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NOx reduction in acid plants

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Drum granulator Commercial installation for innovative forming system.

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Back on the rollercoaster

ommodity markets are often volatile, and sulphur and sulphuric acid can be more so than most, with much of their supply coming from involuntary production, and sulphur supply in particular often dependent on the timing of large scale oil and gas projects. Even so, this year's price rises, in some cases tripling in just over a year, have been especially eye-catching.

The continuing delay to Qatar's Barzan LNG project and a slower than expected start-up for Kuwait's new refineries have helped keep supply tight at the same time that phosphate consumption seems to be strong, and the threat of Chinese export restrictions is keeping phosphate markets nervous. Chinese sulphur imports have been higher than expected, keeping an already tight market tighter still. On the acid side, high sulphur prices discourage sulphur burning acid production, and strikes and shutdowns in Chile and Canada have helped balance new Chinese smelter acid production. And covid continues to impact upon demand for refined fuels and hence refinery run rates, reducing sulphur availability from that segment of the market.

And then there is the start-up of the PT Halmahera Persada Lygend high pressure acid leach (HPAL) plant in Indonesia, which will add up to 300,000 t/a of sulphur demand for nickel production at capacity - whenever that is reached. Although this is no bigger than some of the new phosphate projects that are starting up, it is a sign of one of the major changes that may be happening in sulphur and sulphuric acid markets. It is only the first of several new HPAL plants that are under construction in Indonesia and Australia to feed new nickel sulphate demand for battery production, predominantly in China. The China nickel story used to be based around stainless steel demand, and that encouraged the first wave of HPAL plants in the 1990s and 2000s, part of a wave of acid leaching that swept copper and uranium as well as nickel markets, and added 20 million t/a and more to acid demand. However, on the nickel side they were eventually undercut by nickel pig iron (NPI) production using cheap Indonesian ore, as well as suffering

a plethora of technical issues. Now, though, there is something of a perfect storm created by Indonesia's ban on nickel ore export, a shortage of nickel sulphide deposits encouraging a focus on oxide-based laterite ores, and a rapidly growing need for purer, Class 1 nickel that laterites can find hard to supply, which is driving a huge new concentration of Chinese-funded HPAL projects in Indonesia. Lygend is only the first, and acid demand for nickel production could again rise by several million t/a over the next decade. Indeed, Indonesia's nickel production, which has risen from 24,000 t/a to 636,000 t/a in just five years, turning it into the world's second largest nickel producer (after China), is projected to become the world's largest nickel producer this year, and likely to become dominant in international nickel markets. With smelter acid in fairly short supply, most of the acid requirement for Indonesia is likely to come from sulphur burning acid plants.

This is all for the longer term, however. In the meantime, the global vaccination programme offers the hope that fuels demand will continue to recover, and with it sulphur supply. There are strong signs that this is already happening, and it should eventually feed into sulphur availability and hence prices - especially if one of the Middle East mega-projects also finally starts ramping up. For the time being we seem to be at the top of the rollercoaster, and as we all know, there's only one way to go from there.

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Richard Hands, Editor

BCInsight

This year's price rises... have been especially eyecatching."

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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.

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The upturn in demand for fuel oil and refined products through the second quarter has led to an increase in oil production, with this trend expected to continue through the second half of the year. OPEC+ was planning to continue to reintroduce 2.1 million bbl/d of supply back into the market between May and July. The impact of the vaccine rollout in some countries is evident with fuel demand rising as the weeks go on. Operating rates at refineries in the US have continued to improve and through May and June European refiners restarted idled capacity, also increasing throughput. But in sulphur terms, we have yet to see a major easing in the tight supply situation. Availability in some regions remains squeezed. The Middle East appears to be the first region to be filtering additional cargoes into the market, resulting in softer prices through June and the view that the sentiment that a price correction is under way

The main focus through July will be third quarter contract negotiations. In North Africa, Moroccan end user OCP was in discussions with major suppliers through June. The curtailment of availability of supply from Russian producer Gazprom is likely to limit the downside potential in pricing. While OCP reduced DAP production in the first quarter of this year, sulphur demand remained strong for phosphoric acid production. Consumption in Morocco is expected to remain healthy through the second half of the year, keeping import demand strong. Any shortfall in supply from Russia is expected to be met by cargoes from the Middle East region. The US import duties on OCP phosphate products deterred any sales to the US since April, while alternative markets have been found with global fertilizer demand remaining strong in recent months.

In Russia, fertilizer-based sulphur consumption will drive the region's demand growth in the forecast with expansions at existing phosphoric acid lines ramping up. Phosagro has completed construction at its Volkhov expansion. An extra 395,000 t/a of P_2O_5 capacity will be available by the end of the year, increasing sulphur demand by over 300,000 t/a. Phosagro has also completed construction at its expansion at Balakovo, increasing sulphur consumption. Commissioning will commence in 2022. The rise in domestic sulphur demand is expected to put downward pressure on sulphur exports from the country. In other demand news, Udokan Copper continues to progress with construction at its mine in the far east of Russia. Ore grinding facilities are complete and work continues on the concentrator and leaching site. Phase 1 start-up is expected in the second half of 2022. The company is understood to be considering options for the sulphuric acid requirement. This may be met by captive acid capacity through a sulphur burner or procured directly on the merchant market.

Over in Indonesia, Lygend's Halmahera nickel HPAL site has begun production of nickel and cobalt. It is understood to be receiving sulphur cargoes at Obi Island for use at the site's two sulphur burners. Sulphur demand at capacity will be over 300,000 t/a. Sulphur demand in the country is expected to rise further in the outlook as additional nickel HPAL projects come online at the Morowali Industrial Park on the island of Sulawesi. This is being driven by demand for battery metals for the electric vehicle (EV) sector.

Brazilian spot prices firmed through June with the benchmark assessed at \$225-235/t c.fr at the end of the month. This rise came as freight rates from major f.o.b. markets firmed to all-time highs and offtakers looked to secure cargoes, placing upward pressure on prices. A period of stability is expected in the short term, but the bullish freight market remains a risk to this. Sulphur consumption in the fertilizer sector is expected to remain healthy through the rest of the year although Yara's Serra do Salitre SSP facility is now expected to start up during the first quarter of 2022. Demand from the expansion project will add 300,000 t/a sulphur demand at capacity.

In the US, on the lithium front, there are three main projects in development that could impact the medium to long term sulphur market balance significantly. Lithium Americas' Thacker Pass project sits as the most advanced and is expected to start up from 2024. The project includes two sulphur burners. Cypress Developments also plans a sulphur burner at its Clayton Valley project. A feasibility study is planned to be started in 2021 as well as a pilot plant. According to initial project plans, solid sulphur from west coast refineries would be trucked to the site. Ioneer's Rhyolite Ridge project also includes plans for a sulphur burner.

As Covid-19 restrictions continue to ease across the US, refinery run rates have improved, data from the Energy Information Administration show. In the second week of June, refinery utilisation reached 93%, up from 91% the week prior and 74% this time last year. Sulphur demand is expected to hold firm in the coming months from both the fertilizer and industrial sectors.



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Global sulphuric acid prices have continued to firm in recent months with signs of the price run slowing during June as buyer resistance has kept prices stable in some regions. Strong support remains on the demand front from the processed phosphates sector and industrial and metals markets. Supply remains tight for smelter acid and regional tightness in sulphur continues to put pressure on operating rates at sulphur burners. Sulphuric acid price premiums continue to rise further, disconnecting from the sulphur benchmark as global supply remains stretched from smelters and sulphur burners.

In NW Europe, average prices for exports firmed by \$106/t to \$135/t f.o.b. between January to July this year on the back of tight supply and healthy demand. The Western European supply squeeze is expected to persist into 2022, with the closure of the Inovyn UK acid plant adding to the tighter balance. Covid-19 remains a risk factor and some turnarounds have been delayed from the 2021 schedule to the first half of 2022. The UK acid import requirement is forecast to remain firm with a strong demand outlook from the water treatment sector, this has repercussions for acid trade flows across and from Europe.

Contract negotiations for the third quarter and the second half of 2021 continued into the start of July in the region. Some settlements were understood to have been reached. Smelter-based acid settlements increased by €15/t but some contract discussions were still ongoing. For six-monthly contracts, increases were forecast to be higher given the steep price rises since the start of the year.

North African prices firmed by \$135/t between the start of 2021 and 1 July to \$180/t c.fr. This has been driven by strong demand and a tight market balance. Acid trade to Morocco has been strong with imports to the country totalling 717,000 t in the January-April 2021 period, up by 41% on the year. China has led trade to the country and this trend is expected to continue as smelter-based acid supply grows in the forecast. We currently expect Moroccan acid imports to reach 1.9 million t in 2021 but there is potential for levels to exceed 2.0 million tonnes.

On the demand front robust copper prices have been supporting short term operations at mines as well as the potential for new projects to start up. Latin American demand is forecast to remain firm across the metals sectors. Peru and other countries in the region have struggled with rising infection rates despite rolling out vaccines. Brazil is driving demand from new projects, expanding its phosphoric acid output, which will largely be met by captive sulphur-based acid supply from 2022.

In Chile, third quarter contracts were reported concluded by buyers ranging \$190-215/t c.fr but figures are expected to vary according to the size of the buyer. BHP reports that negotiations with workers regarding the planned August strike at Escondidos are likely to continue into the first week of August. Glencore is suspending its maintenance at AltoNorte until October. It has been expected to be offline in July for 30 days, taking a potential 124,000 t off the market. Sulphur based acid producer Noracid was heard suspending its August turnaround, but this was unconfirmed by the company.

Vale, a large nickel and sulphuric acid producer, halted operations in June at its Sudbury, Canada operations after workers went on strike. Progress was not heard made by 1 July with off-takers concerned around supply sources. The North American balance is set to remain tight in the near term until the plant returns to production. Prices increased notionally in early July to \$190-210/t c.fr in line with other markets but while enquiries continued, trade remained muted.

Chinese smelter acid production is forecast to rise by 5%, or 1.8 million tonnes, in 2021 on a year earlier, but tightness in the copper concentrate market remains a risk. Environmental concerns are also adding uncertainty, with major smelters pledging to reduce concentrate purchases by 8.8% this year. This is because of climate change mitigation strategies, equivalent to 300,000 t of refined metal. Smelters are the leading driver in the short term for capacity growth, with over 6 million t/a of new capacity expected to be added between 2021 and 2022. Prices out of China have been firm and above levels achieved out of Japan/South Korea through the year so far. This was largely because higher liquidity for the spot market from China to test pricing.

Price Indications

Table 1: Recent sulphur prices, maj	or markets				
Cash equivalent	January	February	March	April	Мау
Sulphur, bulk (\$/t)					
Adnoc monthly contract	112	163	189	157	154
China c.fr spot	141	175	223	230	246
Liquid sulphur (\$/t)					
Tampa f.o.b. contract	96	96	96	192	192
NW Europe c.fr	139	160	190	228	228
Sulphuric acid (\$/t)					
US Gulf spot	83	100	135	160	160
Source: various					

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Market Outlook

Historical price trends \$/tonne



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- Significant capacity additions in the Middle East are still awaited. The more positive outlook for fuel demand is providing support to seeing these projects ramp up in the coming months. New supply is expected from Saudi Arabia following the commissioning of a gas project in 2020, sulphur availability is likely to improve from the country through the second half of 2021 and into 2022 as a result.
- News is awaited on the potential for a Chinese export tax with fears over potential measures providing a bullish sentiment to the DAP market.
- China's January-May sulphur imports rose by 10% from a year earlier to 3.61 million t. The outlook for China imports for the year and in the forecast will be a key factor in determining global trade patterns. Total imports for this year are forecast at 9 million t and a similar level for 2022, but it is the lowest level of imports since 2008.
- **Outlook:** The prospect of supply tightness easing out of the Middle East is expected to provide some softening to export prices

but firm freight rates and demand will continue to prop up delivered benchmarks. The downside will be limited by potential DAP price gains and demand, with strong demand from downstream sectors keeping consumption of sulphur healthy. Increased trade for nickel projects is a market bull, following the restart of Ambatovy in Madagascar and the start-up of metals projects in Indonesia, supporting the view that the market will remain balanced in the short term.

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- The expected improvement in sulphur supply in the second half of the year will provide some relief to sulphur burner operators that have struggled with the tight market in recent months. But the tightness from the smelter sector is not expected to improve in the short term.
- Nickel producer Meta Nikel is understood to be assessing whether to embark on a sulphur burner project in Turkey to meet its demand for sulphuric acid. This is currently met by imports of smelter acid, largely from Bulgaria.

- Japanese suppliers report limited potential for spot cargo availability in the short term because of lower sulphur content in copper concentrates and disruptions to operations during the first half of the year. Acid capacity in Japan is expected to remain stable at 8.6 million t/a in the outlook with production at around 6.0 million t in 2021. Exports are forecast to be down to 2.9 million t this year, below 2020 levels because of turnarounds and reduced supply.
- Outlook: Prices are not expected to ease in the short term, despite appearing to have reached a ceiling. The tight supply situation is not expected to ease in the coming months, with turnarounds and industrial action impacting availability. Strong demand from key industries as well as low inventories at smelter acid suppliers is keeping the price outlook firm. Indications for November spot cargoes are at higher prices to levels in early July – suggesting there may be room for further price increases before a peak is reached for the year.

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UNITED ARAB EMIRATES

Saipem wins contract expand Shah sour gas plant

The Abu Dhabi National Oil Company (ADNOC) has awarded a \$510 million engineering, procurement and construction (EPC) contract to Italy's Saipem to expand production capacity at the Shah sour gas plant, as the UAE looks to increase its output of gas by 2030. The Optimum Shah Gas Expansion (OSGE) & Gas Gathering project has been awarded by ADNOC Sour Gas, a joint venture between ADNOC and US energy major Occidental. The contract will increase gas processing capacity at the Shah plant by 13% per cent to 1.45 bcf/d from 1.28 bcf/d by 2023 and supports ADNOC's objective of enabling gas self-sufficiency for the UAE. The Shah gas plant currently meets 12% of the UAE's total supply of natural gas, as well as producing 5% of the world's elemental sulphur. The expansion will cumulatively represent a

45% increase on the plant's original capacity of 1.0 bcf/d when it came on-stream in 2015.

"Shah's expansion will optimise the plant as well as improve both capacity and higher-end product recoveries, further growing our contribution as a safe and reliable supplier of gas to ADNOC and the UAE," said Tayba Al Hashemi, chief executive at ADNOC Sour Gas.

The scope of the development work at the Shah gas plant includes engineering, procurement, construction, pre-commissioning, commissioning, and start-up of facilities to increase plant production capacity. Saipem will also extend the existing gas gathering network and new pad facilities, as well as all associated off-sites and utilities needed to integrate the new facilities with existing installations.

Gulf chemical industry "requires bold leadership"

Securing a bright future for the GCC's chemical industry will require bold leadership that adapts to the new trends emerging in the post-pandemic reality, said speakers at the inaugural edition of the Gulf Petrochemicals & Chemicals Association (GPCA) Leaders Forum. Delivering the inaugural address at the forum, Yousef Al-Benyan, chairman of the GPCA and vice chairman and CEO of SABIC, said that industry leaders would need to change how they think about growth, innovation and operating models. He highlighted a major acceleration - during the pandemic - of already established trends such as digitalisation, a re-energised focus on sustainability and innovation, the circular economy, the move towards decarbonisation and renewable energy, as well as the energy and materials transition among others. The pandemic emphasised the power of collaboration, without which the world would not be anywhere near a global recovery, he remarked. The industry's challenge now shifts to building a new ecosystem that allows us to thrive in the long run, Al-Benyan added, expressing his confidence in the industry's ability to emerge even stronger from this period of change.

Buoyed by a gradual economic recovery within the region and its largest export market, China, the GCC chemical industry believes that it is well positioned for long-term growth. Real growth in the GCC region is expected to be at 2.5% between 2021-2023, while China is targeting 6% growth in 2021. This may be a welcome development but comes with its own challenges, as the Asian country accelerates its move towards

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self-sufficiency in chemicals which will reduce demand for imports from the GCC region.

Dr. Abdulwahab Al-Sadoun, Secretary General of the GPCA, added, "Chemical industry leaders must leverage the lessons learned from the COVID-19 pandemic and lead with a renewed sense of purpose to create value for its shareholders, costumers, society and our planet. The next decade will require companies to embrace people centricity, innovate and adopt agile decision making. To succeed, the industry would also need to drive customer collaboration and formulate effective partnerships. It would need to develop products that meet the future needs of our times and demonstrate leadership in the digital transformation."

ISRAEL

Siwertell to deliver sulphur unloader for Ashdod

Bruks Siwertell has signed a contract with Ashdod Port Company Ltd for the delivery of a Siwertell ST 490-M screw-type ship unloader destined to serve Ashdod, Israel's largest seaport in terms of cargo volumes. The new Siwertell ship unloader has been ordered as part of the port's major expansion plans. It will be rail-mounted and used to discharge sulphur and petcoke at continuous rated capacities of 600 t/h and 500 t/h respectively from vessels up to 60,000 dwt.

A fundamental requirement of the port was environmental protection. Although a valuable and widely used commodity, it is now environmentally unacceptable for sulphur to be spilled during unloading. However, its containment increases the build up of sulphur dust 'hot spots', creating the potential to explode and cause fires. The totally-enclosed Siwertell unloader was the only system that could meet the port's standard and offer safe, high-capacity through-ship performance.

"Ashdod Port Company chose Siwertell technology to secure its substantial and growing dry bulk cargo volumes for a number of reasons," explains Bertil Andersson, Siwertell Sales Manager. "Most significantly, our Siwertell unloaders are the only proven solution for safe, enclosed and continuous sulphur unloading. They also meet the port's strict environmental requirements, handling materials without dust or spillage. All these units are fitted with the Siwertell Sulfur Safety System (4S), which detects and extinguishes fires early, shutting down the system to stop their spread, and safely containing them before they can become a full-blown blaze. To contain explosions, steel casings are reinforced and explosionventing valves are fitted along the conveyors to relieve pressure."

Ashdod's bulk terminal operates 24 hours a day and the new ship unloader is destined to serve this facility. It will be built and transported fully-assembled via heavy-lift vessel for installation at the port. Delivery is scheduled for April 2021.

UNITED STATES

Controls Southeast Inc. and Comprimo join forces on degassing

Comprimo, Worley's Sulphur Technology business, has become an authorised licensor for Controls Southeast Inc. (CSI), an AMETEK Company, for its patented sulphur degassing technology ICOn. To date, there is one ICOn unit in operation and two scheduled to start in 2021. By adding

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ICOn to its portfolio, Comprimo can now offer the Shell degassing (shared license with Shell) or the ICOn technology via CSI.

ICOn degasses the liquid sulphur in a small vessel over a fixed bed catalyst that promotes the release of the dissolved H_2S in the sulphur. It uses less plot space while allowing the choice of multiple design configurations when considering the various inputs/outputs of sparging gases and liquid sulphur. This flexibility in design makes it very suitable for revamp situations. While the Shell degassing is better suited for new build facilities, the selection preference might change depending on the size and individual situation.

"For years, our customers have relied on CSI to help solve their toughest challenges. With our customers' continued focus on sustainability and safety, there was a need for a better way to reduce emissions and make it safer to transport and handle sulphur. Licensing our ICOn sulphur degassing technology to Comprimo's Worley Sulphur Technology business provides our customers with a best-in-class solution that helps address these challenges," said Thomas Willingham, division vice president and CSI Business Leader.

"At the end of the day, it's about helping our customers be good neighbours by contributing to a more sustainable world. Applying degassing technologies lowers emissions and helps ensure the sulphur handling and transportation are safer. We are pleased that ICOn technology from CSI, combined with our Shell degassing license, offers our customers options when it comes to degassing," said Frank Scheel, senior vice president of Comprimo.

SWITZERLAND

Axens teams up with Sulzer on hydrodesulphurisation

Axens, and Sulzer Chemtech have formed an alliance to license a process for fluid catalytic cracking naphtha processing. The combined offering is based on Axens' Prime-G+[®] hydrodesulphurisation technology and Sulzer Chemtech's GT-BTX PluS[®] extraction technology. The combination offers a unique solution to reduce octane loss to a very low level for the gasoline pool. The technology is especially important in countries that are upgrading fuel specifications to meet environmental requirements, and it can be applied in new, or retrofits of existing units in operation to maximise profit.

CHINA

New refinery to begin test runs in Q3

China's Shenghong Petrochemical plans to start test runs at its 320,000 bbl/d crude unit in August or September, according to press reports. The new refinery, in the eastern port city of Lianyungang, will be the only greenfield oil refinery coming on stream in China this year, with a capacity equal to nearly 3% of the country's crude oil imports. Commercial operations at the plant are likely to begin in 1Q 2022, upon completion of downstream facilities. The refiner is reportedly in talks with suppliers to secure about 15 million bbl of crude oil, focusing on low-sulphur, low-acid grades, to be used for its trial runs through the end of 2021.

ARGENTINA

Axens to supply hydrodesulphurisation unit to Buenos Aires Refinery

Shell licensee Raízen Argentina has selected Axens for the supply of a Prime-G+ FCC gasoline hydrodesulphurisation unit for its Buenos Aires refinery. Raízen is developing a modernisation and expansion program for its existing 110,000 bbl/d refinery to meet more stringent motor fuels specifications in Argentina by January 1st 2024. Part of this program, downstream of the FCC unit, is an integrated solution based on Prime-G+ technology. The 10.200 bbl/d unit will be delivered in modular form to enable Raízen to execute the project in a competitive schedule, typically saving up to six months while ensuring the performance of the unit. This is achieved by a high degree of pre-fabrication and pre-commissioning.

"We are confident that having Axens delivering the modular hydrodesulfurisation unit is the key to timely achieving our targets and succeeding in the modernisation and growth of our Buenos Aires refinery," said Julio Ramos, Product Quality Project Manager from Raízen Argentina.

SWEDEN

Topsoe revamps hydrotreater

Haldor Topsoe has completed a revamp of Preem's renewable hydrotreater unit at their refinery in Gothenburg, Sweden. The 6,600 bbl/d hydrotreater is now able to co-process 85% renewable feedstock using Topsoe's HydroFlex[™] technology. HydroFlex converts a wide variety of renewable feedstocks into transportation fuels. The revamp is part of

ISSUE 395 SULPHUR JULY-AUGUST 2021 Preem's endeavours to reduce Sweden's total carbon emissions by 20%, and follows a revamp in 2010 that upgraded the unit to co-process 30% renewable feedstock, again using HydroFlex. The unit was one of the first in the world capable of processing renewable feedstock. Preem is aiming to produce 5.0 million m³ of renewable fuels by 2030, reducing carbon emissions by 12.5 million t/a, corresponding to 20% of Sweden's total emissions.

OMAN

Yibal Khuff to come online in Q3

State-owned Petroleum Develxopment Oman (PDO) says that it is preparing to start operations at Yibal Khuff in the third quarter of this year, adding around 20,000 bbl/d to the country's overall crude output. PDO says that the project is currently 99.7% complete, and will raise crude production by around 21,900 bbl/d according to contractor Petrofac, more than double the 10,000 bbl/d target that PDO set in 2015. It will also deliver 6.1 million m3/d (2.23 bcm/ year) of sour gas for local power generation and Oman's numerous enhanced oil recovery (EOR) projects. The project start-up has slipped from its original target date of 2019, as Petrofac worked to overcome technical challenges arising from handling the field's extremely high sulphur content.

CANADA

Sour gas plant receives permit approval

CSV Midstream Solutions says that it has received Environmental Protection and Enhancement Act (EPEA) regulatory permit approval from the Alberta Energy Regulator (AER) for its proposed Albright Sour Gas processing facility near Grande Prairie, Alberta. The main activity of the plant will be to separate and remove sour gas from crude sour gas for operators at Wembley, in the Wapiti-Montney metropolitan area. It is designed to process 4.2 million m³/d of sour gas, generating 370 t/d of sulphur.

CSV says that it employed an early community engagement philosophy prior to entering the formal regulatory approval process for the development in order to better understand the impact upon local communities of the planned project.

Daniel Clarke, CEO commented; "We are proud of the work our early engagement team has done fostering strong relationships and building upon the heritage and initiatives that currently exist within the community."

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Sulphuric Acid News

DEMOCRATIC REPUBLIC OF CONGO Production begins at Kamoa-Kakula copper mine



Production has begun at Ivanhoe Mines' Kakula copper mine in the DRC. The company says that total production for this year is expected to be 80-95,000 t/a of copper in concentrate, with a phase two expansion to 400,000 t/a due to be completed by Q2 2022. Ivanhoe is working with China's Zijin Mining on the development plan for phases 2 and 3 of the mine, as well as a feasibility study for the Kipushi zinc mine further to the east. Both projects lie close to the DRC's southern border, with Angola and Zambia respectively. Phase 3 of Kamoa will lift capacity to an anticipated 600-800,000 t/a of copper in concentrate, making it the second largest copper mine in the world after Escondida in Chile. Canadian-based Ivanhoe expects to be digging 3.8 million t/a of ore at Kakula with 6% copper content in Phase 1.

The DRC has a long-standing ban on exports of copper concentrate, and so processing of the copper is planned to occur in-country. Around 40% of the copper concentrate from Phase 1 (up to 150,000 t/a of concentrate) will be processed into a 99% copper blister at the nearby Lualaba Copper Smelter under a 10 year contract. Ivanhoe recently announced that an offtake agreement for 100% of Phase 1 production has been signed with the Citic Metals and Gold Mountains International Mining Company Ltd (a subsidiary of Zijin). Each of the companies will be receiving 50% of the Kamoa-Kakula Phase 1 production.

Further down the line, there are plans for a new smelting complex beginning operation in 2026. Ivanhoe signed a power supply agreement with a hydro-electric plant in April this year for the projected Kamoa expansions. The smelter would produce around 300,000 t/a of blister copper, as well as an estimated 1,600 t/d of sulphuric acid a by-product. Ivanhoe's plan is that the sulphuric acid produced at Kamoa would be sold to copper-oxide mining operations in the central African copper belt that currently purchase acid from Zambia or overseas.

CHINA

Contents

Sinopec starts up two new alkylation units

DuPont Clean Technologies says that it has achieved a successful start-up of two *STRATCO*[®] sulphuric acid alkylation units at the Zhongke Refinery and Petrochemical Company LTC refinery in Zhejiang, and the Sinopec Shanghai Company (SPC) refinery in Jinshan, Shanghai. Both are designed

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to process MTBE raffinate feedstock and produce 9,240 bbl/d (360,000 t/a) and 10,240 bbl/d (400,000 t/a) of alkylate, respectively. The low-sulphur, high-octane, low-Rvp alkylate with zero olefins will enable Sinopec to meet the China VI low sulphur fuel standard at these two refineries.

The start-up brings the number of *STRATCO* units in operation with Sinopec organization to six, with a seventh unit due to come online this year. Sinopec Shanghai refinery is the second commercial installa-

ISSUE 395 SULPHUR JULY-AUGUST 2021 tion of the Model 74 Contactor reactor, which reduces the number of total reactors and plot space required, at an overall lower capital cost for the alkylation unit. It has a volume of 68.1 m^3 (18,000 gallons), an increase from the standard size Contactor (Model 63) of 43.5 m³ (11,500 gallons) per reactor.

"In the last few years, DuPont and Sinopec have had the opportunity to start up several *STRATCO*[®] alkylation units together, providing DuPont with the opportunity to develop a strong relationship with each refinery. The success in both startup and operation continues to meet and exceed expectations, enabling the Sinopec organization to make a vast amount of high quality alkylate to improve the overall quality of their gasoline pool. We are very appreciative for the experience we've had with each of these refineries," said Kevin Bockwinkel, global business manager, *STRATCO* Alkylation Technology.

UNITED STATES

Rhyolite Ridge project wins key permit

ioneer Ltd says it has received a Class II Air Quality Permit for its lithium-boron Rhyolite Ridge project in Nevada, a major project milestone, following a detailed review of the project by the state of Nevada's Bureau of Air Pollution Control. The permit was a key requirement for construction to begin at the site.

The project comprises a quarry, overburden storage facility, an ore processing facility responsible for boric acid and lithium carbonate production, and a spent ore storage facility, as well as the first sulphuric acid plant permitted in the state of Nevada. The acid plant features MECS[®]/ SNC Lavalin designed heat recovery technology, which means the plant will generate all of the electricity and heat required for normal operations, according to ioneer. This means the operation will be energyindependent and using co-generated zerocarbon power. The acid plant features state-of-the-art controls that limit emissions to among the lowest in the world for this type of plant, the company claims.

ioneer's Managing Director, Bernard Rowe, said: "The issuance of the Class II Air Quality Permit represents a significant milestone for the Rhyolite Ridge lithiumboron project and supports our detailed plans for a processing plant with low emissions and minimal hazardous air pollutants. After regulatory review and public comment period, we are pleased that Rhyolite

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Ridge is the first project with sulphuric acid production to receive a Class II Air Quality permit in Nevada."

The company expects to mine and process 63.8 million tonnes of ore over the 26-year mine life at an average annual rate of 2.5 million t/a.

WORLD

Copper smelting activity rebounds from low point

Global copper smelting activity reached its highest point this year in May, with South America the top producing region, according to Earth-i and Marex Spectron's SAVANT platform. SAVANT's global copper smelting index averaged 49.4 for May, a return to long-run average levels after a record low point of 39.8 in March 2021. The platform, which monitors about 90% of smelting capacity, put the rise down to copper's price surge stimulating a supply response. Copper prices reached a 10-year high of over \$10,000/tonne in May on the London Metal Exchange.

Marex global head of analytics Dr Guy Wolf said the record low levels of smelter activity in March had led to "an explosive price rally" for refined copper. "The natural supply response to that became evident in the data towards the end of April has continued throughout May - hence the consolidation in copper prices," he said. "We are now entering a fascinating period, where seasonal declines in smelter activity in China and the rest of Asia are to be expected, and other regions showing no signs of slowdown. Given the importance of Chinese demand, it remains to be seen if the external supply can satisfy China's demand during this maintenance window."

FINLAND

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Metso Outotec wins order for precious metals recycling plant

Metso Outotec says that it has received an order for the engineering and delivery of key equipment for the expansion of a precious metals recycling plant, although the customer and the value of the contract were not disclosed. Metso Outotec's equipment delivery consists of a direct current (DC) furnace with feeding equipment and process control system. The order has been booked in Metals' Q2/2021 order intake. Typically, this type of an order is in the range of €8-15 million.

Metso Outotec's pyro- and hydrometallurgical technologies are capable of the processing of secondary raw materials, including valuable metals like copper and platinum. The AusmeltTM and KaldoTM processes can be used for integrated primary smelting and standalone smelting, complemented with efficient gas cleaning systems. Further refining can be accomplished with Metso Outotec's state-ofthe-art electrorefining and electrowinning processing technologies. The DC furnace is based on proprietary technology featuring advanced environmental performance and efficient slag and alloy separation providing high metal recoveries.

"We are excited about this order, as it will strengthen our position in treatment of secondary raw materials. Our DC furnace technology is well suited for secondary smelting applications, including precious metal recycling. This delivery is well in line with our strategy to grow in circular economy," explains Jyrki Makkonen, Vice President, Smelting business line at Metso Outotec.

MOROCCO

Morocco sets up Global Phosphorus Institute

Morocco's Mohammed VI Polytechnic University and the Ibn Rochd Foundation for Science and Innovation (FIRSI) have announced the creation of the Global Phosphorus Institute (GPI), an independent non-profit international institution. According to a press release, the GPI "aims to bring together scientists, policy makers and communicators, industry leaders, educators and a variety of food security stakeholders on a single platform." It also aims "to create and share innovative solutions to balance the need and use of phosphorus in the production of healthy food, animal feed and natural fibres as we protect our environment for a prosperous and equitable society in the spirit of the United Nation's Agenda 2030 for Sustainable Development."

Hicham El Habti, the president of Mohammed VI University and new president of the GPI said: "GPI will promote global, science-based, inclusive dialogue and collaborations on subjects ranging from industrial phosphorus use and recycling to nutrient management and stewardship. Morocco, as the custodian of the planet's largest known reserves of phosphate... has a unique duty to encourage and support global research, innovation

ISSUE 395 SULPHUR JULY-AUGUST 2021 and dialogue on this essential element and its vital role in life on earth.

"GPI looks forward to convening experts with a variety of diverse backgrounds and views to develop a variety of different approaches to phosphorus use," said El Habti. "Sustainable and innovative use of phosphorus is essential to improve life on earth in all its forms."

The global institute has appointed Dr Amit Roy as its first executive director to spearhead the operations (see People section). His initial focus will be creating the Consortium for cutting-edge phosphorus research projects, building global coalitions, and establishing research hubs around the world.

CANADA

Falco and Glencore agreement on copper-zinc project

Falco Resources Ltd says it has concluded an agreement in principle with Glencore Canada Corporation establishing a framework of terms and conditions pursuant to Falco's Horne 5 gold-silver-copper-zinc project in Quebec. The project covers the former Horne and Quemont mines, formerly copper-zinc sulphide mines, which will be de-watered and rehabilitated, as well as the Horne 5 deposit, which lies at a depth of 0.6-2.3 km. The new mine will produce an anticipated average 15,500 t/d of ore over the mine's 15 year life. Ore will be processed by primary grinding in a single SAG mill and ball mill, followed by three flotation and thickening circuits dedicated to recovering copper, zinc and pyrite concentrates. The pyrite concentrate would then be leached along with the pyrite flotation tailings in separate leaching circuits. Pumping out the old mines is expected to take two years from the completion of de-watering infrastructure in H2 2021/H1 2022. Access to the Quemont 2 shaft is contingent upon Falco's agreement with Glencore, which operates the Horne smelting facility only 700m away.

AUSTRALIA

Patent application for new phosphate fertilizer blend

Minbos has lodged an Australian provisional patent application for a new phosphate rock fertilizer blend. The provisional patent claims to produce a 100% organic phosphate fertilizer using less reactive

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phosphate rocks than conventional production. The new patent application has been filed to cover the new blend following analysis of results comparing different product forms from Minbos' Cabinda phosphate granules in field trials in Angola, and greenhouse trials at the International Fertilizer Development Centre (IFDC) in the US.

The company says that its new phosphate rock fertilizer blend promotes the early release of phosphate nutrients from phosphate rock, potentially eliminating monoammonium phosphate from the proposed Cabinda Phosphate granule formulation. This results in a purely organic fertilizer blend. Minbos says its new blend will be trialled during the company's 2021 and 2022 growing season through soil incubation tests, growth chamber trials and greenhouse trial. The company also says that the production of the new phosphate rock fertilizer blend can potentially be applied to the company's granulation plant and be including in the production profile from commissioning in 2022.

"This is a promising development for the company's plans to participate in the development of a regional agricultural powerhouse," said Minbos CEO Lindsay Reed. "The new fertilizer blend has the potential to deliver healthy, organic crop yields for Angola and its farming communities for decades to come."

INDONESIA

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Zhejiang Huayou HPAL project to come in under budget

Zhejiang Huayou Cobalt's first nickel and cobalt project in Indonesia will enter the commissioning stage at the end of this year, with capital expenditure coming in below planned levels, according to the company. The project, on Sulawesi, is one of several Indonesian nickel and cobalt plants using high-pressure acid leach (HPAL) technology. The project is a joint venture between Huayou, stainless steel giant Tsingshan Holding Group and China Molybdenum Co. It is designed to have annual capacity of 60,000 t/a of nickel content and 7-8,000 t/a of cobalt content in their nickel-cobalt mixed hydroxide product.

"We are confident to say to the market that the capex is lower than the original design. The original design is around \$1.2-1.3 billion," said George Fang, Huayou's executive vice chairman, speaking at an online industry conference, though he did not provide a revised figure for the plant's cost. "We are in the final stage of construction. We will finish all construction and start commissioning at the end of this year," he said, noting it will take about another 12 months for the plant to ramp up to full operation. "If there no was no Covid-19, we would have finished half a year earlier."

Huayou is also building another HPAL project in Indonesia, which was announced in May, with annual capacity of 120,000 tonnes in nickel content, double the size of the Huayue plant, in conjunction with battery producer EVE Energy. Fang said that that project is at the start of engineering and construction, and would source nickel from Indonesia's Weda Bay region.

HPAL plant inaugurated

In late June Indonesia's Minister for Maritime Affairs and Investment Luhut Binsar Pandjaitan inaugurated production operation at the PT Halmahera Persada Legend high pressure acid leaching (HPAL) facility on Obi Island, South Halmahera. The HPAL plant has been built at an investment cost of over \$1.0 billion and will produce nickel for electric vehicles. Minister Luhut said that

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by 2030 it is predicted that the global electric vehicle sales are predicted to reach 31.1 million units, and the Indonesian government is targeting production of 600,000 four-wheeled electric vehicles and 2.45 million two-wheelers. "Indonesia has sufficient resources and reserves of nickel and cobalt, supported by other minerals such as copper, aluminium and tin which will become vital for the electric vehicle industry," said Luhut in his official statement.

The HPAL plant will process lower grade nickel ore (limonite) to produce Class 1 nickel mixed hydroxide precipitate (MHP) in the form of nickel sulphate and cobalt sulphate.

INDIA

Chemetics wins new acid plant contract

Chemetics Inc. has been awarded a contract by Bodal Chemicals Ltd for a new 1,050 t/d sulphuric acid plant using solid sulphur as feedstock. The plant will produce both 32-33% oleum and 98.5% Sulphuric acid for the production of dye intermediates. Because Bodal Chemicals was seeking to conserve water use and maximise energy recovery, the new acid plant will be designed using an air-cooled cooling water system and an enhanced boiler feed water preheating system with *SARAMET*[®] acid coolers.

Vancouver-based Chemetics, part of the Worley Group, says that this project award continues the company's success in serving the Indian sulphuric acid market; in the last three years Chemetics has signed contracts for three new sulphuric acid plants and several sulphuric acid concentration plants in India.



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The International Fertilizer Association (IFA) says that **Svein Tore Holsether** has been elected as its new chair of the Association. IFA said in its press release that the selection of Holsether, the president and CEO of Yara International, is a continuation of the industry's commitment to sustainability.

"I am honoured to be appointed Chair of IFA because the fertilizer industry has a key role in finding sustainable solutions to some of the greatest challenges the world is facing. As an industry, we need to lead the way to decarbonise food and build resilient and fair food systems," Holsether said.

Dmitry Konyaev, CEO of Russia's Ural-Chem, has become the new vice chair of the Association. Both Holsether and Konyaev serve on the executive board of directors, which also welcomed two new appointments: **Jeanne Johns**, managing director and CEO of Incitec Pivot Ltd, and **Tony Will**, president and CEO of CF Industries. **Mostafa Terrab**, group chairman and CEO of OCP, Morocco, remains on the executive board of directors as Immediate Past Chair, along with **Zhai Jidong**, vice president international for Kingenta, and **Alzbeta Klein**, director general of IFA.

There are also five new Board Directors elected by the membership: **G. David Delaney**, CEO, Itafos; **Ahmed El-Hoshy**, Group CEO, OCI NV; **Shakeel Ahmad Khan**, CEO, Petronas Chemicals Marketing; **Suresh Krishnan**, managing director, Paradeep Phosphates Ltd and Mangalore Chemicals and Fertilizers; and **Mayo Schmidt**, president and CEO, Nutrien. IFA members also re-elected to the board of directors Raviv Zoller, president and CEO, ICL Group.

Rami Hiulumäki has been appointed vice president and head of Metso Outotec's Group Tax function. Rami succeeds Jarno Siivola, who left Metso Outotec on June 1st to join a new employer. Rami Hiulumäki joins Metso Outotec from Nokia, where he has headed the Group Tax function since 2018. Prior to that, he worked in various tax roles in Nokia, Nokia Siemens Networks and Deloitte. Rami will start at Metso Outotec during 3Q 2021.

The newly launched Global Phosphorus Institute (GPI) has announced the appointment of **Dr Amit Roy** as Executive Director to develop and lead the Institute. His initial focus will be creating a consortium for cutting-edge phosphorus research projects, building global coalitions, and establishing research hubs around the world.

"We are pleased that Amit joins GPI to direct this new global initiative," said Hicham El Habti, president of Morocco's Mohammed VI Polytechnic University and president of the GPI. "His vast experience combined with his enormous breadth of knowledge, research work and experience in managing the International Fertilizer Development Center (IFDC) are valuable assets to GPI. I am confident that his qualifications will make him succeed in building out this Institute"

Amit Roy has been involved in phosphorus research for more than four decades beginning with his graduate work for a doctoral degree. At the IFDC he developed new products and processes for conversion of phosphate rock into fertilizers along with other activities related to food production and agricultural development. As CEO of IFDC, he oversaw a number of major publications including Fertilizer Raw Material Resources of Africa, World Phosphate Rock Reserves and Resources and Sustainable Phosphorus Management, A Global Transdisciplinary Roadmap. These publications helped raise global awareness about phosphorus and inspired similar initiatives around the globe. He also launched more than 20 international IFDC branch offices to establish collaborative global research programs and spearheaded the 2006 Africa Fertilizer Summit held in Abuja, Nigeria.

"I am honoued and excited to develop GPI into the global convener of all things phosphorus," said Roy. "This platform will be available to anyone from the local dairy farmer to the climate scientist to the chemistry student to the food manufacturer interested industries because we must ensure that phosphorus, a non-substitutable vital element, is responsibly managed and available for future generations."

Calendar 2021

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

SEPTEMBER

12-15

2021 Australasia Sulfuric Acid Workshop, BRISBANE, Australia Contact: Kathy Hayward, Sulfuric Acid Today Email: kathy@h2so4today.com Web: www.acidworkshop.com

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Amine Treating and Sour Water Stripping Seminar, KANANASKIS, Alberta, Canada Contact: Paula Zaharko, Sulphur Experts Tel: +1 281 336 0848 Ext 101 Email: Paula.Zaharko@SulphurExperts.com

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'Virtual Vail 2021': Annual Sulphur Recovery Symposium – **Virtual event** Contact: Mike Anderson, Brimstone STS Phone: +1 909 597 3249 Email: mike.anderson@brimstone-sts.com 20-24 Sulphur Recovery Seminar,

KANANASKIS, Alberta, Canada Contact: Paula Zaharko, Sulphur Experts Tel: +1 281 336 0848 Ext 101 Email: Paula.Zaharko@SulphurExperts.com

28-30 **POSTPONED TO MAY 2022**

8th Sulphur and Sulphuric Acid Conference, CAPE TOWN, South Africa Contact: South African Institute of Mining and Metallurgy Tel: +27 (011) 834 1273 Web: www.saimm.co.za

OCTOBER

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Amine Treating and Sour Water Stripping

Seminar, NOORDWIJK, Netherlands Contact: Paula Zaharko, Sulphur Experts Tel: +1 281-336-0848 Ext 101 Email: Paula.Zaharko@SulphurExperts.com

11-15

Sulphur Recovery Seminar, NOORDWIJK, Netherlands Contact: Paula Zaharko, Sulphur Experts Tel: +1 281-336-0848 Ext 101 Email: Paula.Zaharko@SulphurExperts.com

NOVEMBER

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Sulphur & Sulphuric Acid Conf. 2021 Contact: CRU Events Tel: +44 (0) 20 7903 2444 Fax: +44 (0) 20 7903 2172 Email: conferences@crugroup.com

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CRU's **Sulphur + Sulphuric Acid** will run as a fully virtual event in 2021 – connecting you with an even wider audience of sulphur and acid industry professionals from around the globe.

Drawing on the success of the 2020 virtual event you can expect expanded content streams, enhanced networking opportunities and much more – all from the convenience of your plant, office or home.

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



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Crude to chemicals

With demand for conventional fuels projected to peak and fall over the next decade, some refiners are looking to petrochemical production as a way of diversifying their product slate.

ost refineries are reliant on the production of liquid fuels. On average, around 55% of all refinery products are sold as gasoline, diesel and other middle distillates, kerosene etc, as well as bunker fuels, and refineries depend upon the difference between the price of oil that they buy and the price of the fuels that they sell to make their margin. Conversely, petrochemicals like olefins such as ethylene and propylene, aromatics, glycols, and polymers represent currently collectively only 5-20% of refinery output, depending on the refinery's configuration.

Traditionally, the relationship the relationship between refining and petrochemicals has been at one remove; refineries focused on fuels production, and sold the naphtha that they produced to operators of steam crackers, who would then turn it into ethylene, propylene, and other basic chemical building blocks. However, changes in the market for oil products, on both the supply and demand sides, are now encouraging refinery operators to integrate petrochemical production into their product slate.

Market changes

On the demand side, car sales have been tapering off even in the developing world, and vehicles are becoming more fuel efficient, requiring less gasoline per unit. Also, while currently still only a small sector of the market, there is the growing push for hybrid

and electric vehicles - many countries in the developed world are planning to ban the sale of fossil fuel driven vehicles from about 2030. Overall, the US Energy Information Administration predicts that US fuel consumption for light-duty vehicles will decline by 1% annually through 2050. At the same time, there are tightening regulations on sulphur content of fuels and the carbon dioxide that they produce when burnt, which are placing increasing pressures on refineries to invest in expensive process equipment items to remove more sulphur and produce less, e.g., high sulphur fuel oil as against more middle distillates. US fuel oil demand is predicted to fall by 25% this decade.

In contrast to fuels, petrochemical markets continue to be relatively buoyant. In spite of a growing backlash against 'single use plastics' in the developed world, global demand for plastics products and synthetic fibres continues to grow, and with them demand for olefins such as polyester and aromatics like paraxylene. Urbanisation and rising wealth in the middle classes of developing nations are also driving above-GDP growth rates, and China's consumer boom in particular has led to increasing demand for packaging, consumer goods, and car parts.

One the supply side, the past decade has seen a surge in output from US tight oil production. This lighter crude slate has meant higher light distillate yields for LPG, naphtha and gasoline, resulting in higher light products with potential for chemical integration. At the same time, increased output of natural gas liquids from US shale gas production also encouraged ethane cracker investments, with a lower ethylene production cost than naphtha, especially given how low US natural gas prices have gone. But US tight oil production has also moved the US close to self sufficiency in oil and led to significant US oil exports for the first time in decades, bringing down the price of oil globally and shutting out some medium and heavy grades as OPEC cuts production.

IHS Markit suggests that the pull of changing demand means that oil refiners are seeing an opportunity to convert lower value oil into higher value chemicals and therefore seeking to "push" barrels of oil (displaced and new) into chemical markets. This is leading to increasing interest in crude to chemicals technologies, which in effect merge a refinery and petrochemical plant into one; in theory returning higher margins to refiners relative to more traditional fuels products. Figure 1 shows projections by Wood Mackenzie that over the next 15 years most new demand for oil-based products is going to come from the chemical sector.

Three 'generations' of crude to chemicals

There are three 'generations' of crude to chemicals technology, but all have the common feature of increasing the refinery yield of light olefins (ethylene or propylene)

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or aromatics such as benzene, toluene, and xylene. In general, to maximise the conversion of crude oil into petrochemicals, the refiner must utilise streams that would otherwise be used for the production of fuels such as kerosene and diesel to produce naphtha, as well as upgrading heavy bottom of the barrel products into steam cracker friendly feedstocks.

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The first 'generation' depends upon existing refinery units and can typically produce chemical yields of 15-20%. The second generation of technologies now being integrated into new and existing refineries can lift this to 40-50%. Future, 'third' generation designs could potentially convert up to 80% of a crude barrel into petrochemicals.

As far as existing technologies go, a typical refinery begins with fractional distillation, breaking down the crude feed into its constituent parts, ranging from light, shortcarbon-chain molecules such as gasoline, naphtha, and propane to heavy diesel and vacuum gas oil (VGO). VGO is usually then further processed in a downstream hydrocracker or fluid catalytic cracker (FCC), depending on the desired product output. Hydrocracking is targeted towards diesel production and generates no olefins, since any double bonds are hydrogenated, but naphtha from the hydrocracker can be sent either to an ethylene steam cracker to produce olefins or to a reformer to be refashioned into aromatics. To increase chemical output, hydrocracker operators can target naphtha rather than diesel production. FCC units meanwhile break down VGO into gasoline. The process generates propylene at around 5-20% of output, but refiners can run FCCs at higher severities (higher temperatures and longer residence times) to increase propylene yield further.

Crude to chemicals options

A variety of 'second generation' options now exist for refinery crude to chemicals processing. One is the direct processing of crude oil via steam cracking to produce ethylene and a small quantity of propylene. The direct use of crude oil in steam cracking for the production of light olefins has historically been hampered by coke formation and fouling of crackers, but ExxonMobil have a process using light crude which has been in operation in their Singapore refinery since 2014 (see below).

Saudi Aramco has filed patents for the integration of hydroprocessing/de-asphalting with steam cracking for olefin production. The hydro-processing/de-asphalting step produces a highly paraffinic, de-asphalted and de-metalised stream, which can later be processed in the steam cracking unit.

Middle distillates such as diesel and residues from vacuum distillation can be hydrocracked to produce a naphtha range stream, which then be processed to produce aromatic compounds.

Axens offers its *H-Oil* process in association with naphtha fixed-bed hydrocrackers. Light naphtha is routed to a steam-cracker, whose olefinic streams have to be selec-



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tively hydrogenated. Heavy naphtha is dedicated to the aromatics block, designed to synthesise benzene, toluene and xylene. It also has a high severity FCC (HSFCC) process using deep feed pretreatment and its patented permutable reactor system (PRS) upstream of the HSFCC to maximise the overall olefins yield.

Benefits of integration

One of the benefits that can come from integrating petrochemicals production with refining is that it provides an opportunity to integrate and optimise allocation of resources and feedstocks, maximise the process streams that can be shared and exchanged between the two halves of the facility, and allow the sharing of utilities, logistics and energy costs. It may also allow a producer to switch product yields between refining and chemicals, depending on where the greatest value lies at the time. All of this can help to reduce cost and improve overall profitability. It can also decrease capital intensity through scale; refinery scale petrochemicals production can be much larger than standalone petrochemical sites and offer corresponding efficiency gains.

Aramco said that its thermal crudeto-chemicals technology (developed with Axens and TechnipFMC) could cut capital costs by 30% compared to conventional refining by allowing several oil treatment steps to be combined into one operation – removing sulphur, cracking heavy fractions etc into a suitable feedstock for steam cracking via several 'layers' of catalyst.

Asia

The majority of crude to chemicals plants planned or operational have been in Asia and the Middle East. One of the first movers was ExxonMobil, which opened an ethylene cracker in Singapore in 2014 based on crude feedstock rather than naphtha. ExxonMobil has its own proprietary technology which allows the processing of light crude directly by pre-heating of the crude oil, partially vapourising the heated crude in a flash tank and feeding the vapor from the flash tank to the steam cracker to produce ethylene, propylene, and related products.

In India, Reliance has a crude oil to chemicals project under development at its Jamnagar refinery – the world's largest - which plans to more than double crude

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conversion to chemicals. The project will convert the site's entire FCC capacity to Petro-FCC, and will add large naphtha catalytic cracking, steam cracking, and aromatics blocks to raise chemicals conversion to over 35% for the site.

S-OIL at Ulsan in South Korea has recently built the world's first commercial high severity FCC unit coupled with heavy oil hydrodesulfurisation and associated units to reduce high sulfur fuel oil production. The project has raised crude conversion to chemicals from 8% to 13% for the refinery.

China

China's huge demand for petrochemicals and the fall in global oil prices around 2014-15, along with the opening up of crude import licences to private companies, and the ban on Chinese refiners from exporting fuels have all combined to encourage Chinese refiners to cross into crude to chemicals production. The first was Hengli Petrochemical's 400,000 bbl/d refinery and paraxylene complex in Dalian, which came on-stream in 2019. The plant is capable of processing 20 million bbl/year of crude, using Axens technology, including H-Oil ebullated bed hydroconversion technology for processing vacuum residue, a Solvahl de-asphalting unit for processing of unconverted residue, hydrocracking for processing atmospheric gas oil to produce the maximum yield of naphtha and hydrotreating for naphtha processing. Continuous catalytic regenerative reforming maximises aromatics production from naphtha, with paraxylene purification for full isomerization of other C8 aromatics into paraxylene. The plant overall yields around 40% chemicals production, mostly paraxylene for polyester fibre and polyethylene terephthalate (PET) production.

A similar sized project is underway at Zhejiang Petrochemical, which is building a crude-to-chemicals complex in two phases in China's Zhejiang Province. Each phase has a capacity of 400,000 bbl/d of crude processing, with around 50% of this going to make chemicals. UOP is providing technologies for the complex, including hydrocracking to break down vacuum gas oil into naphtha and reforming and extraction to make aromatics from the naphtha. At capacity, it will produce 8.8 million t/a of paraxylene, as well as 500,000 t/a of propylene using UOP propane dehydrogenation technology.

Shenghong Petrochemical is another large project, looking to process 300,000

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bbl/d of crude, again with paraxylene as the main chemical output. The first crude distillation unit at Zhejiang Phase 1 came onstream in November 2020, and the second in March 2021.

Saudi Aramco

One of the largest crude to chemicals projects on the horizon was to have been at Yanbu in Saudi Arabia, where state oil company Saudi Aramco and state petrochemical giant Sabic - itself now 70% owned by Aramco – were planning a \$20 billion petrochemical complex based on processing 400,000 bbl/d of Arabian light crude into 9 million t/a of downstream chemicals and base oils, with an on-stream target date of 2025. The facility would sell 45-50% of its output as chemicals, including olefins, aromatics, glycols, and polymers. It was seen as an acknowledgement by the world's largest oil producer that the future of oil was in petrochemicals. Aramco had targeted \$100 billion in chemical investments out to 2035, to convert 3 million bbl/d of oil - one third of its output - into chemicals. The company has been developing its own patented crude to chemicals technology in partnership with Chevron Lummus Global and McDermott. The company has also signed an agreement with Axens and TechnipFMC to work on a high-severity FCC process for chemicals.

However, in October 2020 came signs that Aramco and Sabic were reassessing this plan, with an announcement that they were instead considering integrating Aramco's existing refineries in Yanbu with a mixed feed steam cracker and derivative olefins units. The companies said in a joint statement that this would increase cost efficiency and competitiveness as well as creating value opportunities for petrochemicals. The reassessment was prompted in the covid-related collapse in global oil demand and prices, and a need for Aramco to cut costs, particularly on the capex side.

According to Sabic, however, the two companies maintain that they are still committed to "advancing crude to chemicals technologies through existing development programs with the goal to increase cost efficiency."

A glut of chemicals?

The scale of production from refinery crude to chemicals plans can be large. A 400,000 bbl/d refinery producing chemicals at 45-50% of output will be generating 10 million t/a of petrochemicals, compared to 2 million t/a for a typical naphtha-based ethylene cracker. East Asia in particular could face a problem with the combined paraxylene output of China's new crude to chemicals plants and consequent oversupply in the Asia-Pacific aromatics market; China imports 11 million t/a of paraxylene per year, and will temporarily more than achieve self sufficiency (although demand is continuing to increase), displacing product from South Korea, Taiwan and Japan.

On the other hand, olefins markets are likely to be less affected, as they are generally already quite large. Furthermore, while large crude to chemicals projects can cost billions of dollars, increased crude to chemicals production might lead to a rethink in the scale of a typical refinery. Refineries are often large because margins are slim, but the higher margins achievable from chemicals might mean smaller facilities were more profitable.

Changing the industry

Crude to chemicals offers the possibility of radically reconfiguring the refining industry, at least as far as some of the large scale operators are concerned. The impact on the sulphur industry may not be a profound one – most sulphur is already recovered from a barrel of oil. However. it has the potential to prevent any future decline of the refining industry in the face of falling fuel demand, as well as switching refining activity towards more advantaged feedstock locations as well as places where petrochemical demand is rising. Research and analysis company FutureBridge suggests that the type and level of refinery and petrochemical integration will primarily be driven by feedstock advantage, and hence will vary from region to region. In the US and the Middle East, which are not dependent on crude oil imports where there is sufficient availability of cheap natural gas liquids, direct production of crude oil to chemicals could become the prevailing option, whereas for regions, such as Europe and Asia, dependent on crude oil feedstock import and with limited availability of NGLs, the adoption of crude-to-chemicals technology will be governed by the capital efficiency of the project and demand for the petrochemicals output.

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Sulphur forming project listing 2021

Sulphur's annual listing of new or recently completed sulphur forming projects worldwide covers both new sour gas and refinery sulphur forming projects as well as upgrades at existing units.

System manufacturer/ supplier	Operating company	Operating site	Units	Product type	Scheduled throughput	New project/ expansion	Scheduled completion
Enersul	Banco	Sitra	3	granule	1 500 t/d	new	2021
RELGUIM	Бароо		0	Branalo	1,000 0 4		2021
IPCO	Duval	Antwerp	na	pastille	na	new	2020
CANADA				paotino			
Matrix PDM	Heartland Sulphur	Scotford	1	prill	2.000 t/d	new	2020
EGYPT			-	pini	2,000 0 0		
IPCO	Midor	El Amreva	3	pastille	230 t/d	new	2021
Enersul	HPCL	Vizag	2	granule	1.000 t/d	new	2021
IPCO	Econova	n.a.	3	pastille	580 t/d	expansion	2020
IPCO	Econova	n.a.	1	granule	700 t/d	new	2021
IRAQ							
IPCO	Missan Oil Co	Halfaya	n.a	pastille	200 t/d	new	n.a.
KAZAKHSTAN							
Enersul	Caspian General Contr.	n.a.	3	granule	1,500 t/d	new	2020
KUWAIT							
Enersul	KNPC	Mina al Amina	1	granule	1,200 t/d	expansion	2020
Enersul	KNPC	New Refinery Project	4	granule	4,800 t/d	new	2021
MALAYSIA							
Enersul	Petronas RAPID	Pengerang, Johor	5	granule	2,000 t/d	new	2021
OMAN							
IPCO	Duqm Refinery	Duqm, Oman	3	granule	900 t/d	new	2022
QATAR							
Enersul	Qatargas	Ras Laffan	2	granule	2,400 t/d	expansion	2021
RUSSIA							
Enersul	Syzran Refinery	Samara	1	granule	350 t/d	expansion	2021
SINGAPORE							
Enersul	SPCA Advance Pte. Ltd	Singapore	4	granule	2,400 t/d	new	2022
SPAIN							
Enersul	Petroleos del Norte	Bilbao	1	granule	350 t/d	expansion	2021
THAILAND							
Enersul	Thai Oil	Sriracha	3	granule	1,500 t/d	new	2022
UNITED ARAB EMIR	ATES						
Enersul	ADNOC	Shah	2	granule	2,320 t/d	new	2022
US VIRGIN ISLANDS	5						
Matrix PDM	Limetree Bay Refinery	St Croix	1	prill	1,000 t/d	new	2020

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Fig. 1: Global alkylation capacity by region, million bbl/d

The continuing spread of alkylation technology and the preference for the sulphuric acid route are leading to increased demand for acid in refineries.

Ikylation is a refinery process which converts light olefins into a highquality gasoline blendstock by reacting them with isobutane. The most common is C4 alkylate, made by alkylating butylene with isobutane. However, alkylate can also be made from propylene and isobutane, or pentene and isobutane. It is particularly desirable because of its combination of properties; zero sulphur content, no aromatic content, low vapour pressure and high octane number, and is used as a blendstock in the manufacture of cleaner burning, premium quality gasoline. In the US, a creeping ban on the use of MTBE - the major alternative octane improver - and the increasing use of ethanol as a gasoline component have also led to increased demand for alkylate as a balancing component. It is reckoned that in California the proportion of alkylate used in gasoline rose from 17% (when MTBE was permitted) to 23% now that up to 10% ethanol is blended.

Although alkylation has traditionally mainly been a North American phenomenon, its use is spreading worldwide – our news this issue notes that DuPont has licensed its *STRATCO* alkylation process to two more Chinese refineries, making six plants in China now using that process.

Sulphur vs HF

Acid is used to catalyse the alkylation reaction, and the two main ones used are sulphuric and hydrofluoric (HF) acid. There are two main HF processes, licensed by UOP and ConocoPhillips, while sulphuric acid licensors include DuPont (the major licensor), ExxonMobil/Axens, CB&I (now Lummus), and a Kellogg process which is no longer offered commercially – KBR instead now has a solid acid alkylation technology called K-SAAT. with installations in both China and the US. Chevron and Honeywell have developed a non-acidic process using an ionic liquid called ISOALKY, though there is so far only one commercial reference. The China University of Petroleum has also developed an ionic process which is marketed by Wall as Ionikylation, and which has been used in several Chinese refineries.

Installation and operating costs are similar for sulphuric and hydrofluoric acid alkylation. Sulphuric acid is cheaper than HF but is more complex to regenerate and has higher usage rates. In the early days of the processes sulphuric acid was preferred, but during the 1980s and 90s, HF gained predominance, and by the turn of the century there was roughly a 50-50 split between their installations. However, the number of new HF installations has fallen dramatically over the past 20 years, due to increasing safety concerns, and only about one third of US refineries now use HF. While both sulphuric and hydrofluoric acids are highly corrosive and can cause terrible burns on skin contact, the danger with HF is that it is more volatile, and can form an expanding toxic vapour cloud that travels along the ground and which can affect a much wider area, and which also has the potential for explosion, whereas sulphuric acid merely pools as a liquid. With the acids being used in close proximity to hydrocarbons such as LPG, there is a potential for explosions which can rupture acid tanks and release large volumes of acid. A series of HF accidents and near misses at US refineries, and culminating in an explosion and fire at the Philadelphia Energy Solutions (PES) refinery in Philadelphia in 2019, have led the US Chemical Safety Board (CSB) to call upon the Environmental Protection Agency (EPA) to review its regulation of HF in alkylation and other applications and look for substitutes. So far, however, an EPA response to the CSB request has not been forthcoming. Meanwhile, the CSB's final report on PES is still pending approval. Operators argue that the use of modifiers in HF can reduce the formation of vapour clouds and water spray systems can be used to contain any release. Nevertheless, there have been several conversions from HF to sulphuric acid or other systems. DuPont markets its ConvEx

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ALKYLATION

technology for converting HF alkylation plants to sulphuric acid which can also be used to expand unit capacity at the same time.

In China, which has had a number of the alkylation installations outside of the US, there are only two HF alkylation plants operating, and considerable scrutiny of the process by the Environmental Protection Ministry.

Another factor favouring sulphur is that as refineries have been pushed towards increased sulphur removal from crude feeds, so the volumes of elemental sulphur available at refineries have increased, making for a ready potential feedstock for on-site sulphuric acid production, and helping to control the cost and any logistical difficulties of importing acid.

Spent acid regeneration

With the cost of merchant acid increasing, and costs of safe disposal of spent acid likewise, the option to regenerate spent acid is becoming an increasingly attractive one, with a number of companies now providing acid regeneration services, either on a merchant basis or via a captive acid regeneration unit. Where refiners have taken the option of on-site acid generation, it can be relatively straightforward to build acid regeneration capacity into the existing sulphuric acid plant.

Capacity

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Total US alkylate capacity is just over 1.3 million bbl/d, according to the Energy Information Association, just over half of it in the PADD 3 region (US Gulf Coast). This has been a slow, steady rise from around 1.0 million bbl/d in 1990. Over the same period, alkylation capacity outside the US has risen to around 1.1 million bbl/d, according to OPEC figures (see Figure 1), with installations at, e.g. Reliance's refinery in Jamnagar where an 83,000 bbl/d unit – one of the largest in the world – now operates. Chinese capacity now represents about 100,000 bbl/d of this, with a number of alkylation sections added to refineries over the past decade to help meet China-VI (<10ppm sulphur content) gasoline standards.

Additional alkylation capacity out to 2025 is projected to add another 200,000 bbl/d of capacity, with OPEC projecting a further 600,000 bbl/d of capacity being added in the decade from 2025-2035, by which time global alkylation capacity will reach 3.2 million bbl/d. This represents a modest but still noteworthy average annual growth rate of about 1.8-2.0% over the period.

Sulphuric acid demand

While HF functions almost as a 'pure' catalyst, for the sulphuric acid alkylation route there is a fractional conversion of acid, and hence 'consumption' is relatively high; around 10-12 kg of acid per barrel of alkylate produced at best, and potentially as high as 15-25 kg/bbl alkylate if the cracker is being run at high severity. Not all of this is pure consumption; acid concentrations must be kept high (>90%) in order to prevent acid 'runaway', where catalytic activity rapidly declines and polymerisation is enhanced, and so the acid must be continually topped up with fresh acid and spent acid removed from the system. But this effective consumption of acid means that the total market for sulphuric acid as an alkylate catalyst is thus around 10 million metric tonnes per year; only a small fraction of the global market for sulphuric acid (less than 4%), but still an important end-use.





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- Advanced ammonia Claus
- Sulphur degassing
- · Thermal and catalytic oxidisers
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 (main burners, thermal reactors, WHB, condensers)



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Sulphuric acid projects 2021

Sulphur's annual survey of recent and planned construction projects in the sulphuric acid industry includes several large-scale acid plants both for phosphate processing and to capture sulphur dioxide from smelters.



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Company	Site	Application	Capacity	Licensor	Contractor	Type of project	Start-up date
ALGERIA							
Sonatrach	Oud el Kebrit	Sulphur burning	4,500 t/d	n.a.	n.a.	New	2022
BRAZIL							
Klabin	Ortigueira	WSA	150 t/d	Haldor Topsoe	Andritz	New	n.a.
CHILE							
Codelco	Chuquicamata	Smelter off-gas	2 x 2,050 t/d	DuPont MECS	SNC Lavalin	New	2020
Enap Refinerias SA	Hualpen	WSA	140 t/d	Haldor Topsoe	Tecnicas Reunidas	New	2024
CHINA							
Shandong Chambroad	Shandong	WSA	419 t/d	Haldor Topsoe	n.a.	New	2020
Wanhua Chemical	Yantai, Shandong	Spent acid regen	630 t/d	Chemetics	n.a.	New	2023
PetroChina	Jihua	Spent acid regen	450 t/d	Chemetics	n.a.	New	2022
CNOOC	Hainan	Spent acid regen	460 t/d	Chemetics	n.a.	New	2022
Shandong Yulong	Yantai, Shandong	Spent acid regen	95 t/d	Chemetics	n.a.	New	2023
DEMOCRATIC REP	UBLIC OF CONGO						
Kamoto Copper Co	Lualaba	Sulphur burning	1,900 t/d	DuPont MECS	Desmet Ballestra	New	2021
EGYPT							
El Nasr	Ain Sukhna	Sulphur burning	2 x 1,900 t/d	Outotec	Intecsa	New	2020
WAPHCO	Abu Tartur	Sulphur burning	5,000 t/d	Outotec	n.a.	New	2024
Sprea Misr	Ramadan City	Sulphur burning	500 t/d	Nuberg	Nuberg	New	2022
FINLAND							
Boliden	Harjavalta	Smelter off-gas	2,000 t/d	Outotec	n.a.	New	2020

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Company	Site	Application	Capacity	Licensor	Contractor	Type of S project	Start-up date
Bodal Chemicals	Sakhva	Sulphur burning	1.050 t/d	Chemetics	n.a.	New	2022
Arti Chemicals	Vapi	Sulphur burning	570 t/d	Chemetics	n.a.	New	2023
MBAPL	Rajua	Sulphur burning	300 t/d	n.a.	n.a.	New	2022
Rama Phosphates	Indore	Sulphur burning	170 t/d	n.a.	n.a.	New	2021
INDONESIA							
PT Pertamina	Balikpapan	WSA	74 t/d	Haldor Topsoe	n.a.	New	2020
PT Pertamina Cepu	Jambaran-Tiung Biru	Sulphur burning	n.a.	Chemetics	n.a.	New	2021
PT Halmahera Lygend	Obi Island	Sulphur burning	2,700 t/d	n.a.	n.a.	New	2021
PT Smelting	Gresik	Smelter off-gas	1,330 t/d	Chemetics	n.a.	New	2024
Eramet	Weda Bay	Sulphur burning	3,000 t/d	DuPont MECS	CC6	New	2025
LITHUANIA							
Orlen Lietuva	Mazeikiai	Spent acid regen	75 t/d	DuPont MECS	n.a.	New	2025
MOROCCO							
OCP	Jorf Lasfar	Sulphur burning	2 x 5,000 t/d	Chemetics	Intecsa	New	2022
PERU							
Petroperu	Talara	WSA	560 t/d	Haldor Topsoe	Cobra	New	2021
RUSSIA							
PhosAgro	Volkhov	Sulphur burning	2,400 t/d	n.a.	n.a.	New	2022
NorNickel	Norilsk	Smelter off-gas	n.a.	Outotec	n.a.	Revamp	2022
SAUDI ARABIA							
Ma'aden	Ras al Khair	Sulphur burning	5,000 t/d	n.a.	n.a.	New	n.a.
SOUTH AFRICA							
Anglo Platinum	Polokwane	WSA	148 t/d	Haldor Topsoe	Hatch	New	2020
SWEDEN							
Boliden	Ronnskar	Smelter off-gas	n.a.	Outotec	n.a.	Revamp	2020
UNITED STATES							
ioneer	Nevada	Sulphur burning	3,500 t/d	DuPont MECS	SNC Lavalin	New	2023

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4 5 **Reducing NOx emissions** 6 7 8 in metallurgical oleum 9 10 tower production 11 12 13 14 A. Goudarzi of CECO Industrial Solutions discusses the science behind NOx content and how it 15 impacts sulphuric acid producers. In a recent project in Korea, TWIN-PAK[®] candle filter technology was successfully used to reduce NOx emissions in metallurgical oleum tower production. After 16 installation of the candle filter mist eliminators the plant was compliant with environmental 17 regulations enabling the producer to operate the plant without penalties or shutdowns. 18 19 verchanging regulations and air 20 pollution control is a major global 21 concern, organisations are looking for smart solutions to reduce emissions 22 to meet stipulated limits by governing bodies. Elevated temperatures required 23 for metallurgical roasters often create higher levels of nitrogen oxides (NOx) which require abatement or exceed emis-25 sion limits. As the gas flows through the operation from the roaster to the final 26 stack output, mitigating NOx levels has 27 become a major global initiative which has transgressed to the metallurgical sul-28 phuric acid industry. CECO Filters in development with a major Korean metallurgical 29 producer "Company K", utilised the last 30 line of defence, candle filter mist eliminators. to remove NOx outputs to meet the 31 local requirements. 32 Fig. 1: Top compartment retrofit 33 34 35 SOURCE: CECO INDUSTRIAL SOLUTIONS 36 37 38 39 40 41

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Using CECO Filters TWIN-PAK[®] & Graded Bed[™] technology the operator was able to further enhance performance to meet regulations.

NOx content and how it impacts sulphuric acid producers

The reaction between nitrogen and oxygen results in nitric oxide (NO) and nitrogen dioxide (NO₂) formation – otherwise known as NOx or nitrogen oxides.

$$N_2 + O_2 \rightleftharpoons 2NO$$

 $2NO + O_2 \rightleftharpoons 2NO_2$

A common day problem for most metallurgical sulphuric acid producers is high levels of NOx formation and output at the stack.

There are three common sources of NOx formation:

- above 815°C NOx formation starts to increase exponentially and reach higher than 800 ppm at temperatures of 1,650°C;
- unbalanced oxygen concentrations and higher combustion residence times;
- wet electrostatic precipitators (WESP) are commonly known to spark NOx formation.

With stricter controls on air pollution regulations and implementation of NOx emission reductions to mitigate the impact on our ecosystem, more producers are experiencing stringent changes in environmental permitting and are required to take action to comply with new local norms. These changes have been geographically noticeable throughout the last decade.

Table 1: Stream 1 – inlet para	meters
Volumetric gas flow rate	100,000 Nm³/h
Temperature	70°C
Gauge pressure	1800 mm H ₂ 0 (g)
Mist loading	4,000 mg/Nm ³
NOx content	< 80 ppm
Allowable pressure drop	< 130 mm H ₂ 0 (g)

Source: CECO Industrial Solutions

NOx requirement at stack

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< 60 ppm

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NOx has an affiliation to sulphuric acid and absorbs onto molecules to form nitrosylsulphuric acid. This enables candle filters with highly dense fibres to create a liquid film layer of sulphuric acid to absorb NOx contaminants in the gas streams passing through the candle filter media bed.

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 $NO + NO_2 + 2H_2SO_4 \rightleftharpoons 2NO \cdot HSO_4 + H_2O$

 $N_2O_3 + 2H_2SO_4 \rightleftharpoons 2NO \cdot HSO_4 + H_2O$

An optimised solution to a common problem

A Korean producer faced local laws swiftly changing on NOx emissions from 120 ppm to 60 ppm. They contacted CECO Filters for mist eliminator solutions to help resolve the problem. CECO proposed adding candle filter mist eliminators to the oleum tower. The current tower didn't house any filters and required retrofitting the top compartment of the tower to install filter units.

The oleum production presented pressure drop concerns and restrictions through the existing plant set-up and the customer was limited to solutions with a compact design to fit into the existing constraints and increased throughput capacity while meeting the pressure drop limitation for the existing blowers (Fig. 1 & Table 1).



Fig. 2: TWIN-PAK[®] candle filter

Source: CECO Industrial Solutions

TWIN-PAK® candle filters

TWIN-PAK[®] was developed specifically to address conventional candle filter restrictions through arrangement reconfiguration by optimising performance through increased filtration area to give additional capacity flow, reduced pressure drop, better filtration efficiency and output performance, ideal for retrofitting solutions, as well as compact design solutions for greenfield projects to reduce capital expenditures without impacting operation expenditures and maintaining an overall economical solution by optimising the total cost of ownership for operators.

In this project, the TWIN-PAK[®] filter arrangement offered greater reductions in pressure drop compared to conventional filters, decreasing the pressure drop by 50% (180 mm H₂O (g) to 90 mm H₂O (g)), as well as creating more surface area to enable better NOx absorption (Fig. 2).

Graded Bed[™] candle filter media technology

Candle filter technology operates under wetted or partially flooded mechanisms to effectively remove sub-micron oleum mist using closely packed fibrous media in multiple density arrangements to enhance performance. CECO's Graded Bed[™] technology was cleverly designed to balance the level of flooding contained within the media and create a fine oleum film layer for contact.

The affiliation of absorption between sulphuric acid or oleum and NOx gases is utilised to reduce NOx concentrations in the gas stream to effective levels and in compliance to local norms (Fig. 3).

Pilot testing and results

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During the validation and prior to testing of media, CECO worked with the customer



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Fig. 5: Installation photographs







< 32 ppm

based on CECO's graded bed filtration arrangements. As the project evolved, it became apparent that the client's need was primarily focused on available pressure drop and the constraints which they faced for the retrofit solution. The client opted for the lowest case pressure drop design with a value of less than 100 mm H_2O .

CECO supported and provided pilot testing filters to ensure that the filter was able to achieve the reductions of NOx and meet the pressure drop requirement. This was done to validate the theoretical data and convert theory into empirical data using pilot testing and validation of performance. The results from the pilot testing were positive and provided confirmation of the pressure drop at given flow rates and also, significantly reduced NOx removal rate. CECO collected multiple data points and developed further empirical knowledge of absorption rates of NOx and sulphuric acid at multiple operating conditions (Figs. 4 & 5).

After installation and adding additional filtration area, the commissioning results from CECO Filter's TWIN-PAK® technology confirmed the units were able to remove NOx levels more effectively to 32 ppm or less from 80 ppm (at commissioning stage), while reducing the pressure drop from 130 mm H₂O (conventional filters) to 90 mm H₂O with TWIN-PAK[®] filters. The oleum output levels were also enhanced by higher efficiency performance, ultimately, providing a smart solution that reduces the total NOx output of the plant in accordance with environmental regulations and enabling the producer to operate the plant without penalties or shutdowns (Fig. 6 & Tables 2 & 3).

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NOx content

Table 3: Stream 3: Stack output

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Source: CECO Industrial Solutions



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New showcase drum granulator commissioned

Sulphur processing and handling equipment manufacturer IPCO has completed the commissioning of a groundbreaking new drum granulator in Italy that will serve as a global showcase for this patented system. **C. Metheral** of IPCO, describes the innovative approach and key features of the SG20 sulphur granulation system.

Above: IPCO SG20 drum granulator in Italy.

he IPCO SG20 is a fully automated sulphur granulation system based on rotating drum technology. Its high productivity 'once through' operation delivers a solidification capacity of up to 800 t/d. The unit has been delivered to a long-standing customer in Italy, a company operating multiple sulphur solidification lines, and an agreement is in place that will enable prospective customers to visit the site and assess the system in operation.

The SG20, a scaled-down version of the company's 2,000 t/d SG30 model, is designed for medium-range capacities. The newest model is notable for its remarkably quiet operation, well below standard noise limits, and for easy access to all components for monitoring and maintenance.

The system delivers a high quality product satisfying the shape criteria and Stress Level I and II friability parameters of the SUDIC product specification. This ensures efficient, clean and environmentally safe storage and handling during transportation. The SUDIC specification also limits

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moisture content; excess moisture not only adds weight, leading to unnecessary transportation and melting costs, but also results in increased acidity, risking corrosion in storage, handling and transportation equipment.

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The same operating principles apply to both models. This is a single-pass process, which eliminates any need for screens or recycle conveyors to send sulphur back through the drum. The sulphur seed or nuclei particles are created outside the drum by freezing sprays of liquid sulphur in a water bath. Generating the particles externally simplifies the process and allows wider flexibility with the incoming liquid sulphur temperature. It also provides an innovative way to recycle the sulphur waste stream from the wet scrubbing system, which is explained later.

Fig. 1 shows a basic process flow diagram of the drum granulation process.

Innovative approach to drum granulation

The IPCO patented SG system has been designed to resolve the drawbacks often associated with traditional drum granulation technology, in particular cleaning, maintenance and process control. IPCO's experience in the supply of sulphur solidification and handling equipment extends all the way back to 1951 and this gives the company an unparalleled insight into the problems encountered by operators and maintenance personnel. The design of the SG series involved identifying the root cause of each issue, and then working out how it could be eliminated or, at the very least, its effects minimised.

Substantial reduction in sulphur build-up

Older drum technologies have always required regular shutdowns to clean out the build-up of sulphur within the system. This could be as frequent as every 12-24 hours, with an obvious and significant impact on overall system productivity. And even when systems could be run for longer than this, the cleanout process would be much more challenging, leading to longer shutdown periods.

Having identified the points within the system where sulphur build-ups occur (Fig. 2), and studying each one, IPCO has designed the system to minimise this issue. The specifics remain confidential





Fig. 2: Major build-up (left) vs. minor build-up (right) inside ducting.



Fig. 3: Unheated nozzles (left) can be prone to plugging; heated nozzles (right) stay clear.

but the result is a dramatic reduction in cleaning requirements: the SG20 can run continuously for a full week before requiring a shutdown. Even then, the cleaning requirement is minimal compared with traditional drum granulation systems.

Heated sulphur nozzles

Liquid sulphur has to be maintained at a specific temperature range (around 120 to 160°C), so any cold spot in a processing system has the potential to cause problems. In the case of traditional drum granulators, the problem area in this respect has often been the sulphur spray nozzles, due to the fact that they extend outside the steam-jacketing (Fig. 3).

If liquid sulphur remains in the nozzle when the system is shut down it will

freeze in the tip, blocking flow at the next start-up. Even if the nozzle is clear, sulphur vapour from inside the header can condense and freeze in the tips if the system is shut down for an extended period. In either case, rectifying the problem will require an operator to manually clean out the nozzle or replace it before starting up the system. A single frozen or plugged nozzle can make the difference between premium granules and off-spec product.

IPCO has overcome this issue by incorporating the industry's first heated sulphur spray nozzle. Again, the technical specifications are protected by IPCO, but the outcome is that the nozzles in the SG series will not freeze up, and the time-consuming task of sending an operator into the drum to resolve the problem has been completely eliminated.

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Redesigning the drum to minimise roller wear

The drum granulation process is based on the use of a rotating drum to form curtains of falling granules. As the nuclei particles travel along the drum, they are progressively enlarged to the required size by means of sulphur sprayed from a bank of nozzles running the length of the drum.

In older systems, the drum would be positioned at an angle so that gravity would advance the granules towards the outlet end of the system. However, granulation drums are large and heavy pieces of equipment and the need to rotate on an angle inevitably creates high levels of stress on the rollers that support the drums, resulting in alignment issues requiring ongoing maintenance.

IPCO's SG series granulators (Fig. 4) take a different approach. Instead of turning on an angle, they operate on a completely level base, using angled internal flights to advance the product instead of gravity. This means no unnecessary wear and tear on the rollers, and no maintenance to keep the unit aligned.

Dust emissions and scrubber waste

Drum granulators work by removing heat from the product to convert it from a liquid state into a more easily handleable solid. In the case of sulphur solidification, this heat exchange is carried out using air and water: air is pulled into the drum, water is evaporated into the air as the sulphur cools, and the air is then discharged to the atmosphere. However, as the exhaust air contains sulphur dust, it has to be treated in order to prevent atmospheric pollution.

Managing this has traditionally meant choosing between two options, the steamjacketed cyclone and the wet scrubber with dust collection system, and there are drawbacks to both.

The steam-jacketed cyclone melts the sulphur dust that has been captured to create sulphur vapour. The result is high levels of dust emissions, a major problem for systems operating in environmentally sensitive areas. The process also requires high volumes of steam in order to heat up the air stream while melting the sulphur dust.

The second technology, the wet scrubber with dust collection system, captures the fine sulphur particles with water to form a sludge, which in turn needs processing. The usual approach is to melt and filter the waste, then feed it back into the liquid sulphur supply system. Although a more complicated process than the steam-jacketed cyclone, it results in lower dust emissions.

IPCO has taken a new approach. As a wet scrubbing system has the lowest sulphur dust emissions (and therefore lowest impact on the environment), this was chosen as the basis of the solution. However, instead of requiring a second stage of processing, the waste stream is recycled directly into the external seed generation system (Fig. 5).

Injecting the sulphur dust captured by wet scrubbing back into the process, it is consumed as seed in the drum (Fig. 1). This is a simple and energy efficient solution, one that requires no extra work in terms of operating and maintaining the sulphur melting/filtering equipment.

Managing H₂S emissions

As is the case with all sulphur produced as part of the oil refining process, the sulphur processed at this facility in Italy contains levels of hydrogen sulphide (H_2S). The drum granulation process involves spraying liquid sulphur through nozzles, which releases a portion of this H_2S into the air stream.

Levels of H_2S vary depending on the liquid sulphur supply and acceptable stack emission levels will differ around the world too. European regulations place strict limits on H_2S so measur es have to be taken to prevent it from entering the atmosphere.

The solution here is the addition of an H_2S scrubbing system, an option that can be incorporated to ensure compliance with the most stringent of emission requirements, anywhere in the world (Fig. 6).

Consistent operation

While technology is key to successful sulphur forming, there are many other factors at play, all of which can impact on the quality of the end product.





Above: Fig. 4: SG20 drum (left). Fig. 5: Scrubber waste discharge to seed generation system (centre). Fig. 6: Exhaust stack (right).

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HOTOS: IPCO

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Throughput rates, liquid sulphur feed temperature, geographic region, ambient temperature, humidity levels, seasonal conditions, the weather; all need to be taken into account as part of the solidification process and this can place a high degree of responsibility on the operator. It is possible to set up a drum granulator to operate to fixed parameters but this is likely to result in sub-optimal performance if and when conditions change.

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The ability to adjust operating parameters relies on the operator having sufficient experience to understand how the system will react under varying conditions. Get it right and the result will be consistently high-quality sulphur granules; get it wrong and product quality will suffer, water will be wasted, and build-ups will occur, resulting in shutdowns.

While operator training and follow-up support visits can help build the necessary skills over a period of time, there is a risk of a system operating at less than 100 percent efficiency – and producing less than premium quality product – until the required level of in-house expertise has been developed.

IPCO has overcome this by developing a process simulation solution that takes all guesswork out of realising the full potential of its patented drum granulation system.

The SG series operator guidance system – an industry-first in the field of sulphur drum granulation – was developed by analysing a wealth of operating data collected from both the SG20 and SG30 systems, and building a process simulation that can be applied to any operating conditions.

Summary

In designing the SG series, IPCO has taken all the inherent advantages of drum granulation – highest capacity, highest quality end product – and enhanced the technology in ways that overcome the challenges previously associated with this approach to sulphur forming (Table 1).

Cleaning and maintenance requirements have been significantly reduced, resulting in increased equipment availability. Emissions of both sulphur dust and H_2S are well within the limits of prevailing environmental legislation. Noise levels are far below standard limits. A new approach to drum design minimises stress of rollers to increase equipment life, and, perhaps most important of all, operation has been simplified: the unit can be stopped and started at the touch of a button, and a game-changing operator guidance system means that a high-quality product can be produced at all times, regardless of operator experience.

IPCO is a world leader in sulphur processing and handling, having delivered complete end-to-end systems to hundreds of companies around the globe since 1951. In addition to granulation drums, IPCO's well-known Rotoform system meets small to medium capacity requirements for sulphur, offering excellent product uniformity, environmentally friendly operation and



Sulphur production by SG20 being stockpiled.

premium quality pastilles of uniform shape and size. More than 700 Rotoform pastillation systems have been installed for sulphur processing to date.

Together, the drum and pastillation options make up IPCO's premium forming product range, giving customers access to all technology options under a single brand.

The IPCO SG20 drum granulation system installed in Italy is available for customer visits on request. Interested parties are invited to contact their local IPCO office to organise a visit.

Feature	Advantage	Benefit
Minimised build-up	Reduced housekeeping	Increased equipment availabilityLess labour
Heated sulphur nozzles	No frozen nozzle tips	Increased equipment availabilityLess labour
Completely level drum	Minimal shearing forces on rollers	Increased equipment lifeLess maintenance (no alignment)
Combustion of wet scrubbing with	Lowest sulphur dust emissions	• Easier environmental permitting
external seed generation	Recycled scrubber waste	Eliminates scrubber waste streamLower steam consumption
H ₂ S scrubbing solution for drum granulator	Reduced H ₂ S emissions	• Easier environmental permitting
Operator guidance system	Precise control in all scenarios	 Reduced training and experience requirements Efficient use of utilities
	Simple operation of equipment	 Easy to maintain product quality and officient use of utilities

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The three "Ts" reconsidered

Are the three "T"s (temperature, turbulence, time) of Claus unit ammonia destruction still meaningful with improved understanding of the thermal reactor? CFD models appear to be adequate at higher temperatures, e.g. 1,200°C, but not at lower temperatures, e.g. 800°C and 1,000°C. **A. Keller**, on behalf of the Amine Best Practices Group, reviews how meaningful the rules of thumb for Claus unit ammonia destruction really are.

here is a near ad-nauseum collection of technical papers concerning the destruction of ammonia in Claus thermal reactors (as reaction furnaces are now being called). There have been arguments for the use of "oxidising" conditions in "front zones" of the thermal reactors while others have maintained that oxidising zones encourage the formation of sulphur trioxide causing plugging in downstream equipment. Papers abound advocating split furnace zones or "good mixing" burners. Ultimately, nearly all of these papers get to the same rules of thumb for adequate ammonia destruction in a Claus burner/thermal reactor:

- Time: 0.8-2 seconds of thermal reactor residence time is needed;
- Temperature: 1,200-1,250°C (2,192-2,282°F) is the minimum temperature requirement;
- Turbulence: Mixing in the burner and furnace need to adequately combine the air and acid gas being burned.

Known as the three "Ts" for good ammonia destruction, they have been considered close to gospel for the practitioners of Claus sulphur recovery, but they unfortunately rest on some fairly shaky assumptions.

Concerning residence time, most chemical engineers would compute this simply as the volume of the thermal reactor space divided by the volumetric rate of the gases through the reactor as if this were merely a turbulent flow in a pipe exercise. As we shall see later on, this is not meaningful for the bulk flow of gas in the burner/thermal reactor, nor is it meaningful in terms of

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how the ammonia destruction takes place.

Concerning temperature, most operations departments rely on pyrometers peering into or embedded thermocouples indirectly reporting a value purporting to be the temperature in the thermal reactor. We shall also see this number may not be meaningful in terms of how the ammonia destruction takes place.

Concerning turbulence, it is presumed that better mixing bringing oxidiser and fuel together improves ammonia destruction. It is up to each Claus burner/thermal reactor technology provider to convince each potential client that their burner/thermal reactor design is best suited to this task. We shall also see where some technology offerings have been criticised, but fortuitous design circumstances allowed these technologies to perform adequately.

Most of the shaky assumption blame can be placed squarely on the industry's lack of digital computing power prior to the 1990s. With the advancement of solidstate electronics through the 1980s into

ISSUE 395 SULPHUR JULY-AUGUST 2021 the 1990s, computing speed increased exponentially. Chemical engineers now had the computing power to make computational fluid dynamic (CFD) modelling practical.

Models have moved from around 30 thousand cells for a Claus burner/thermal reactor to over 30 million cells. With the details that these models can develop, is it worth asking if the gospel notions of the three "Ts" are still worthy of their gospel quality?

Temperature and composition effects on ammonia destruction

The landmark study by Alberta Sulphur Research Limited (ASRL) on the chemical conversion of ammonia in Claus thermal reactors in the late 1990s¹ corrected many of the known rules of thumb of that day concerning ammonia destruction. What is being discussed in this work is not meant to change or alter any of the conclusions made in their analysis, but to put their results into the perspective of burner/



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thermal reactor performance and to reconsider the three "Ts" rules of thumb.

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Some important conclusions from the ASRL work that are useful for understanding CFD models of different burner/thermal reactor systems can be summarised as:

Reduction of SO_2 by ammonia to form nitrogen, water, H_2S , or elemental sulphur is kinetically favoured over thermal decomposition of ammonia to nitrogen and hydrogen or direct oxidation of ammonia by oxygen.

Above 1,200°C, the kinetics of SO_2 reduction by ammonia results in nearly complete ammonia destruction in much less than one second residence time.

Fig. 1 is a schematic, provided by ASRL to a member company, of the tubular reactor placed in a temperature-controlled furnace to perform this study. The geometry of this reactor was used by the member company to construct a CFD model of the reactor to validate the turbulent, plug-flow assumption used to determine experimental residence time used to correlate conversion.

The experiment was conducted with some fixed assumptions, plug flow and isothermal conditions. The CFD modelling fixed assumptions were the mixing parameter and all reactions having achieved chemical equilibrium inside of any of the differential cells being computed.

Let's examine some of the modelling results testing both sets of assumptions.

Fig. 2 is a comparison of yields of various species measured in the lab versus those predicted by the CFD model. The cases were run to try to match the residence times computed from the laboratory work showing a small discrepancy. At the lower temperature, the CFD assumption of achieving equilibrium is invalid according to the measured results. At the higher temperature, the CFD assumption of reaching equilibrium is fairly consistent with measured results.

In Figs 3, 4 and 5, we see three data extractions from the model depicting the reactor temperature profile, ammonia concentration profile, and SO_2 concentration profile for Test 2a.

In Fig. 3, temperature is shown in kelvin (K). 418K is 144°C or 293°F, depicted by the blue colour at the bottom of the scale. 1,472K (1,119°C or 2,190°F) as depicted by the reddish orange colour near the top of the scale is the furnace and outer tube temperature. Ammonia, entering the annular

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space closest to the heating source on the outside of the reactor tube wall, is heated more rapidly than the $Ar-SO_2$ mixture entering in the middle tube.

In Fig. 4, the scale on the side shows the ammonia concentration in the inlet and the change in concentration as the ammonia is first heated then reacted. The rapid heating of the ammonia without water being present leads to some thermal decomposition as the ASRL study showed in a separate experiment. Reaction of the remaining ammonia with SO_2 is fairly rapid when the two streams are combined and reach 1,286K (1,013°C or 1,855°F) to 1,348K (1,075°C or 1,967°F).

In Fig. 5 the scale depicts the mole fraction of SO_2 in the Ar- SO_2 mix dissipating as it contacts the ammonia in the reaction zone. The Ar- SO_2 mix is being heated more slowly than the ammonia, but the heating does nothing to the stable SO_2 molecule. At the point of mixing with the hot ammonia, SO_2 is rapidly consumed.

Unlike the confirmation of the chemical reaction results obtained in the laboratory, the CFD modelling dispels some of the three "Ts" assumptions. We certainly don't

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CLAUS UNIT AMMONIA DESTRUCTION



Fig. 4: CFD generated ammonia concentration profile for Test 2a (reactor entrance)





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have plug flow. Not everything is perfectly mixed and at a constant temperature, and near complete destruction is taking place below 1,200°C. Most importantly, ammonia appears to react quickly near the mix point and does not require the entire residence time of the tube.

CFD application in commercial units

We can apply these small-scale lessons learned to commercial-sized burner/thermal reactor systems. The emphasis in doing this must be kept on the notion of the three "Ts" and their application to the burner/thermal reactor design.

We will examine two well-known technology offerings. The first is a low mixing intensity burner with a two-zone thermal reactor using amine acid gas split between the two zones (see Fig. 6). The second will be the single-zone thermal reactor using a high mixing intensity burner (see Fig. 7).

For each offering, there are six images extracted from the CFD models done. These are wall temperature, gas temperature, oxygen mole fraction, SO_2 mole fraction, ammonia ppmv, and velocity.

Low intensity mixing burners

In Fig. 6b we see that the first zone, which is supposed to be hotter than the second zone is much cooler, on average. What is most important to note is that ammonia contained in the acid gas is being heated up by hot gas recirculating in a narrow annular space prior to contact with the SO_2 generated by the combustion.

In Fig. 6f, note that the scale was to primarily show low values for completeness of destruction purposes. Regions in red represent higher concentrations.

Burning with excess air would give a hotter flame as more H_2S is converted to SO_2 and water in a highly exothermic reaction. However, the profiles show that if a box were drawn around the first zone (assuming perfect mixing), technically it would be an oxidising environment. However, we see that oxygen leaves the first zone only because it remains unmixed.

Next, we notice that SO_2 is plentiful where the acid gas and air are mixing and burning, but not so plentiful in the recirculation zone of first thermal reactor zone. SO_2 made in the initial flame is rapidly consumed to make sulphur and water by reacting with H₂S. It also appears from the ammonia concentration profile that SO_2 is also aiding in

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ammonia destruction close to where the incoming acid gases and air collide.

Without the benefit of CFD modelling, a prescient conclusion/recommendation from the ASRL work clarifies this:

This study has, however, shown that SO_2 reacts quite readily with ammonia forming N_2 , water or H_2 , and sulphur or H_2S , displaying reaction rates which exceed those of either dissociation or oxidation. Also, it was shown that the ammonia/ SO_2 reaction is able to proceed in the presence of water. These observations and others described in the main text suggest the following protocol for ammonia destruction in the Claus furnace.

- Utilise a burner/furnace configuration which allows the SWSG to impinge on a hot SO₂-rich flame.
- This could be accomplished by feeding all the oxygen required for ammonia and H₂S conversion with the AG through a main burner with the SWSG impinging on the flame.

What we have here is a "which comes first, the chicken or the egg?" scenario. The burner/thermal reactor that was modelled was vintage 1980, the ASRL work was done in 1998, and the CFD modelling was done in 2007. The burner/thermal reactor was destroying ammonia effectively for almost two decades prior to the ASRL work, yet it implemented the ideas developed from the study. CFD modelling showed the burner/thermal reactor designed using the three "Ts" philosophy did not work exactly according to the three "Ts" rules, especially time and turbulence, but it still did the job.

Let's look at the last suggested protocol from the ASRL work now.

 Employ furnace temperatures exceeding 1,250°C and furnace residence times of >1.5 sec.

Without the benefit of CFD done on the laboratory reactor (late 2012), this conclusion was likely the result of making the assumptions of plug flow/perfect mixing and somewhat genuflecting to the three "Ts".

High intensity mixing burners

Now let's turn our attention to high intensity mixing burners with thermal reactors. High intensity is defined by incorporating swirl vanes internal to the air and acid gas streams prior to the burner tip. We will

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again see two types, air enveloping acid gases and acid gases enveloping air.

The design in Fig. 7a is a one zone furnace with choke ring. Acid gas enveloping air produces the central cone-shaped combustion zone seen in the first low intensity burner model. A series of model profiles similar to that analysis follow.

Again, profiles for oxygen, SO_2 , and ammonia mole fraction are used to illustrate the impact of the burner-thermal reactor design on ammonia destruction taking into consideration adherence to three "Ts" thinking. Figs 7b-d are for the acid gas enveloping air case.

The range of the scale didn't allow intermediate concentration to show up as before.

Essentially the model shows the ammonia cannot stand up to the high temperature and high SO_2 content in the narrow combustion zone denoted by the rapid consumption of oxygen. The time element of the three "Ts" does not seem to play a significant role in ammonia destruction.

This burner/thermal reactor performance is more of a function of the other two elements, temperature and turbulence. However, three "Ts" thinking, whether using temperature measured by thermocouple or pyrometer or adiabatic flame temperature as a guideline for operations, appears to be unimportant. The important temperature is in the combustion zone where the ammonia destruction action is. This temperature, as the CFD models show, can be several hundred degrees higher than measured or computed temperatures.

This leaves us with only one of the three "Ts"-turbulence in this case.

There is a great failing with the CFD models though. Measured ammonia never agrees with the equilibrium assumptions made for computing reaction chemistry. This is likely a failure of the assumptions used to build the mixing part of the model.

Fault for not achieving sufficient destruction is typically attributed to not having all three "Ts" in place. Without CFD modelling, decisions that may cause severe performance related problems or damage to the burner-thermal reactor may be enacted.

Concluding remarks

We now come back to the original question, "How meaningful are rules of thumb for claus unit ammonia destruction?". We see with the CFD modelling that the real question we should have asked is: Were our assumptions leading to the three "Ts" valid?

Laboratory work and actual plant operations, confirmed by CFD modelling, say the assumptions were incorrect. Both laboratory and plant CFD models appear to demonstrate the following:

Ammonia destruction has two components. The first is preheat of the ammonia containing gas by the hot gases recirculating in the thermal reactor. All the models show the hottest place in the thermal reactor is at the combustion boundary. Both allow the ammonia containing gases to quickly reach the desired temperature "T".

The second part is SO_2 reaction with ammonia. The CFD models confirm H_2S is the fastest consumer of oxygen. Once oxygen is consumed by the H_2S in the flame, only SO_2 remains to attack the ammonia.

In the end, several different styles of burner-thermal reactor arrangements accomplish similar levels of performance because they foster the conditions of preheat and SO_2 formation in the combustion zone setting up ideal conditions for ammonia destruction.

If ammonia is not being destroyed, there could be many things going on. CFD modelling can identify what is expected. It is difficult to model the myriad of plugging, destroyed burner parts, or other impediments to ammonia destruction that may occur.

As with many rules of thumb, the three "Ts" are an expression of experience driven common sense. Sometimes there is a tendency to make common sense scientifically absolute. The three "Ts" are meaningful, but as the ASRL laboratory work and the CFD models show, they are not scientifically absolute.

Acknowledgement

This article is an abridged form of the paper "How Meaningful Are Rules of Thumb for Claus Ammonia Destruction?", presented by Al Keller, on behalf of the Amine Best Practices Group at Brimstone "Virtual" Vail Symposium September 15-17, 2020.

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Upgrading for greater efficiency

New state-of-the-art equipment has been installed in the thermal stage of one of Europe's largest Claus SRU units. Substoichiometric firing and a furnace designed with CFD calculations and a modern compact boiler system design based on detailed heat engineering and FEM calculations were key to the success of the retrofit. **P. Foith** of CS Combustion Solutions reports on the retrofit and how the novel combination of a CS low pressure swirl burner, additional mixing using a VectorWall[™] and a new waste heat boiler design achieved the desired results.

successful retrofit was recently completed at a 700 t/d Claus plant in Germany, overcoming the problems of poorly operating existing equipment in the existing thermals stage of the SRU unit. The original burner, reactor and waste heat boiler all had issues.

The original burner at the site was a multi flame burner with low pressure drop on the Claus gas side. Due to construction issues the burner had undefined mixing between the air and Claus gas, the flame stability during start-up and lower load cases was poor and there was corrosion due to gas condensation. In the original design there was a ceramic block for each individual flame (48 flames) with undefined mixing of oxidation air and Claus gas. The ceramic blocks was not centrical, hence the Claus gas was not evenly distributed.

Even though the original reactor was equipped with a checkerwall in the first third of the chamber it had inhomogeneous temperature distribution, hot spots damaging the refractory and problems with long burner flames as the checkerwall was positioned too close to the burner.

Besides temperature distribution, the other main purpose of the checkerwall was to improve the H_2S to S conversion, which was also not being met. The checkerwall was therefore very inefficient.

The original waste heat boiler (WHB) was a smoke tube boiler with an internal by-pass with a capacity of 75 tonnes per hour @ 36 bar(g) and 250°C. The steam drum was installed directly on the boiler. The biggest issue was welding cracking,



which arose due to thermal stress caused by an inhomogeneous temperature profile. The main challenges of the retrofit were:

- process parameters upstream and downstream should not be affected (remain the same);
- only low pressure is available on the Claus gas side (high turbulence is difficult with low pressure availability);
- low pressure availability on the air side;
- high H_2S to sulphur conversion rate;
- overall size and dimensions should remain the same (reactor and waste heat boiler).

The target was for a maximum pressure drop of 100 mbar(g) through the complete unit (burner, reactor and waste heat boiler). Of utmost importance was to generate suff-

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iciently high turbulence and mixing of air and Claus gas, despite the low-pressure availability. In addition, the aim was to get as close as possible to the theoretical maximum achievable H_2S to S conversion of 70% at these process parameters of 1,338K to meet the guaranteed conversion rate of 65%, as well as increasing the maximum sulphur capacity to 120%.

The following steps were taken to meet these requirements:

CS low pressure swirl burner: To minimise the pressure drop over the burner and ensure proper mixture of Claus gas with oxidation air, the original burner was replaced with a low pressure double staged swirl burner, based on existing and proven CS burners (Fig. 1).

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- Additional mixing section by using a VectorWall[™]: The swirl and turbulence was further increased by utilising a VectorWall[™] with low pressure drop (Fig. 2). The new reactor has the same dimensions as the original one but is equipped with a VectorWall[™] instead of a checkerwall. The VectorWall[™] generates separate mixing zones for even distribution over the entire cross section.
- New waste heat boiler and CFD analysis: A new waste heat boiler was specially designed by a partner to keep the pressure drop as low as possible. Like the original waste heat boiler, it was a smoke tube type boiler with the steam drum installed on top. The design of the heat exchangers, bypass and internal piping focused on keeping the pressure drop as low as possible, while ensuring the necessary steam capacity. Multiple CFD analyses were done to verify the design and to ensure that the guaranteed H_2S to S conversion rate of 65% or above, as well as an increase of the maximum sulphur capacity to 120% were met.

Results

The result of the retrofit was a complete new thermal process stage for a Claus plant with a sulphur output of 700t/d. The state-of-the-art design is low maintenance, has a low pressure drop throughout the overall unit and achieves a sulphur conversion of \geq 65%.

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Temperature measurement in sulphur recovery

Temperature monitoring and measurement of the Claus thermal reactor in sulphur recovery units is one of the most challenging applications in the oil and gas industry. Recently, market interest in unpurged thermocouples has increased with the introduction of new unpurged thermocouple designs utilising alternative thermowell materials such as monocrystalline sapphire.

DELTA CONTROLS CORPORATION

Purged vs unpurged thermocouples in Claus thermal reactors

T. Keys, M. McCallister, and M. Coady

emperature measurement in the main reactor of the sulphur recovery unit (SRU) is not only a primary process variable, but also critical for the overall safety and reliability of the reactor. Recently, many legacy reactors with limited to no temperature instrumentation may be required to handle more throughput than originally designed. In addition, many reactors are adding supplemental oxygen resulting in increased operating temperatures. With higher reactor operating temperatures, the importance of temperature monitoring is greatly increased. As standard process temperatures rise through the use of oxygen enrichment and reach maximum

capabilities of the refractory, it is and will be increasingly important to have accurate and reliable temperature indication.

SRU temperature measurement technologies

There are currently two technologies suitable for reliable temperature monitoring in the main reactor: infrared pyrometers and thermocouples. It is recommended to use both technologies for maximised reliability.

Pyrometers designed for sulphur recovery are specifically engineered for the optical characteristics of the reactor and high temperature environment. Thermocouples

Table 1: Chart of thermocouple temperature ranges

Гуре	Composition	Temperature Range
В	Pt-30% Rh versus Pt-6% Rh	0°C to +1,820°C
E	Ni-Cr alloy versus a Cu-Ni alloy	-270°C to +1,000°C
J	Fe versus a Cu-Ni alloy	-210°C to +1,200°C
K	Ni-Cr alloy versus Ni-Al alloy	-270°C to +1,372°C
1	Ni-Cr-Si alloy versus Ni-Si-Mg alloy	-270°C to +1,300°C
1	Pt-13% Rh versus Pt	-50°C to +176°C
\$	Pt-10% Rh versus Pt	-50°C to +1,768°C
Г	Cu versus a Cu-Ni alloy	-270°C to +400°C

Source: NI

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SRU thermocouple challenges

Thermocouples, both purged and unpurged, are presented with numerous individual challenges in the sulphur recovery environment, and when presented together compound to create significant reliability challenges. Proven thermocouple designs utilise a series of alumina ceramic thermowells and noble metal thermocouple elements.

The high temperatures permit only a few thermocouple types to fall in the readable range (see Table. 1). Also many metals commonly used on thermocouple sheaths, or thermowells, are not suitable due to melting temperatures below +3,000°F (+1,649°C). In addition to high temperatures, the process is highly corrosive with process gases hydrogen sulphide, sulphur

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ISSUE 395 JULY-AUGUST 2021 dioxide, and other sulphur species present. Noble metal thermocouple types such as B, R, and S may be subjected to a multitude of detrimental effects, including hydrogen embrittlement, platinum oxide sublimation (see Fig. 1), and other degradation reactions. These reactions lead to signal degradation or, ultimately, failure.

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An alumina thermowell does not provide complete protection from the process gases. The porosity of the aluminium oxide at operating temperatures allows small amounts of process gases to diffuse through the thermowell, particularly at operating temperatures. If these gases are allowed to accumulate inside the thermowell, they will corrode, contaminate, or otherwise degrade the thermocouple within a few weeks.

Purged thermocouple technology

The proven method of protecting thermocouple elements is to purge the thermowell with an inert gas, usually nitrogen, in order to sweep away any process gases that diffuse through the primary thermowell (see Fig. 2). The gas is piped to the upper chamber of the thermocouple where it then travels down the holes of the element support where the thermocouple wires are positioned. The gas envelops the sensing junction at the end of the support. Any diffused process gas is mixed with the nitrogen, then directed to the outlet. Due to the slow rate of process gas diffusion through the thermowell, a purge flow of approximately 11 L/h is sufficient to provide protection without significantly cooling the thermocouple.

Disadvantages of purged thermocouple technology

Purged thermocouple designs, when properly installed and maintained, are the proven solution for reliable temperature indication from turnaround to turnaround. However, purged thermocouples are not without compromise. Installing and maintaining the purge system will require additional costs and complexity that may be considered a disadvantage. The purge gas system also introduces additional potential failure modes for the thermocouple as the purge gas must remain free of contaminants such as moisture or hydrocarbons that may damage the thermocouple elements. The system requires periodic maintenance to verify correct pressure and flow settings as well as functionality.

Unpurged thermocouple technology

Plants may attempt to reduce operational and capital expenditure costs by installing unpurged thermocouples that are unsuitable for the challenges of the reactor environment. Most of these attempts result in a failed thermocouple after a relatively short time resulting in the main reactor losing critical temperature indication and introducing associated safety concerns.

Recently, market interest in unpurged thermocouples has increased with the introduction of additional unpurged thermocouple designs utilising alternative thermowell materials such as monocrystalline sapphire. Sapphire is grown from a single crystal, rather than slip cast or recrystallised like alumina resulting in a molecular monocrystalline crystal lattice structure that is uniform throughout the thermowell. Traditional high purity alumina ceramic has a higher molecular porosity that can allow process gases to diffuse through the ceramic at the high operating temperatures in the main reactor. Sapphire is compositionally identical to high purity alumina as both are composed of aluminium oxide, Al₂O₃. However, the monocrystalline structure of sapphire is not porous at high temperature and therefore the diffusion of process gases through its crystalline matrix is much slower than through alumina ceramic. While monocrystalline structures are absent of grain boundaries, it is unlikely that process gas diffusion is completely prevented.

The utilisation of a sapphire thermowell in an unpurged thermocouple design exclusively is not sufficient for long term reliability of the instrument. The seals that surround the thermowell are critical to the prevention of process gas diffusion into the assembly. Even the most effective seals will not have a zero leakage rate. While contaminants may be impeded by the sapphire thermowell, the seals surrounding the thermowell are subject to trace amounts of leakage. The trace contaminants can accumulate inside the thermocouple assembly eventually causing degradation of the thermocouple elements

The Delta Controls Model HTV thermocouple (Fig. 3) reliably addresses the seal leakage problem by implementing a newly developed, patent-pending seal

Fig. 1: Effects of platinum oxide sublimation. The thermocouple element thins to a needle point and platinum deposits up the ceramic element support as crystals. A) Mass loss thinning as a result of platinum oxidation. The bottom wire has full cross section remaining. B) Platinum crystals deposited on a ceramic element support.



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Source: Delta Controls

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mechanism designated as QSeal[™]. The design utilises a series of protection mechanisms to prevent process gas diffusion, gas accumulation, and seal leakage from compromising the temperature indication. The issues are first addressed with careful selection of advanced seal materials that minimise diffusion through the seal structure. Secondly, a high compression wedge seal design mechanically reduces contaminant bypass around the seal. Finally, and most importantly, the seal system design prevents any contaminants that bypass the primary seals from accumulating within the thermocouple assembly to concentrations higher than the ambient atmosphere. Secondary seals, which are exposed to a nearly ambient atmosphere, isolate the open end of the sapphire thermowell; therefore, contaminant leakage through secondary seals is negligible. Multiple redundant seals, in addition to the primary and secondary seals, ensure process containment is maintained in the event of thermowell breakage.

Disadvantages of unpurged thermocouple technology

While thermocouples utilising a sapphire thermowell have been in high temperature applications for many years, the designs have only recently been evaluated for use in sulphur recovery thermal reactors. Due to the recent implementation of this technology, it is unproven in terms of reliability and longevity in sulphur recovery service.

The absence of grain boundaries in monocrystalline sapphire can slow the diffusion of process gases through the thermowell, but it is unknown whether the diffusion rate is sufficiently minimised to prevent thermocouple deterioration for the targeted five to seven years between turnarounds. Another potential concern is the effect of the atmosphere contained within the thermocouple assembly will have on the longevity of the device. A number of deleterious reactions are known to occur with platinum at high temperatures. These reactions are not a problem in a purged thermocouple, where the purge gas is constantly replacing the atmosphere within the thermocouple assembly with inert nitrogen. How problematic contained atmosphere is remains to be seen.

Trials are underway, but an insufficient number of sapphire protected thermocouples have been installed long enough to clearly demonstrate turnaround to turnaround reliability. Until the technology has matured and demonstrated reliability, it is recommended that sapphire protected thermocouples only be installed in addition to other proven temperature measurement technologies such as purged thermocouples or pyrometers.

In conclusion, unpurged sapphire thermocouples show promise as an alternative to purged thermocouples; however, overcoming Fig. 3: Unpurged thermocouple



the associated application challenges in sulphur recovery service require more than changing the thermowell material. Careful attention must be paid to the seal materials, seal design, and overall architecture of the thermocouple assembly to assure safety, longevity, and reliability.

Unpurged sapphire thermocouples have only been used in SRUs for a relatively short time. It will be 5 to 10 years before enough field data has been collected to evaluate whether unpurged sapphire thermocouples are as reliable as purged thermocouples in SRUs.

The Claus thermal reactor is a challenging environment for the long term reliability of all temperature indicating devices. It is imperative that an accurate temperature measurement be continuously reliable for efficient and safe operation. Low reliability thermocouple design consequences include not only financial costs, but also potential loss of safety critical SIS indication while in operation and increased down time of the SRU. As proven in hundreds of worldwide installations for nearly 50 years, a properly designed and installed purged thermocouple reliably serves this purpose.

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DAILY THERMETRICS

A complete temperature measurement system

D. Keles

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Removal of sulphur from natural gas or crude oil is one of the most critical operations within a plant. Traditionally, this occurs within a thermal reactor that is a part of the sulphur recovery unit. The reaction occurring is called as Claus reaction, which removes the sulphur from process stream occurs at elevated temperatures and is exothermal, therefore excess heat is created throughout the process run.

Even though there are several reactors involved within the Claus process, one of the most important is the thermal reactor (also called the Claus reaction furnace or main combustion chamber) since the operating temperatures could be as high as 1,500-1,600°C (2,700-2,800°F). In this reactor, thermal energy is utilised to react hydrogen sulphide with oxygen to yield elemental Sulphur as well as water.

Since the reaction within the thermal reactor is most efficient at higher temperatures, temperature measurement control of this reactor is extremely critical to ensure safe operation, considering the highly toxic gas that is contained. An important point to consider here is the condition of refractory walls which could degrade over time at the elevated temperatures, which increases the criticality of temperature measurement for the maximized lifetime of the refractory and therefore the reaction furnace. If not properly monitored, refractory lining could potentially melt which was the case in modern history catastrophes. The normal limit for refractory lining is 1,650°C, however some refractories are rated much high temperatures of up to 1,800°C. Monitoring the refractory temperature is critical to prevent the vessel shell from overheating and containment of toxic gas.

Temperature measurement challenges

Traditionally, the monitoring of this crucial temperature in the furnace is done either with infrared pyrometers or special high temperature thermowells using a noble temperature sensor. High temperature thermowells are usually seen as unreliable as most of the technologies available in the industry were not successful in finding answers to common problems within the Claus thermal reactor. For this reason, most operators prefer using pyrometers, despite their high maintenance costs. In



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general, pyrometers are practical, however one should be careful with the readings as it could potentially be showing temperatures with a high error (up to 20%) due to sulphur build up or potential drift.

The current high temperature assemblies available in the market, or in other words the ceramic thermowells, are widely susceptible to hydrogen sulphide migration which corrupts the noble metal thermocouples within. The main reason for this is the porous outer ceramic material that is utilised, which allows toxic gas to pass through and potentially reach the noble thermocouple wires.

To prevent this from happening, a nitrogen purge system is added to remove this highly toxic gas, but this introduces a temperature difference, generates high operational costs and an extremely hazardous working condition due to the constant monitoring and control required to operate the unit safely.

Moreover, the outer ceramic that is utilised is not well suited for the Claus thermal reactor, which is prone to failure in the unlikely event of refractory shift or thermal shocks, not to mention the complex installation procedures that consume valuable time during turnarounds, as well as difficulties if the thermowell nozzle has a smaller flange or is located on the horizontal axis.

Proven temperature measurement technology

In the light of these drawbacks, the Daily Thermetrics team has worked tirelessly to come up with the latest iteration of their design which provides high reliability and is easy to operate, providing operators with peace of mind (Fig. 1).

The new design with its optimised sensor provides protection from the damaging effect of toxic gas without the added complication and costly requirement for nitrogen purging. The design is therefore maintenance-free.

While designing the assembly, the first area to look at was the outer protection tube, which is designed to be from sintered silicon carbide supported by a high temperature metal support tube to ensure the highest resistance to thermal shock and

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shifting refractory. This outer protection tube already has an excellent track record within high temperature applications. It is resistant to 1,950°C and proven to provide the ideal solution due to its excellent thermal conductivity.

Another area to consider was whether nitrogen purging is necessary, since there was the belief in the industry that purging is a must or the thermocouple wires could not survive in the toxic gas environment. However, taking a deeper look at the options available, it was obvious that an impermeable layer which would seal around the noble thermocouple wires could eliminate this need.

After a careful search, a monocrystalline sapphire tube was selected to provide the optimum solution which again is proven in extreme temperature applications. Due to its homogenous structure,

in contrast to porous structure of ceramic protection tubes, its completely impermeable to any toxic gas penetration, therefore eliminating the need for the costly and high maintenance item of purging equipment.

The assembly offers a process rated containment system to ensure full plant safety at all times. The design itself has primary, secondary and tertiary process sealing that are rated greater than 1.5 times the pressure rating of the process connection. This triple seal system is tailored to mitigate any risk factors:

- first seal fitting for outer protection tube for stability throughout operation;
- second seal fitting for the sapphire tube to ensure process containment in case of potential failure;
- third seal fitting for the thermocouple;
- fourth seal fitting for the individual noble thermocouple wires.

The assembly itself is an integrated well which requires no specialty tools or instructions for installation and could be described as a plug and play system. An additional advantage of this assembly is the flexibility for all existing nozzles due to variable flange sizing down to 2 inches (5 cm) as well as an optional leak detection thermocouple that could be added within the containment chamber for the unlikely events (Fig. 2).

Daily Thermetrics has been providing high temperature assemblies for the some of the most arduous applications within the energy industry such as Claus furnaces, partial oxidation reactors, waste

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heat boilers, incinerators and many more for more than 40 years.

However, in the last couple of years, working intimately with process licensors, engineering contactors and end clients, Daily Thermetrics has developed a complete temperature measurement system for the Claus thermal reactor, which includes the patented Mag VSS[™] magnetic skin sensor that is attached on the thermal reactor surface via the magnetic pull force with the Daily ImpermaWell[™] (Fig. 3).

This skin sensor assembly has 150 pounds of pull force (68 kg) and is rated up to 540°C surface temperature. It is a general recommendation to install two of these skin sensors at every metre on the reaction furnace length for the monitoring of refractory shift or falling that could potentially happen during the operation.

The main advantage is the easy attachment of the assembly as it does not require any welding and its position can be adjusted as desired.

Overall, the Daily $\operatorname{ImpermaWell}^{\scriptscriptstyle {\rm M}}$ is an innovative solution utilising proven technologies and with references in a variety of applications. Combining top shelf materials and expertise from various applications, Daily ImpermaWell[™] has already been proven in commercial applications and obtained approvals by clients. This maintenance-free design reduces the total cost of ownership, provided that no purging equipment is needed, and increases plant safe operation as process sealing is at the process connection and no toxic process gas is allowed to enter secondary equipment. Ultimately, it provides reliability and peace of mind.



Source: Daily Thermetrics

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