams, as well as a good analysis of the fuel gas/natural gas used for start-up and hot standby operation. The installation of an onstream analyser for the fuel gas/natural gas can also be considered in order to have an onstream adjustment of the stoichiometric air to FG/ NG ratio, thereby ensuring that both excessive substoichiometric and super stoichiometric combustion of the fuel gas/natural gas does not occur.

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Fig. 12: CarSul on sulphur pump.

In addition, it was clear from the information that the installers had used a solvent to make the installation of the heat cement easier and that it is essential to have proper training and supervision of the installation of the ControTrace<sup>®</sup> elements as in this case it led to ignition of the heat transfer cement.

Anecdotally, upon removal of the sulphur pumps from the sulphur pit, the sulphur pump appeared to be covered with a substantial amount of CarSul (Fig. 12), which could indicate that the combustion of the natural gas was more sub-stoichiometric than previously suspected or heavier hydrocarbons than expected were present in the natural gas.

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