

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29

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Nickel and copper in Southeast Asia

New Asian refining capacity

Emissions reduction in sulphuric acid plants

Seven deadly sins of tail gas treating

CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

COVER FEATURE 3

Emissions reduction in sulphuric acid plants

COVER FEATURE 4

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10

Asian refining

A major source of new sulphur production over the next few years.



16

Emissions reduction

Using a neighbouring plant during start-up and upsets.

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SULPHUR

www.sulphurmagazine.com

NUMBER 376

MAY | JUNE 2018

CONTENTS

10 New Asian refining capacity

Asia continues to add refining capacity which will generate additional tonnages of sulphur over the coming few years.

12 Nickel and copper in Southeast Asia

The demand for sulphuric acid in metal processing has been complicated by Indonesia's export ban on nickel ores and move to develop copper smelting capacity and an environmental crackdown on nickel mining in the Philippines.

14 Middle East Sulphur

CRU ran its second Middle East Sulphur Conference in Abu Dhabi in March 2018, in partnership with UniverSUL Consulting.

16 Emissions reductions for adjacent acid plants

NORAM is offering a new solution to greatly reduce emissions from sulphuric acid plants during start-up and transient operating conditions. This article describes the new emissions reduction process and compares it to current emissions reduction procedures.

20 The seven deadly sins of tail gas treating units

Sulphur Experts discusses the most common design, operation, and reliability problems encountered in Claus tail gas treating units that impact emissions, compliance or reliability of the unit and guidance for achieving compliant and reliable operation.

26 Ensuring low emissions with technical services

Good technical services can be a valuable tool to achieve better sulphuric acid plant performance and meet stricter emission limits. M. Granroth of Topsoe reports on the effective use of technical services for catalyst loading design, optimisation of plant operation and plant debottlenecking and troubleshooting.

REGULARS

- 3 Editorial
- 4 Price Trends
- 5 Market Outlook
- 6 Sulphur Industry News
- 7 Sulphuric Acid News
- 9 People/Calendar

CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

COVER FEATURE 3

Emissions reduction in sulphuric acid plants

COVER FEATURE 4

Seven deadly sins of tail gas treating

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Sulphur to clean oil spills?



Sulphur's extraordinary combination of physical and chemical properties make it an endlessly fascinating substance, both on its own and in combination with other elements. In this issue, in our report on the Middle East Sulphur conference, we review work on sulphur incorporated into common polymers like polyethylene and polypropylene by the Petroleum Institute of Abu Dhabi, and sulphur's potential role in solar power generation being conducted by the German Aerospace Institute. But another potential use came along just this month, with an announcement by researchers in Australia that they had developed a sulphur polymer that could be potentially used to clean spilled oil from the surface of the sea.

It could be an effective solution for smaller, localised oil spills.

The work, published in *Advanced Sustainable Systems*, was led by a team from South Australia's Flinders University in Adelaide in a joint project with scientists from Portugal's Institute of Molecular Medicine and Cambridge University in the UK. They have developed a new polymer from sulphur and canola cooking oil, both waste products, the one from the hydrocarbon processing industry, as we are all aware, and the other from waste cooking oil from the fast food industry. The polymer reportedly acts like a sponge to remove crude oil and diesel from seawater, absorbing 2-3 times its own mass in oil, and also being completely reusable – it can be squeezed like a sponge to remove the oil and then reused. Both cooking oil and sulphur are hydrophobic – they do not interact with water. The research team found that the polymer created by combining the two not only absorbed oil but turned it into a gel. "We actually didn't expect the aggregation effect," Chalker said. "It's one of the interesting things that came from working in the laboratory."

The BP Deepwater Horizon explosion in 2010 released 4.9 million barrels of crude oil into the Gulf of Mexico, and has prompted new research efforts into ways of dealing with them, such as carbon nanotubes. In the meantime, large spills continue. According to the International Tanker Owners' Pollution Federation, 7,000 tonnes of crude oil were spilled into oceans last year, and the Indonesian port city of Balikpapan, part of the island of Borneo, declared

a state of emergency after a spill along the coast earlier this month.

Currently, there are several ways to clean up crude oil spills. If there is no risk of polluting coastal regions or marine industries, the oil can be left to break down naturally. For heavier spills, the oil is contained with booms and skimmers that are deployed to remove the substance off the water's surface. Biological agents or dispersants can be introduced to speed up the oil's degradation. Absorbent materials can also be used, including polymers like polyurethane and polypropylene. But a new class of sorbent materials like this could be – once produced at scale – an inexpensive alternative for cleaning up oil spills, given the relatively low cost of waste cooking oils and sulphur which forms the basis of the polymer. That low cost means it could be an effective solution for smaller, localised oil spills in countries where clean-up resources can be limited and where spills threaten groundwater, drinking water and important food staples such as fish. "Our goal is for this to be used globally. It is inexpensive, and we have an eye for it to be used in parts of the world such as the Amazon Basin in Ecuador and the Niger Delta that don't have access to solutions to oil spills," said Chalker.

Of course, laboratory tests are one thing, but field trials are another, which the product will move on to later this year, and, as any chemical engineer knows, scaling up a process can also throw up all manner of unforeseen complications. Nevertheless, the team say that they have already attracted interest from industry, and have high hopes for its eventual commercialisation.

Richard Hands, Editor



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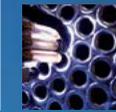
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CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

COVER FEATURE 3

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COVER FEATURE 4

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MARKET INSIGHT

Oliver Hatfield, Director, Fertilizer Research Team, Integer Research (in partnership with ICIS) assesses price trends and the market outlook for sulphur.

SULPHUR

The last two months have seen the sulphur market shift from relative bullishness and seller optimism about prices, to uncertainty, followed by more recent pessimism. These sentiments have been reflected in the recent movement of market prices. Having revised prices downwards in February the three main sulphur exporters from the Arab Gulf each posted a significant increase in their monthly listed prices for March. Muntajat raised its reference in March to \$134 per tonne, an increase of \$15 per tonne compared to February, having posted reductions from \$185 in December and \$144 in January. However, Muntajat then adjusted its April price downwards to \$118 f.o.b., and similar movements were reported elsewhere.

Early in March the sulphur market consensus was that the supply side was relatively tight. Buying interest from key importers like India and particularly China was relatively modest, but the view was that there was sufficient underlying latent demand to justify higher prices. A reduction in Chinese port stocks during the first few weeks of March was seen as a signal that buyers were waiting on the sidelines for sellers to drop their prices. Chinese port stocks started the month of March with a total of 1.38 tonnes, but the total had dropped by around 120,000 tonnes by month end. Sellers might reasonably have

expected to hold firm with their price ideas as it would be just a matter of time before the buying interest materialised.

Sellers were expecting strong demand after the Chinese Lunar holidays but this turned out to be disappointing, and by early April the anticipated rush of interest had not materialised. In fact the Chinese market looked to be well supplied despite relatively modest import buying. In the first week of April Chinese port stocks had reportedly reached 1.35 million tonnes, an increase of 100,000 tonnes in just a week. Although we don't yet have import numbers for March, Chinese imports for the first two months of 2018 were around 1.8 million tonnes, more than 100,000 lower than the previous year. Although just a few months of data are not sufficient to draw strong conclusions, it could be that the Chinese market situation is beginning to move to a position where it needs less imported sulphur.

Integer has been highlighting the potential for reduced Chinese imports for some time. A key part of this evolution stems from major shifts taking place in the global phosphate business. While Morocco and Saudi Arabia are ramping up export capacity of processed phosphates, consuming more sulphur and acid, this increasingly applies competitive pressure to the Chinese phosphate industry, parts of which are at the marginal end of the phosphate business economically. The major expansion of Chinese processed phosphates production

over the last twenty years was the major factor in the expansion of Chinese sulphur imports from below 3 million tonnes in 2000 to in 11-12 million tonnes in recent years. However, Chinese processed phosphate production is becoming decreasingly competitive and production has stopped growing. Meanwhile Chinese domestic availability of sulphur in elemental and metallurgical sulphuric acid form is steadily rising, and sooner or later China will reduce its need for elemental sulphur imports. Note that Integer will be looking in detail at the Chinese sulphur and sulphuric acid markets in the May and June publications of our regular analytical services. It could be that we are seeing this trend developing in 2018.

Incredibly, this article has nearly got to the end without mentioning the fact that the Kashagan project in Kazakhstan has officially started moving sulphur volumes. The North Caspian Operating Company (NCOC) reported that it had exported around 140,000 tonnes of sulphur between November 2017 and mid-March 2018. Without this additional export volume, market sentiment in the last few months would no doubt have been more bullish, but the project has been so long delayed that there is still significant scepticism about its capacity to reach its potential of around 100,000 tonnes a month of sulphur exports.

Looking ahead to the next few quarters, there is still a lack of really clear market direction. Availability at most key buyers is steady to tight, while on the other side, buyers are also reasonably well stocked and comfortable. We expect to see several important influences. Interest will continue as always to focus on Chinese sulphur stocks and ongoing import requirements, which are likely in turn linked to the

ability of Chinese phosphate producers to stay competitive, which will be difficult. Ma'aden's expanded phosphate capacity in Saudi Arabia is the most cost competitive to the Indian imported processed phosphate market.

SULPHURIC ACID

As we enter the second quarter of 2018, the tone of the international sulphuric acid market has continued to be firm extending a period of mainly steady or rising prices which goes way back to the middle of 2016 and beyond. Availability from export suppliers has been tight with relatively little volume available for spot sales. Even availability of virgin acid volumes, which frequently act as swing supply, dampening price inflation or shoring up falling prices, have been limited in the last few months. The spot price of acid for export in Europe reached around \$45 per tonne around double the price at the start of this year, and more than three times the price level of a year ago.

In Asia, which hosts several major acid exporters, spot supply availability has been universally reported as constrained. A month ago, some easing of supply limitations was foreseen in the second quarter but in more recent weeks, reports suggest that there will be no respite for buyers until Q3 at the earliest. Scheduled maintenance continued to remove available export supply tonnes from South Korea during the last few months with Korea Zinc and LS-Nikko copper both reporting downtime. The Pasar smelter in

the Philippines extended its long period of downtime due to prior typhoon damage.

Export volumes from China are an interesting indicator of the acid export supply side, since the main exporting company, Two Lions, is attracted in to the export market when acid prices are buoyant and sulphur prices make arbitrage possible. Having shipped two cargoes for Chile in March, and with around 60,000 tonnes reportedly booked to OCP in March and April, Two Lions reported that it would have little material available for international buyers until May. Chinese sulphuric acid exports for the first two months of 2018 reached 90,000 tonnes compared to a negligible amount at the same time last year.

In the European acid market, with more supply being committed to contract tonnage in the first quarter of 2018, spot availability was thin. For contract business, although buyers were pursuing a price rollover for second quarter contracts, sellers were looking for substantially higher numbers. Some early contract agreements were reported to have been made at an increase of around €5 per tonne, with buyers unable to persuade their negotiating counter-parties that falling sulphur prices were of significance.

In Morocco in Africa, phosphates major OCP continued to balance its overall sulphuric acid needs between own produced and imported product. The company reportedly booked around 130,000 tonnes of sulphuric acid for arrival in each of March

and April, having recorded imports of 270,000 tonnes in January and February, about 50,000 tonnes more than at the same time in 2017. Although severe weather delayed discharge over several days in March, production and overall raw material needs were not disrupted. In the second quarter of 2018, OCP is reported to be looking for 200,000 tonnes of sulphuric acid imports. As mentioned in our sulphur market commentary in this piece, the company will add an additional processed phosphate unit at its Jorf Lasfar hub in the second quarter, which may boost its overall acid import requirements further.

Not surprisingly with export supply so limited, many acid buyers have been looking to postpone purchases in the hope that prices will soften. In India, one buyer scrapped a tender in March for 10,000 tonnes because it considered offers of \$59 per tonne to be too high. Indian supplies were shortened further after major acid producer Vedanta experienced a delay returning its 1.3 million t/a acid plant at Tuticorin after maintenance. Similarly in Brazil and Argentina, a prior reluctance to pay higher prices seems to have evolved in exasperation at the lack of ability to secure spot tonnes, despite renewed interest. First quarter imports to Brazil for 2018 totalled just 59,000 tonnes compared to 162,000 tonnes for the same period in 2017. At least part of this reduction can no doubt be explained by limited supply availability and price elasticity.

Price indications

Table 1: Recent sulphur prices, major markets

Cash equivalent	November	December	January	February	March
Sulphur, bulk (\$/t)					
Vancouver f.o.b. spot	175	145	120	117	115
Adnoc monthly contract	184	195	140	140	140
China c.fr. spot	190	150	135	135	135
Liquid sulphur (\$/t)					
Tampa f.o.b. contract	110	110	116	116	116
NW Europe c.fr.	123	123	136	112	112
Sulphuric acid (\$/t)					
US Gulf spot	60	60	65	65	95

Source: various

Fig. 1: Month average spot sulphur prices, Jul 15 to Mar 18



Source: Integer, ICIS

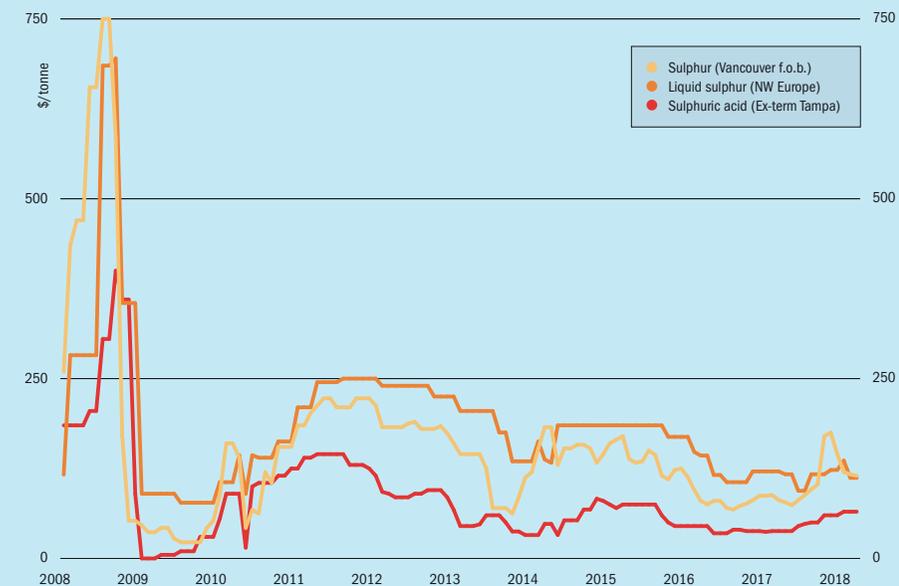
Fig. 2: China sulphur port inventory, Mar 2014 to Mar 2018



Source: Integer, ICIS

Market outlook

Historical price trends \$/tonne



Source: BCInsight

SULPHUR

- The sulphur market direction remains unclear over the coming months. Availability at most key buyers is steady to tight, but buyers are reasonably well stocked and comfortable.
- Interest will focus on Chinese sulphur stocks and ongoing import requirements, which are likely in turn linked to the ability of Chinese phosphate producers to stay competitive, which will be difficult. Ma'aden's expanded phosphate capacity in Saudi Arabia is the most cost competitive to the Indian import market. Chinese phosphate exporters are gradually losing market share in India and elsewhere, reducing their demand for sulphur.
- Chinese phosphate producers also continue to struggle with environmental restrictions on operations, and Chinese DAP operating rates are down in the 55-60% range.
- Now that significant tonnages are coming from Kashagan, this could have a major impact on market supply. If export

volumes from that project do get close to their potential, it may move the market to a long position. According to NCOC, 250,000 tonnes of sulphur had been exported from Kashagan to the end of March 2018, and export shipments are currently running at 50,000 tonnes per month, while NCOC says that a grand total of 1.5 million tonnes of sulphur has been produced. However, given the long history of delays to the project, there is considerable scepticism about whether the project's target of exporting of 100,000 tonnes of sulphur per month can be met in the near future.

- A ramp up in export availability from Russia, as we move seasonally away from winter logistics disruptions, also has the potential to contribute to an export supply surplus.
- On the other hand, OCP, normally the biggest buyer of Black Sea sulphur tonnes, is scheduled to increase its sulphur needs further when it ramps up the last of the four additional world scale processed phosphate units it is adding at Jorf Lasfar in April/May.

SULPHURIC ACID

- The sulphuric acid market looks set to remain tight for the second quarter of 2018 at least. Limited supply availability remains the main theme and buyers are likely to remain frustrated by reduced availability of spot tonnes and relatively little competition between sellers.
- Smelter outages in East, Southeast and South Asia have reduced acid availability and are expected to lead to more spot buying and increased prices.
- So far the supply response from virgin acid exporters has been insufficient to arrest price inflation. The disconnect between sulphur and sulphuric acid prices is getting to the point where significant arbitrage opportunities will become available to buyers and sellers that have the capability to switch between products.
- However, this kind of substitution can take significant time, and the acid market is likely to remain firm in the meantime.

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Sulphur 376 | May-June 2018

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CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

COVER FEATURE 3

Emissions reduction in sulphuric acid plants

COVER FEATURE 4

Seven deadly sins of tail gas treating

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INDIA

Petrofac wins SRU contract

Petrofac has been awarded a contract by the Hindustan Petroleum Corporation for the sulphur recovery unit block package of the Visakh Refinery Modernisation Project at Visakhapatnam, Andhra Pradesh state. The lump-sum engineering, procurement and construction (EPC) project, valued at around \$200 million, includes licensing and commissioning. Petrofac says that the unit will be constructed within the existing refinery under the terms of the 30-month contract.

"We are delighted to be supporting HPCL in the delivery of this important package at the Visakh Refinery," said group managing director for Petrofac's engineering and construction growth business, Sunder Kalyanam. "It is particularly satisfying to be expanding our EPC activities in-country with this award and our recent contract award in Kerala. Both demonstrate our growth strategy in action and the continued strength of our capability in the refinery sector."

NIGERIA

Nigeria to cut sulphur in imported fuel this year

The Nigerian National Petroleum Corporation (NNPC) says that it will slash the permitted sulphur levels in diesel fuel imports in July this year from 3,000 ppm to just 50 ppm. The move comes a year later than the original July 2017 deadline agreed with several other west African nations, including Togo, Benin, Cote d'Ivoire and Ghana. Sulphur levels in gasoline will be cut to 300 ppm from 1,000 ppm in October 2018, and again to 150 ppm in October 2019, according to NNPC. Nigeria, which imports 60% of west Africa's fuel imports, was part of the countries that pledged in December 2016 to adopt low sulphur diesel standards under United Nations Environment Programme (UNEP) guidance. Nigerian refineries have been granted waivers on fuel they sell within Nigeria while they upgrade their facilities to produce low sulphur fuels by 2020, although NNPC is also seeking a one year extension on this to 2021. Nigeria's new Dangote 650,000 bbl/d refinery is due on-stream around that date, and will change the complexion of the African petroleum industry, significantly reducing exports from the continent's largest oil producer.

Ghana is also building a new 150,000 bbl/d refinery at Takoradi as well as expanding its existing Tema Oil Refinery, and Angola aims to construct a 200,000 bbl/d refinery in Lobito by 2022 along with a smaller plant in Cabinda. Gabon's Societe Gabonaise de Raffinage (Sogara) is seeking a waiver from the government to continue producing high sulphur gasoil after cleaner fuels standards

are enforced across Africa in 2020. The refinery in Port Gentil currently meets the 50 ppm standards for gasoline, but is expected to continue producing 1,000 ppm gasoil after 2020 given current difficulties around acquiring financing for a new desulphurisation unit.

KUWAIT

KNPC to double refining capacity by 2035?

According to local press reports, state-owned Kuwait National Petroleum Co. (KNPC) is considering a \$25 billion plan to more than double its refining capacity from its current 936,000 bbl/d to 2 million bbl/d by 2035. The first phase of this will come with existing plans to expand capacity to 1.4 million bbl/d once the 615,000 bbl/d Al-Zour refinery comes on-stream in late 2019 or early 2020, following the permanent closure of the 200,000 bbl/d Shuaiba refinery in March 2017. The next phase would be to increase capacity to 1.7 million bbl/d by 2025, and then 2.0 million bbl/d by 2035 via the construction of a new refinery. Kuwait also hopes to increase crude oil production from the current 3.2 million bbl/d to 4 million bbl/d, including 350,000 bbl/d from the Neutral Zone that Kuwait shares with Saudi Arabia.

In March, Jacobs Engineering Group was awarded the contract for a pre-feasibility study, with the option of proceeding to a detailed feasibility study, for KNPC and its subsidiaries in support of KPC's strategic directions and downstream long term plans for the period up to 2040. Jacobs says that it will evaluate how domestic refining capacity can be best expanded, in a cost-effective way, while providing

advantaged feedstocks for integrated petrochemical production. The studies will cover evaluation and optimisation of alternative process configurations, technical studies, licensor evaluation, cost estimation, financial modelling and risk assessment and management, with a focus on increasing refining capacity and optimum petrochemical integration.

"As refiners across the industry look to the chemical market for profit growth, Jacobs leverages its proven, differentiated capabilities that have helped refiners explore options and define strategies for optimised refinery-petrochemical integration," said Jacobs Petroleum and Chemicals President Vinayak Pai. "This new award is an affirmation of our refining, petrochemicals and Oil-to-Chemicals (OTC) expertise and perfectly aligns with our strategy to expand services in the Middle East region."

IRAN

Shiraz refinery to produce Euro-V diesel

Iran's Shiraz refinery says that it has concluded negotiations and signed an agreement with Honeywell UOP to secure licenses for technology to produce higher quality 'Euro-V' (15 ppm sulphur) diesel fuel. The refinery is aiming to produce its entire 26,000 bbl/d diesel output as Euro-V standard via desulphurisation technology.

UNITED ARAB EMIRATES

Ethiad transports 16 million tonnes of sulphur

Abu Dhabi's Ethiad Rail DB says that it has transported 16.2 million tonnes of granulated sulphur since its rail line began commercial operations in January 2016, according to acting CEO Saeed Al Suwaidi, speaking at the Middle East Rail conference in Dubai in March. He added that the first stage of Ethiad Rail had achieved 94% punctuality during its commercial operations, hitting 100% in January 2018. He also hailed its safety record, saying not a single day had been lost to accidents, as well as its impact on road safety.

The UAE's fellow members of the Gulf Cooperation Council (GCC) said at the same conference that they "remain committed to the Gulf railway project", originally to have been completed in 2018 but rescheduled for 2021. Only the first 264km stage, running between the Shah



PHOTO: ETHIAD RAIL

Sulphur being transported by Ethiad Rail in Abu Dhabi.

sour gas plant in the desert and the export port of Ruwais in the Emirate of Abu Dhabi is currently operational. Saudi Arabia has designed and is working on 200km of rail track to link to Ruwais, but Qatar, Bahrain and Kuwait are still designing their portions. Kuwait is working on a 110km length of rail to connect to the GCC network, with an additional 160km of freight line to connect Kuwait City with its port.

KAZAKHSTAN

Kashagan sulphur output tops 1.5 million tonnes

The North Caspian Operating Company (NCOC), the consortium which operates the giant Kashagan offshore oil and gas field in Kazakhstan's sector of the Caspian Sea, gave a further update on sour gas processing from Kashagan at the end of March. According to NCOC, 1.5 million tonnes of sulphur has now been extracted from sour gas treated at the onshore gas processing facility. Exports of sulphur by rail began in October 2017, and reached 100,000 tonnes by the end of 2018. NCOC now says that as of March 29th 2018 another 150,000 tonnes of sulphur has been exported, taking the 6 month total to 250,000 tonnes. At the moment some of the sulphur being extracted is still being sent to sulphur blocks according to Bruno Jardin, managing director of NCOC. However, once the plant reaches capacity, the intention is for the entire sulphur output to be formed and exported. The company will also re-melt and processes sulphur accumulated in the sulphur blocks into granules.

CANADA

Gas output up, but not from sour wells

The Alberta Energy Regulator (AER) says that overall natural gas production increased by 1% during 2017. However, the proportion of gas production represented by sour gas remained relatively constant at around 19%, where it has stayed since about 2012, after falling from 31% of production in 2000. Production from the Montney and Upper Mannville Formations continued to grow, accounting for 45% of Alberta's raw natural gas production in 2017. There were under 117,000 producing gas wells in 2017, down from 120,000 in 2016, as producers focus on drilling fewer, more productive wells.

In a sign of increased processing around the Montney formation, Birchcliff Energy Ltd. and AltaGas Ltd. recently said that they have entered into a definitive 15 year agreement for a long-term natural gas processing arrangement at AltaGas' sour gas processing facility in Gordondale, Alberta. Under the Processing Arrangement, Birchcliff is being provided with up to 120 million cfd of

natural gas processing on a firm-service basis, and Birchcliff's take-or-pay obligation is 100 million cfd. A new 280 million cfd sour gas facility, designed to serve Montney shale producers working in the Pipestone region of the Western Canadian Sedimentary Basin, is also under development by a unit of Calgary-based Sem-Group Corp, designed to process raw sour gas with up to 10% hydrogen sulphide.

SAUDI ARABIA

SNC-Lavalin wins new Wasit contract

SNC-Lavalin has been awarded a contract by Saudi Aramco for the installation of additional facilities for the Wasit gas processing facility in Saudi Arabia's Eastern Province. Under the scope of work for the multi-million dollar contract, SNC-Lavalin will construct the Arabiah condensate handling facility and sour water disposal unit project at the Wasit Gas Plant, including the installation of process equipment as well as related civil and structural, piping, electrical and instrumentation and control systems. Work is already underway with a target completion date of late 2019. Wasit will be one of the largest gas plants to come on-stream in Saudi Arabia, and forms part of the Kingdom's Vision 2030 economic roadmap, feeding into the national master gas network to meet domestic energy demand.

"SNC-Lavalin has an impressive track record of successful project delivery during our 40-years of working with Saudi Aramco and we are pleased to continue our long-term relationship on another important project," said Christian Brown, President, Oil and Gas, SNC-Lavalin.

Production of Stercosul® – ATS liquid fertiliser

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CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

COVER FEATURE 3

Emissions reduction in sulphuric acid plants

COVER FEATURE 4

Seven deadly sins of tail gas treating

SULPHUR
ISSUE 376
MAY-JUNE 2018

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WORLD

Price increases for sulphuric acid catalysts



PHOTO: MECS

Sulphuric acid catalyst.

On March 7th DuPont Clean Technologies (DuPont) announced a general global price increase of \$0.50/litre for its MECS® sulphuric acid catalyst products, effective immediately. Cristina Kulczycki, global product manager, MECS Acid Catalysts said; "Our focus continues to be on supporting members of the sulphuric acid industry with new products, technologies and services that allow them to be more agile, flexible and competitive."

On April 4th, Haldor Topsoe followed suit with an increase in prices for its sulphuric acid catalysts to €0.40/litre (\$0.492/litre), also effective immediately. Topsoe said that the increase was "driven by a substantial increase in the price of vanadium, which is a necessary raw material for sulphuric acid catalysts". Sulphuric acid is produced by oxidation of sulphur dioxide to sulphur trioxide in the presence of a vanadium pentoxide catalyst, and vanadium pentoxide prices have risen from below \$6/lb a year ago to over \$14/lb at the start of April 2018.

EGYPT

Fluor awarded FEED contract for sulphuric, phosphoric acid plants

Fluor has been awarded the front-end engineering design (FEED) contract by Egypt's state energy firm Enppi for the offsites and utilities portion of the main plant complex and support services for the Waphco phosphoric acid production plant at Abu Tartour, in the Egyptian province of New Valley, for an undisclosed sum. The contract signing ceremony was held in Cairo with Tarek El Molla, Egypt's minister of Petroleum and Natural Resources.

"Fluor appreciates the importance and relevance to Egypt of this major industrial project and will use its experienced resources and subject matter expertise to deliver this complex engineering project to meet our client's goals," said Tony Morgan, president of Fluor's Mining & Metals business. "Working with Enppi as an inte-

grated team, Fluor will fast-track the FEED for the plant, which will use resources from the Abu Tartour mine to produce merchant-grade phosphoric acid."

The project scope includes all process facilities including a sulphuric acid plant, utilities with a cogeneration system, storage and other required units. Once completed, the facility will produce 500,000 t/a of wet process phosphoric acid.

INDIA

Sterlite faces protests over smelter expansion

Sterlite Industries, which operates a 400,000 t/a copper smelter at Thoothukundi near Tuticorin in Tamil Nadu state, has faced mass local protests over plans to build a second 400,000 t/a smelter at the same site at an estimated cost of \$450 million. Sterlite obtained clearance to set up the new smelter in 2009, although its location within the

SIPCOT industrial park meant that there was no public consultation on the decision. The smelter has faced a history of environmental breaches and closures. In 2009 the government of Tamil Nadu ordered the plant closed due to public protests and alleged environmental violations, but in 2013 the Indian Supreme Court stayed the order. Sterlite was instead fined \$15 million in 2013 for environmental violations.

Sterlite Copper is the copper-producing unit of UK-based Vedanta Resources plc. It also operates a 1.2 million t/a sulphuric acid plant and 220,000 t/a phosphoric acid plant at the site. Its CEO P. Ramnath has said that the protests are being "fanned by foreign-funded activists", and that the new copper complex would include "zero discharge systems, utilisation of waste for sustainable applications, energy efficient systems and stringent emission monitoring".

SOUTH AFRICA

Acid spill after truck fire

A truck has spilled 30,000 litres of sulphuric acid in the Victoria Falls district of South Africa following a fire in the tanker trailer. Local police said that the truck was heading to the Zambian border post at Kazangula, and that the cause of the fire, which happened about 20km short of the town, had not been determined, although an electrical fault was suspected. A similar accident last year led to a spillage of 34,000 litres of sulphuric acid into the nearby Inyatue River.

Phosphate cargo auctioned after OCP refuses to take part in trial

The cargo of 55,000 tonnes of phosphate seized in Port Elizabeth in May 2017 is to be auctioned following the conclusion of a trial in South Africa's High Court. The shipment, from Moroccan phosphate producer OCP, was intended for Ballance Agri-Nutrients Ltd in New Zealand. The cargo was shipped from the port of Boucraa in Western Sahara on the NM Cherry Blossom, and the self-proclaimed Sahrawi Arab Democratic Republic (SADR), operated by the Polisario Front which claims jurisdiction over Western Sahara, said that the shipment had been illegally taken from Western Sahara and asked for the ship to be impounded when it called in South Africa. South Africa is one of 45 countries which still recognise SADR's control over Western Sahara.

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CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

COVER FEATURE 3

Emissions reduction in sulphuric acid plants

COVER FEATURE 4

Seven deadly sins of tail gas treating

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The South African court decided in its verdict that "phosphate ownership has never been legally held by the Office Chérifien des Phosphates (OCP) and/or Phosphates de Boucraa SA," and said that they are not authorised to sell phosphate from Western Sahara to New Zealand. OCP declined to take part in the case. The court has opened an exclusive bid auction to sell the cargo, running 30 days to April 18th, with a starting bid set at \$1.0 million. Additional orders issued by the court denied OCP the power to auction cargo and the right to recover the capital costs of the shipment.

A shipment detained in Panama in June 2017 under a similar action by Polisario was released after a Panama court decided that there was insufficient evidence that the shipment belonged to Polisario.

ALGERIA

Phosphate complex set for late 2019 opening

Algeria is still targeting the end of 2019 or start of 2020 for the start-up of phosphoric acid production at Souk Ahras in the east of the country, according to Sonatrach CEO Ould Kaddour. The \$6 billion complex is being developed by Sonatrach and Algerian phosphate companies Asmidal and Manal, in conjunction with Indorama and two Chinese partners, the China International Trust and Investment Corporation (CITIC) and Wengfu Group. It will be fed from the Bled el Habda phosphate mine in Tebessa province, which is currently under development, and where there are a reported 2 billion tonnes of phosphate reserves. The complex will include 4,500 t/d of sulphuric acid production, 1,500 t/d of phosphoric acid production and 3,000 t/d of diammonium phosphate production. It is part of an ambitious expansion programme for the Algerian phosphate sector to increase production to 10 million t/a, via four phosphate processing projects approved in 2017, including two projects in Souk Ahras, one in Tebessa and one in Skikda.

MOROCCO

OCP revenues up 14% in 2017

Morocco's state-owned phosphates giant Office Chérifien des Phosphates (OCP) has released figures for 2017 showing that its revenues grew 14% compared to 2016 to reach a total of 48.5 billion dir-

hams (\$5.29 billion), compared to 42.48 billion dirhams (\$4.63 billion) in 2016. The company's sales of phosphate rock increased 40% year on year, while the group's revenues from selling fertilizers jumped by 24% compared to 2016. This performance helped the OCP offset a fall in international prices, the company said in a statement. In 2017, fertilizer sales totalled 54% of the Group's turnover, while phosphate rock and phosphoric acid took 21% and 15% respectively. The group said this positive performance was the fruit of the first phase of its investment plan, which was completed in September 2017. The plan helped double production capacity, triple fertilizer sales, build a pipeline and develop the Jorf Lasfar port. Exports to Africa increased by 50%, from 1.7 million t/a in 2016 to 2.5 million t/a in 2017. The Group's EBITDA remained stable in 2017 with a slight decrease of its margin by 26% compared to 2016.

AUSTRALIA

Offtake agreement for Ammaroo phosphate project

Australia's Verdant Minerals says that it has signed a non-binding memorandum of understanding (MoU) on offtake from its Ammaroo phosphate project. According to the company, Wilson International Trading has agreed to potentially purchase 350,000 t/a of phosphate rock concentrate or other phosphate products produced at Ammaroo. Wilson is looking to secure 1 million t/a of phosphate rock for Greenstar Fertilizers in India. Verdant said that the MoU is "an important step in the process of establishing firm markets for Ammaroo phosphate rock," and that in conjunction with ongoing work to definitively establish the project's economic feasibility and to obtain a license to operate, product analysis and discussions also continue with a number of other buyers of phosphate rock in the Asia Pacific region.

Ammaroo, in Australia's Northern Territory, contains the billion-tonne, 40-kilometer-long Ammaroo phosphate JORC resource. A bankable feasibility study and environmental impact assessment are currently under development, following the completion of a draft environmental impact assessment in October 2018. Verdant says the bankable feasibility study remains on track for completion in Q1 2018.

Feasibility study for Ardmore phosphate project

Australian company Centrex says that it is moving to a feasibility study on the A\$60 million Ardmore phosphate project near Dajarra, after an initial scoping study said a ten-year open pit mining operation would produce 776,000 t/a of premium 35% P₂O₅ phosphate rock product per year. Centrex Metals CEO Ben Hammond says that Ardmore is one of the few remaining high-grade phosphate projects in the world. Australia and New Zealand currently import 1 million t/a of phosphate rock, mainly from North Africa.

"Ardmore can produce a premium grade of phosphate concentrate and unlike most products on the market it is ultra-low in cadmium which is a toxic metal which can be absorbed by plants and end up in our food," Hammond said. The feasibility study is expected to be published in the middle of 2018.

MEXICO

Offshore mining approval offers hope for New Zealand project

The Mexican Superior Court has issued a unanimous ruling in favour of Exploraciones Oceánicas (ExO), overturning a previous denial of the company's environmental permit application to extract phosphate sand at its Don Diego project, in the Bay of Ulloa. ExO is a subsidiary of Odyssey Marine Exploration, a pioneer in the exploration and development of seabed mineral resource deposits.

The Don Diego project contains high-grade phosphate sands within Mexico's Exclusive Economic Zone, beyond its territorial waters. The current resource assessment defines the deposit as containing 588 million tonnes of phosphate ore at 18.1% P₂O₅, held under 1.14 metres of overburden and with an ore thickness of 2.8 metres.

The development has been welcomed by Chatham Rock Phosphate, which shares a director with Odyssey, and which is aiming to develop a similar project off New Zealand, as it establishes a precedent for the consenting of marine phosphate mining.

"This is the best news for Chatham since we were granted our mining permit back in December 2013, as it establishes a precedent for marine phosphate mining after extensive and detailed environmental

assessment," Chatham president and CEO Chris Castle commented. The Don Diego approval also follows the granting of an environmental consent to Trans Tasman Resources in New Zealand's territorial waters last year, Castle noted.

Chatham is also developing a similar project in Namibia's offshore waters, where mining permission was first granted and then withdrawn in 2016, but says it plans to re-apply for consent there by the end of 2018.

CHILE

KBR to upgrade Enap refinery

KBR has been awarded a contract by ENAP Refinerías SA to install KBR's ROSE™ solvent deasphalting technology at ENAP's Bio Bio refinery in Concepcion. Under the terms of the contract, KBR will provide technology licensing and basic engineering design for ENAP's upcoming 30,000 bbl/d refinery upgrading project. The unit will split residue from a mix of crude oils into deasphalted oil and asphaltene, allowing the refinery to upgrade a larger proportion of its oil intake into high-grade products. The new unit will not change the refinery's total processing capacity but will allow a different product mix and will give the refinery more flexibility to respond to market developments and reduce the environmental footprint of its products.

The award is part of a suite of over \$250 million of environmental upgrades at the Bio Bio refinery being conducted by Enap, including a sour water stripper with a capacity of 1,600 m³/day and a new, third sulphur recovery unit with a capacity of 140 t/d of sulphuric acid to enable optimisation of the sulphur recovery process by reducing the SO₂ emissions and increasing reliability and operational flexibility of the site's overall sulphur recovery system.

CANADA

Update to sulphuric acid rail transportation regulations

On March 15th, Transport Canada released a notice on the intent to issue a new January 2018 edition of standard TP 14877 "Containers for Transport of Dangerous Goods by Rail" to replace the current 2013 (with Corrigendum) edition. The move is the result of public consultation following the 2013 Lac Mégantic disaster, when a runaway 74-car train carrying crude oil derailed in the centre of

the town, leading to fire and explosions which killed 42 people. As well as mandating new construction requirements for tank cars, including the addition of stainless steel, normalized steel for dangerous goods classified as a toxic inhalation hazard (TIH) and improved thickness requirements for new tank car construction, the regulations update technical requirements for flammable liquids and improve harmonisation between tank car requirements in Canada and the USA, including tank car design requirements and a new mechanism to secure One Time Movement

Approvals. It also updates the dangerous goods list to align with the 19th edition of the UN Model Regulations, and includes adjusted special provisions to reflect updated transportation requirements for Sulphuric Acid (UN1831) and Hydrogen Peroxide (UN2014 / UN2015).

The amendment to adopt the proposed revised standard is expected to be published in the Part I Canada Gazette (CGI) in the autumn for a 60-day comment period. Transport Canada says that it hopes to have the CGI final amendment version adopted in the fall of 2019.

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CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

COVER FEATURE 3

Emissions reduction in sulphuric acid plants

COVER FEATURE 4

Seven deadly sins of tail gas treating

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People

The Sulphur Institute (TSI) has announced that **Tom Simpson**, Director of Sulphur Purchasing at Nutrien Ltd, has assumed responsibilities as vice chairman of the Board. Simpson's appointment comes in advance of TSI's Annual General Meeting and will continue through April of 2019. Robert McBride, president and CEO of The Sulphur Institute said, "We are excited to have Tom on board as TSI's Vice Chair. He is a veteran of the sulphur industry and we look forward to his leadership on the Management Team and Board of Directors."

Simpson is no stranger to TSI, having participated in several Sulphur World Symposia, and has contributed his industry insights during many working group sessions. "It is an honour to be named TSI's Vice Chair. I look forward to working with the Institute and its members to advocate on behalf of the sulphur industry," said Simpson. In addition to his role as TSI's vice chair, Simpson will lead TSI's Programme Committee, providing vision and direction to the working groups and monitoring the progress of key programmes and services.

Itafos says that **Rafael Rangel** will resign as chief financial officer, effective immediately, to "pursue opportunities

outside the company". The board of directors has appointed **George Burdette** to serve as CFO effective upon Mr. Rangel's departure.

Mr Burdette comes to Itafos with over 12 years of corporate development, financial, commercial and investment management experience. He led or supported over \$8 billion of acquisitions, divestitures, mergers and financings in the US and various emerging markets. Prior to joining Itafos, he was head of Americas project finance at First Solar where he was responsible for project financing and commercial initiatives in the US, Latin America, and South Africa. Prior to First Solar, Burdette had a range of experience in private equity and corporate roles at both Zaff Capital and AEI, covering corporate development, financings and enterprise risk management working together with Brent de Jong (Itafos Chairman) and Brian Zatarain (Itafos CEO). Mr. Burdette holds a BA in International Business and French from Wofford College and an International MBA from the University of South Carolina.

"We thank Rafael for the contribution he made to Itafos during his tenure," Brian Zatarain, chief executive officer, said. "With the acquisition of the Conda Phosphate Operations and GB Minerals Ltd, Itafos is well-positioned to continue the implementation of its strategy of building a pure-play phosphate fertilizer company. Mr. Burdette is the right person to join our leadership team as we enter this new phase of growth."

Phosphate Operations and GB Minerals Ltd, Itafos is well-positioned to continue the implementation of its strategy of building a pure-play phosphate fertilizer company. Mr. Burdette is the right person to join our leadership team as we enter this new phase of growth."

PhosAgro has announced that its board of directors has re-elected independent director **Sven Ombudstvedt** as its chairman. The board also re-elected as its deputy chairman **Andrey G. Guryev**, vice president of the Russian Union of Chemists. The board of directors also appointed the leadership and members of the board committees. The Audit Committee will be chaired once again by independent director and PhosAgro board member **Marcus Rhodes**; PhosAgro CEO and board member **Andrey A. Guryev** was re-appointed chairman of the Strategy Committee; independent director and PhosAgro board member **James Rogers** will lead the Remuneration and Human Resources Committee, the Environmental, Health and Safety Committee will be chaired by PhosAgro board member, executive director and CEO of Apatit **Mikhail Rybnikov**; the Risk Management Committee will be chaired by **Ivan Rodionov**.



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Calendar 2018/19

JUNE

7

European Sulphuric Acid Association (ESA) Spring Meeting, TALLINN, Estonia
Contact: Patricia De Hertogh, Cefic, Brussels
Tel: + 32 2 676 7253
Email: pdh@cefic.be

8-9

42nd AIChE Annual Clearwater Conference 2018, CLEARWATER, Florida
Contact: Perry Alonso, AIChE Central Florida Section
Email: vice-chair@aiche-cf.org

18-20

86th IFA Annual Conference, BERLIN, Germany
Contact: IFA Conference Service
28 rue Marbeuf, 75008 Paris, France.
Tel: +33 1 53 93 05 00
Email: ifa@fertilizer.org

OCTOBER

14-17

Middle East Sulphur Plant Operators Network (MESPOLN), ABU DHABI, UAE
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Fax: +971 2 645 0142
Email: info@universulphur.com

NOVEMBER

5-8

Sulphur 2018 Conference, GOTHENBURG, Sweden
Contact: CRU Events
Tel: +44 20 7903 2167
Email: conferences@crugroup.com

28-30

European Refining Technology Conference, CANNES, France
Contact: Sofia Barros, Senior Conference Producer & Project Manager World Refining Association
Tel: +44 20 7384 7944
Email: sofia.barros@wraconferences.com

FEBRUARY 2019

25-28

Laurance Reid Annual Gas Conditioning Conference. NORMAN, Oklahoma, USA
Contact: Tamara Powell, Program Director
Tel: +1 405-325-2891
Email: tsutteer@ou.edu

MARCH

17-19

AFPM Annual Meeting, SAN ANTONIO, Texas, USA
Contact: American Fuel and Petrochemical Manufacturers (AFPM)
1667 K Street, NW, Suite 700, Washington, DC 20006, USA.
Tel: +1 202 457 0480
Email: meetings@afpm.org
Web: www.afpm.org

25-27

Phosphates 2019 Conference, ORLANDO, Florida, USA
Contact: CRU Events
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CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

COVER FEATURE 3

Emissions reduction in sulphuric acid plants

COVER FEATURE 4

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Asia continues to add refining capacity which will generate additional tonnages of sulphur over the coming few years.



New Asian refining capacity

The Singapore Refining Corporation refinery at Singapore.

Over the past few decades, global oil demand has continued to grow, apart from a contraction over the period 2007-2009 caused by the banking crash and slowdown in the global economy. There are no signs that this is likely to change in the near future. Furthermore, the location of oil consumption has gradually shifted. In 1980, the 'western hemisphere' – Europe, Africa and the Americas – consumed about 75% of oil, and Asia only about 25%, but by 2017 this had become virtually 50-50. This shift has led to a boom in refining in Asia in an attempt to keep up with the rapid increase in refined product demand which has come from the industrialisation of China, India and Southeast Asia.

Refined product demand is continuing to grow globally. The International Energy Agency forecasts that total global demand

for refined products will increase by 3.2 million bbl/d over the next five years. However, this overall figure masks a wide split between OECD and non-OECD growth. OECD demand is forecast to fall by 1.3 million bbl/d, while non-OECD growth will be 4.5 million bbl/d. Other assessments broadly agrees with this forecast, putting non-OECD growth in demand for refined products at 4.8 million bbl/d over the next five years. Around two thirds of this growth will be for gasoil/diesel and gasoline. Furthermore, 85% of this growth will be in Asia. China represents 1.1 million bbl/d of growth out to 2023, with gasoline representing about half of that, while the rest of non-OECD Asia (predominantly India, but also including the developing economies of southeast Asia) adds another 1.6 million bbl/d of growth over the next five years, with diesel the major component at about one third of new demand.

Refining capacity

The shift in refining capacity can be seen in Figure 1, which summarises net new refinery capacity additions by region. Of a total of 7.5 million bbl/d of effective new refinery capacity which is projected to be added to 2023, 2.0 million bbl/d will be added in the Middle East, 1.6 million bbl/d in China, and 1.9 million bbl/d in non-OECD Asia, according to the International Energy Agency. This figure takes into account closures in some places and regions which will offset some of the new capacity building. However, consultants Stratras Advisors have a much higher estimate for new Asian refining capacity, as shown in Table 1 (Asia here defined as Russia and the FSU as well as China, South and East Asia and Southeast Asia, but excluding the Middle East). This begins with established refinery

capacity on January 1st 2017, and so the 2017-2020 figure is boosted by the large jump in Asian refining capacity which happened last year, including 460,000 bbl/d in two refineries in China. Stratras also notes that some of the figures as speculative based on likely refinery configurations – some of these projects are in the early planning stages and have not yet provided specific plans in terms of capacity, particularly for downstream secondary processing capacity. In particular there are a number of large, new refinery projects planned in China for which configuration details are not available.

The report also notes that while average regional capacity utilisation is about 80%, a large portion of underutilised capacity comes from simple so-called 'teapot' refineries in China, which lacks secondary processing capacity.

Changing refinery configurations

As the global supply of crude continues to grow relatively sourer, and regulations on sulphur content in fuels tightens in developing markets such as India and China, so Asian refineries are likely to become more complex and add more hydroprocessing capacity at a more rapid rate than elsewhere in the world, as noted in Table 1. There are large variations in refinery capability and complexity in the region. Japan has one of the most complex refining systems in the world with a high conversion ratio vs. crude oil capacity and one of the highest hydroprocessing ratios globally. While there is a strong push to further increase the depth of refining in Japan, its hydroprocessing capacity exceeds crude oil distillation capacity. Conversely, while Chinese state-owned refineries have a very high level of conversion (47%) but is much more limited in hydroprocessing. Stratras predicts that additions in hydrogen generation capacity will increase by 2.5% year on year in Asia, via both naphtha and especially (65%) steam reforming, while the need to produce better quality fuel and deal with sourer crudes will lead to sulphur production increasing at 3.5% year on year, adding up to 5 million t/a of new sulphur production out to 2025, as shown in Table 1.

China

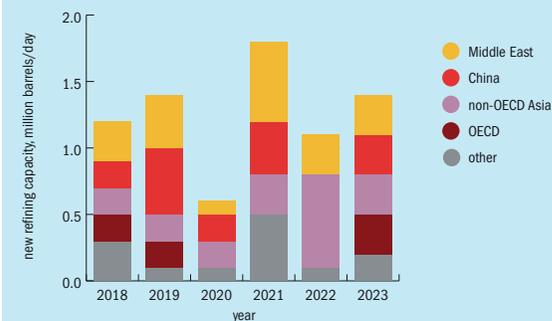
China will have the highest addition of new hydrotreater capacity additions in the world over the next few years. About 1.6 million bbl/d of new hydrotreater capacity

is scheduled to be added between 2018 and 2021, almost one quarter of global hydrotreater expansion over that period, and there are six new refineries scheduled for start-up, including Dayushan Island, Jieyang and Dalian III (see Table 2). Even so, while China is currently a net exporter of refined products, rising domestic demand, growing by about 5% per year means that the country could still become a net importer again into the 2020s, although the rate of increase of demand is forecast to start slowing from the mid-decade as the country moves from an industrial economy to a more service-oriented economy.

Much depends on the fate of the 120 independent 'teapot refineries', mainly in Shandong province, with capacities ranging from 20-100,000 bbl/d. These refineries have had operating rates as

low as 30% in recent years, and their lack of complexity means that they are likely to be unable to cope with increasingly stringent new fuel regulations. They represented 4.3 million bbl/d of downstream capacity, or just over 25% of China's 15.1 million bbl/d of total refining capacity in 2017. The reason for their low operating rates was that they were originally forbidden from importing oil to operate, but in 2015 the Chinese government began to issue 1.6 million bbl/d of oil import licenses to these refineries, possibly in an attempt to put pressure on other refiners in the country to become more efficient. The result was a surge in oil imports into China and a flood of refined products. However, these refiners are still denied export licenses, meaning that they cannot take advantage of China's current refined product surplus to export

Fig. 1: New refining capacity by region, 2018-23, million barrels/day



Source: International Energy Agency

Table 1: Asian refinery expansion projects, million barrels per day

	2017 capacity	New capacity to 2020	New capacity 2020-25
Crude distillation	34.50	6.10	5.89
Coking	3.35	0.74	0.89
Hydrocracking	3.66	0.81	0.98
Hydroprocessing			
Gasoline	1.37	0.30	0.37
Naphtha	3.38	0.75	0.90
Middle distillates	8.76	1.94	2.34
Heavy oil/residual fuel	3.82	0.84	1.02
Sulphur (million t/a)	10.20	2.30	2.70

Source: Stratras Advisors

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

COVER FEATURE 3

Emissions reduction in sulphuric acid plants

COVER FEATURE 4

Seven deadly sins of tail gas treating

Table 2: New Asian refineries, 2017-2025

Country	Company	Site	Capacity bbl/d	On-stream
Brunei	Zhejiang Hengyi Group	Pulau Muara Besar	175,000	2019
China	Petrochina	Anning	260,000	2017
	CNOOC	Huizhou	+200,000	2017
	Rongsheng Petrochemical	Zhoushan 1	400,000	2018
		Zhoushan 2	400,000	2020
	Hengli Group	Dalian	400,000	2019
	Sinopec	Zhanjiang	200,000	2020
		Kaojing	400,000	2024
India	HPCL	Barmer	155,000	2023
	IOC/HPCL/BPCL	Babulwadi	700,000	2023?
Indonesia	Pertamina	Various	+1,000,000	2025?
Malaysia	Petronas	RAPID	279,000	2020
Philippines	Petron	Bataan	+180,000	2020
Taiwan	CPC	Dalin	+47,000	2017
Vietnam	Petrovietnam	Nghi Son	186,000	2018

overseas. In the face of mergers in the Chinese refining market and the new rash of mega refineries that are forecast to come on-stream over the next few years, some of the teapot refiners are banding together in a \$5 billion joint venture. The new alliance, called Shandong Refining & Chemical Group, gathers six independent oil processors and a provincial government-backed fund as investors, and was registered in late September 2017. It aims to eventually gather 2 million bbl/d of processing capacity under its umbrella, and is actively seeking an export license.

In the meantime, the Chinese government is moving instead to strengthen its environmental and tax regulations and is using them to weed out inefficiencies in the sector and remove excess capacity. The National Development Reform Committee (NDRC) is pledged to shut down all refineries with a capacity of less than 40,000 bbl/d, and has given refiners until August 2018 to comply with tax and environmental regulations or face closure – independent refiners and blenders in China have been using loopholes in the consumption tax rules to avoid tariffs entirely or only pay partial taxes. China is also looking to liberalise domestic prices for gasoline and diesel fully by 2020. China has already lost 1.2 million bbl/d of outdated refinery capacity over the past two years, and at least another 1-2 million bbl/d of capacity seem likely to be forced to close over the next few years.

India

In India, demand for refined fuels has grown by 6% per year from 2010-2018, and is forecast to grow by a further 4% year on year out to 2025. Diesel will drive a significant proportion of this demand growth, resulting in India becoming a net importer – mostly of LPG and naphtha – after 2020. The major drivers for India's fuel demand growth will be the continued robust sales of passenger vehicles, substitution of liquefied petroleum gas (LPG) as a cooking fuel, growing urbanisation and the country's demand for infrastructure and consumer goods. Apart from demand for gasoline in passenger cars and diesel for road haulage, India's appetite for jet fuel is also expected to grow as the country upgrades airport infrastructure and plans to build about 200 new airports in the next 10 years. As a result, looking to the longer term, the country's Petroleum Minister Dharmendra Pradhan said recently at a Refining and Petrochemicals Technology Conference that India will need to invest \$300 billion over the next 10 years in order to double its oil refining capacity, which currently stands at 247 million t/a (4.25 million bbl/d), but which will need to reach somewhere between 460-600 million t/a (ca 8-10 million bbl/d) by 2040, depending upon whose figures you believe (the lower figure comes from the state-owned Indian Oil Co, the higher from the Petroleum Ministry).

As the initial part of the development, the government has authorised several brownfield projects which are expected to add 55 million t/a (1 million bbl/d) of additional capacity at existing refineries by 2025, but there are also two major new greenfield refineries under development to add a further 69 million t/a (1.2 million bbl/d) of capacity. Outside the scope of current projects, Reliance is also believed to be developing a second refinery to run alongside its current massive refinery at Jamnagar by 2030 – the company is looking to increase its refining capacity to 2 million t/a by that time. In January 2018, Reliance up-rated the capacity of the existing Jamnagar refinery to 1.24 million bbl/d.

The largest of these new refineries is under development by state-owned oil firms Indian Oil Corporation (IOC), Hindustan Petroleum Corp. Ltd. (HPCL) and Bharat Petroleum Corp. Ltd. (BPCL). These three have signed a \$40 billion joint venture agreement to set up what could become the world's largest refinery and petrochemical complex in the Ratnagiri district of Maharashtra. IOC will be the lead partner with a 50% stake while HPCL and BPCL will each take a 25% stake. The refinery is to be built in two phases, with the first, 40 million t/a (700,000 bbl/d) phase taking 5-6 years to build from acquisition of the land, and therefore not likely to be active before 2023. The other new refinery will be a 9 million t/a (155,000 bbl/d) refinery for HPCL at Barmer in Rajasthan, which is also slated for completion by 2023.

Saudi Aramco has indicated that it is interested in buying a stake in existing Indian refineries and expansion projects, as well as the planned giant refinery on India's west coast, according to Saudi Arabian Energy Minister Khalid al-Falih. The company has signed an agreement to initiate talks for a possible stake in the proposed Ratnagiri refinery, and the minister told Indian journalists during a recent visit that Aramco is also looking at other opportunities to buy into existing refineries in India, as well as upgrades of existing refineries.

Southeast Asia

Outside India and China, the wider Southeast Asian market is expected to mirror the growth in Asia's largest consumers. Refined products demand in Southeast Asia grew by 3% per year from 2010-2018 with forecasts predicting 2% per year

growth until 2025. Net imports of transport fuels are expected to rise, driven by strong demand growth of 4.1% per year, leading to increased pressure to build new refinery capacity.

At present, Malaysia is the largest source of new refining capacity, with its RAPID refinery at Pengerang, Southern Johor, as part of the Pengerang Integrated Complex, and the Kuantan Port refinery. This will represent about 6% of total global planned hydrotreater capacity additions out to 2021; there will be 368,000 bbl/d at Pengerang and 45,000 bbl/d at Kuantan. The Philippines and Vietnam will also add new refining capacity. Philippines refiner Petron is expanding its existing 180,000 bbl/d refinery at Bataan by 90,000 bbl/d in 2019, and is said to be looking at a further 90,000 bbl/d expansion in 2020. The expansions have replaced earlier plans to develop a new greenfield 250,000 bbl/d refinery south of the existing Bataan refinery, possibly in Southern Luzon, the Visayas or Mindanao. Meanwhile Vietnam's state-owned Petrovietnam has developed a new \$9 billion, 200,000 bbl/d refinery at Nghi Son in cooperation with Kuwait Petroleum Europe BV, which has a 35% stake, and Japanese firms Idemitsu Kosan (also 35%) and Mitsui Chemicals (4.7%) – Petrovietnam holds the remaining 25% stake. The country's pre-existing Dung Quat refinery can only supply about 30% of the country's total domestic fuel demand, and the Nghi Son refinery, which will process Kuwaiti crude oil, will up this to 80% of fuel demand. The refinery was due to start up in February 2018, and after some delays, commercial products began flowing in April. Vietnam exports some crude oil but its shipments have been decreasing as production declines from older fields and as some production has become uneconomic amid lower oil prices.

Sulphur

All of these refinery projects are expected to increase Asia's sulphur output considerably; possibly by up to 5 million t/a by 2023, according to the figures in Table 1, potentially about half of that in China. Will this impact upon Chinese imports of sulphur? Not necessarily. China continues to be the world's largest importer of elemental sulphur – in 2016 it imported 11.9 million tonnes as compared to 5.2 million tonnes for Morocco, the next

largest importer. Although 2017 saw a decline in this, China still imported 11.1 million tonnes of sulphur last year. Chinese demand for sulphur has been reduced by cutbacks in the phosphate fertilizer industry due to environmental regulations, and Chinese domestic sulphur supply has increased from Chuandongbei and Puguang sour gas processing and the commissioning of the Anning refinery. But while phosphate production in China is levelling off, and expected to peak in 2020, consultancy CRU says that it expects that there will still be some increase in demand

for sulphur in China due to substitution of pyrite-based acid production for sulphur burning acid production, as well as increasing industrial demand for acid. Meanwhile, while sour gas-based sulphur production may increase by 600,000 t/a over the next five years, another 1 million t/a or so may come from new refinery projects, depending on start-up dates, which are likely to slip from the current dates in Table 2. Overall, this might well keep new supply and demand in China roughly balanced and hence imports remaining at their current high levels.

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CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

COVER FEATURE 3

Emissions reduction in sulphuric acid plants

COVER FEATURE 4

Seven deadly sins of tail gas treating

SULPHUR
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Nickel and copper in Southeast Asia

The demand for sulphuric acid in metal processing has been complicated by Indonesia's export ban on nickel ores and move to develop copper smelting capacity and an environmental crackdown on nickel mining in the Philippines.

Indonesia and the Philippines are the two largest producers of nickel in the world, and between them represent 30% of global nickel mining capacity, and this proportion is growing rapidly. Indonesia will produce 25% of the world's nickel ore in 2018, with a larger proportion than ever being processed locally to nickel pig iron (NPI). Global nickel mine output is expected to increase by over 10% for the second straight year in 2018, according to the International Nickel Study Group (INSG). However, virtually all of the growth will come Indonesia, where mined production will increase by 50%; and the Philippines, which should rise by 10%. Thanks to its export restrictions, Indonesia is also processing more nickel and will add the large majority of the additional 100,000 t/a finished metal capacity that should be online by 2020.

Indonesia

In 2009, Indonesia enacted a new mining law. The law was a response to the boom in mining across the country which had in turn been triggered by China's rapid industrialisation and demand for raw materials. As lucrative as it had become for Indonesia, it also triggered fears that the country was being exploited by large international mining companies, and that it was not capturing enough of the value chain for itself. The goal of the law, therefore, introduced by the government of Susilo Bambang Yudhoyono in 2009, was to get mining companies to build downstream minerals processing capacity in Indonesia rather than shipping

raw ore to China to be smelted, and it gave companies five years to increase their processing of ores within the country or face a ban on the export of raw mineral ores and concentrates (in the case of copper). After the January 2014 deadline, the government would ban raw mineral exports, and only minerals at specified purity levels would be allowed to leave Indonesia.

The law was not taken very seriously by the mining companies and there was little or no investment in downstream smelting capacity – it was assumed that, presented with a fait accompli by the mining companies, the government would re-think its ban. This meant that in January 2014, when the five year grace period ended, they suddenly found themselves facing a complete ban on the exports of nickel ore and bauxite – copper was given a reprieve in order to try and force the hand of Freeport MacMoran, which owned Indonesia's main copper mine at Grasberg and which was in negotiations with the government. There was some hope that the 2014 presidential election might lead to a change in policy – president Yudhoyono was constitutionally barred from seeking a third term in office, and the presidency fell in 2014 instead to opposition PDI-P candidate Joko Widodo. However, the policy remained unchanged, with Widodo strongly supporting the ban as part of his own nationalist economic agenda.

Although the nickel market was dealing by 2014 with a slowdown in Chinese growth and overcapacity, the ban had an immediate impact on nickel markets, reversing the decline in prices that had

happened since 2009. It did also force companies to begin investing in processing capacity in Indonesia, attracting billions of dollars in investment, and the volume of refined nickel began to increase. Most of the capital came, perhaps unsurprisingly, from China, with investors partnering with local companies in joint ventures.

However, in January 2017, there was an abrupt about face from the Widodo government, and the ban was reversed via a new law which allowed exports to resume under certain conditions: they must dedicate at least 30% of their smelter capacity to process low grade ore (up to 1.7%) and they must show progress in the construction of smelters. With this change, the Minister of Energy and Mineral Resources said that the country may export up to 5.2 million tonnes of nickel ore per year. Over the previous three years, Indonesia's trade deficit had been growing, and state owned PT Aneka Tambang (Antam), which exported the largest proportion of Indonesia's nickel ore, had suffered huge financial losses and had to be bailed out by the government. The government instead looked towards consolidating state owned mining companies under a single company, PT Inalum, the state aluminium miner.

Philippines

The Philippines was until recently the world's largest producer of nickel. However, as Figure 1 shows, its output fell dramatically in 2016 and 2017. Part of this was due to the low price of nickel on the international mar-

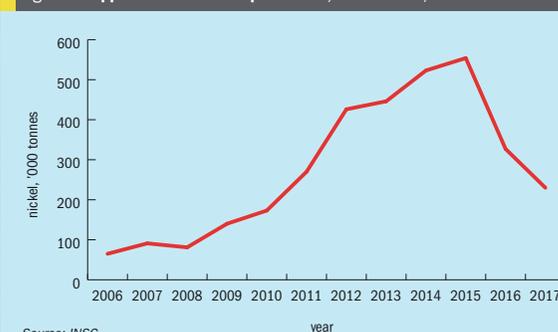
ket, heavy monsoon rains that made operating difficult, and a run down of production at some mines as deposits were exhausted, but mainly due to an environmental crackdown on mining in 2017. This came at an inopportune time for the country – as a result of the Indonesian export ban, since January 2014 the Philippines had become virtually the sole supplier of nickel ore to Chinese NPI producers. The country exported 27.1 million tonnes of nickel ore in 2016. However, in February 2017 Regina Lopez, then Philippines Minister of Environment and Natural Resources, announced the results of a comprehensive review of the Philippines' mining industry, leading to two nickel mines being suspended and 17 closed. A second review of the country's mines, covering all 41 mines operating in the country, including the 26 previously ordered closed or suspended, was announced in May 2017. Lopez was ousted from her position in May before the second round of inspections could be instigated and replaced by Roy Cimatu. Mr Cimatu has taken a much more conciliatory approach, and many of the targeted mines were able to continue operating while legal challenges were held. However, he too supports president Duterte's plan to ban open pit mining.

Nickel Asia is the largest nickel producer in the Philippines. Its mines include Rio Tuba, Taganito, Hinatuan and Cagdianao. Other nickel miners in the country include Benguet, Platinum Group Metals, Berong Nickel and Eramen Nickel, which is owned by Eramen Minerals. All of those companies have faced government-ordered mine

PHOTO: CORNELL UNIVERSITY

The Grasberg copper mine, West Papua, Indonesia, the world's second largest.

Fig. 1: Philippines mined nickel production, '000 tonnes, 2006-2017



CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

COVER FEATURE 3

Emissions reduction in sulphuric acid plants

COVER FEATURE 4

Seven deadly sins of tail gas treating

SULPHUR
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Indonesia's Southeast Sulawesi province is currently operating five of a planned 15 furnaces, and is targeting output of 600,000 t/a of NPI in its first phase. But elsewhere, even relatively cheaper heap leach projects have been put back, and Australia's Ravensthorpe HPAL plant has been forced to close. Indeed, nickel is forecast to face a continuing shortfall in production as the stockpile built up during the previous years is gradually eaten up, and by 2022-25 could face a deficit of 50-100,000 t/a of production and higher prices.

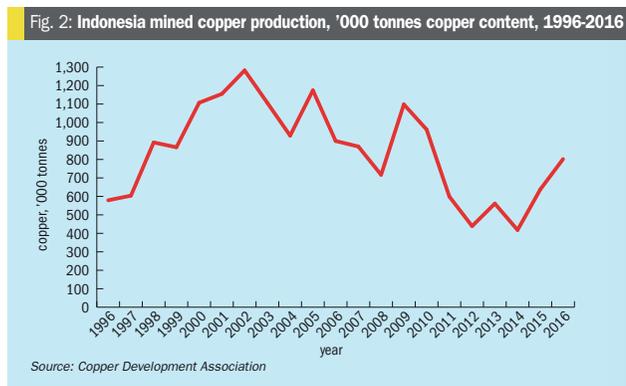
Electric vehicles

But a new wrinkle is emerging in the nickel market – the growing use of nickel in rechargeable batteries for electric vehicles – now around 3% of demand. This requires high grade nickel sulphate, and neither Indonesia nor the Philippines has the ability to produce it in the purity required by the battery market. China is looking towards this in a major way and has started altering tariffs accordingly, doubling the import tax on nickel cathode for smelting purposes but more than halving the import tax on nickel sulphate from 5.5% to 2%. Over 60% of imported nickel sulphate in China is now used in the production of batteries. Just as Chinese stainless steel pushed the nickel market towards NPI, so the demand for high grade nickel sulphate for batteries may create a two-tier market with premium prices being paid for plating/battery chemicals, and may force a new look at acid-based processing.

Copper

While Indonesia produces 25% of the world's nickel, its share of global copper production is much smaller, at about 3.5%. However, until about 10 years ago it was a bigger producer than China, and it is still the second largest copper producer in Asia. As Figure 2 shows, though, this production has been extremely variable over the past two decades.

The major copper producer in the region is PT Freeport Indonesia, the local subsidiary of Arizona-based Freeport-McMoRan, which owns 67% of the world's second largest copper mine (also the world's largest gold mine) at Grasberg in Indonesia's Papua province on New Guinea. Grasberg produced 450,000 tonnes of copper in 2017, and generated 22% of Freeport's revenues in 2016, although the main pit is almost exhausted and new mining is com-



ing from underground levels in which Rio Tinto is also involved – Rio Tinto has a partial stake (13%) in Grasberg, and an agreement to offtake 40% of production above a certain level, and 40% of all production after 2021.

As part of its attempt to force the development of downstream processing, Indonesia has been trying to get Freeport to develop a second copper smelter in the country. At present the only smelter is Gresik, 25% owned by Freeport, which can process 1.1 million t/a of concentrate to make 300,000 t/a of copper. Indonesia's refined copper requirement is 390,000 t/a, and the country would like a new \$2 billion 300,000 t/a smelter. While negotiations continued, Freeport and Rio Tinto were exempted from the 2014 ban on export of copper concentrate, but in 2017 exports of concentrate were halted, leading to an estimated \$1 billion in lost revenue for Freeport.

Freeport and Rio Tinto are now both in discussions to sell their stakes in Grasberg to the newly consolidated Asahan Aluminium (Inalum). Freeport has agreed in principle that up to a 51% stake in PT Freeport Indonesia (PT-FI), would be sold to "Indonesian interests," based on a new mine licence replacing existing contracts which will allow Freeport to continue operating the mine until 2041. The price has yet to be determined however – Freeport valued the 41% stake under discussion (Indonesia already owns just over 9% of PT-FI) at \$1 billion last year. The government turned the screw again in February 2018 by delaying re-issuing Freeport's copper export license, which has to be renewed on an annual basis since the 2017 law change which

said only companies keeping to smelter development timescales can still export. However, in April it agreed that Freeport can export 1.1 million tonnes of copper concentrate to February 2019. Any deal will be considered a boost for President Widodo, who faces re-election in 2019 and who has insisted that mining companies must divest majority stakes in order to continue operating in the country. The divestment is expected to be complete by May 2018.

New smelters

As for the new smelter, PT-FI has said submitted a proposal to develop a second \$2.2 billion facility at the Java Integrated Industrial and Port Estate in Gresik, with an annual input capacity of 2 million tonnes of copper concentrate, but the company says that it is still open to building a new smelter in Sumbawa, West Nusa Tenggara, and is engaged in a joint feasibility study with PT Amman Mineral Nusa Tenggara. State gold and copper mine Amman has also started developing its own copper smelter with an input capacity of 660,000 t/a in Sumbawa, although development progress remains limited so far.

If all three smelters went ahead, an admittedly unlikely occurrence, this could see Indonesia's refined copper output rise by 1 million t/a over the next few years, and with law requiring a maximum of 280 ppm of SO₂ emissions, sulphuric acid output could rise by 3 million t/a, far outstripping current imports of around 400,000 t/a. Even the single new Gresik smelter would turn Indonesia into a net acid exporter. PT-FI has pledged to complete this development by 2022. ■

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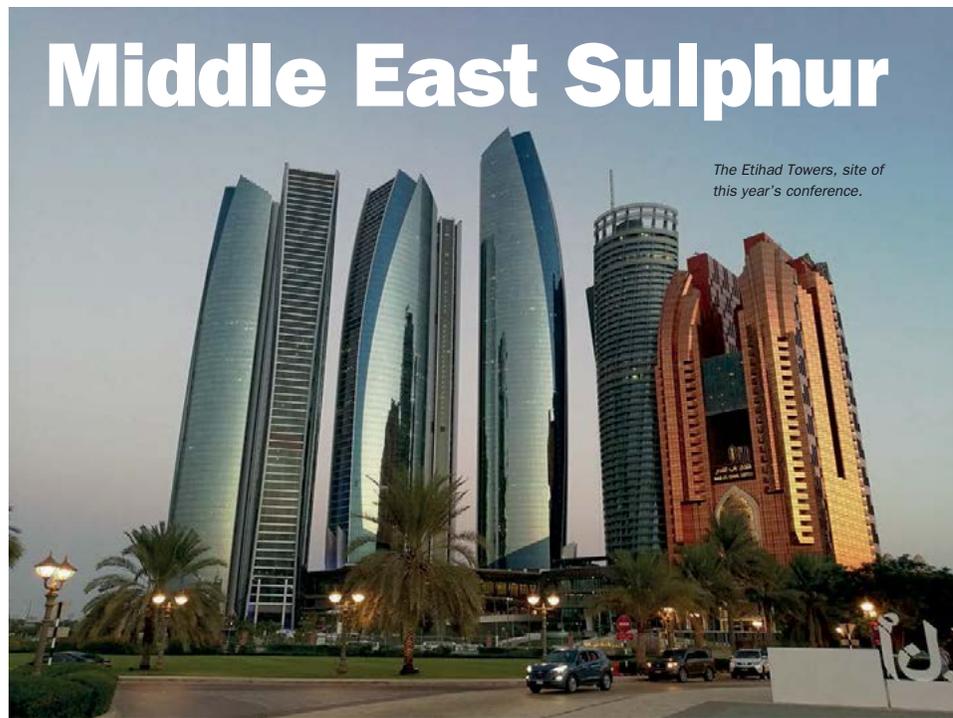
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The Etihad Towers, site of this year's conference.

Middle East Sulphur

CRU ran its second Middle East Sulphur Conference in Abu Dhabi in March 2018, in partnership with UniverSUL Consulting.

As we discussed in our article in the previous issue (*Sulphur* 375, Mar/Apr 2018), the Middle East, and Abu Dhabi in particular, is becoming the new centre of the sulphur world, and that is reflected in an increasing number of conferences as well as project activity. In March it was the turn of CRU to return for their second Middle East Sulphur conference, run in partnership with Angie Slavens' UniverSUL Consulting. In her opening address, Angie noted that ADNOC's sulphur capacity now exceeds 8 million t/a, and represents 14% of the world's sulphur production, a step-change from the 1-2% it represented in the 1980s.

Much of that new capacity has come on-stream in the past five years, and there is still more to come.

The sulphur market

CRU's Peter Harrison discussed the sulphur market, beginning with the price rally at the end of 2017. He pointed to a lack of Chinese buying in the first half of the year, which meant that they had had to catch up during 3Q and 4Q 2017. This coincided with supply issues in Canada leading to a decline in exports in Q2 and Q3 and led to the price spike, but these have now been resolved and together with additional volumes from new projects like Kashagan and Tengiz the sulphur prices is likely to be back down to \$100/t for 2018. China's buying for 2017 was actually overall down compared to 2016, and the same is likely to be true of 2018, and likewise Canadian exports were also up in 2017 overall, but demand elsewhere was stronger, in Morocco, Brazil and Indonesia, and over-

all demand grew faster than supply during 2017. The same trend is likely to continue through 2018, Peter said. Sulphur demand out to 2022 is forecast to rise to 71.5 million t/a, mainly for phosphoric acid, and mainly in Morocco, China, Saudi Arabia, India and Russia, with some increases in industrial uses and metal processing as well in spite of the closure of the Ravensthorpe nickel plant in Australia. In China there will be increased substitution of pyrite based acid production for sulphur burning as the government pushes for a clean-up of process industries, while Russia is benefiting from the low rouble leading to increased cost competitiveness and more domestic fertilizer demand. On the production side, the peak of supply additions is now past, and most sulphur supply growth over the 2019-22 period will be from the Middle East, with Barzan now scheduled for 2020-21 and the Shah expansion in Abu Dhabi possible in 2021-22.

Regionally, sulphur production from sour gas in North America continues to be in

decline, with some slight growth from refining and especially from Canadian oil sands bitumen processing which will lead to a slight increase in sulphur supply overall. In the CIS, there is also a decline in Russian gas-based sulphur, while a redesign of the Norilsk project will reduce anticipated sulphur output there from its original 800,000 t/a to around 200,000 t/a, and the start-up date has been pushed back to 2023. Kashagan is now exporting from Kazakhstan, at a rate of 50-75,000 tonnes per month, but Turkmenistan's sour gas plant is running below capacity due to sales gas issues. Exports are expected to increase from 2020 and a rail link is planned to Iran, but there is generally difficulty in getting sulphur out of the region and high costs of transportation, as well as quality issues. In Uzbekistan, Kady'm is due to start in 2018, adding another 200,000 t/a of sulphur, but this will be stockpiled and there are no exports anticipated.

In the Middle East, the Shuaiba refinery in Kuwait closed in 2017 but the Clean Fuels Project is due later this year and the Al Zour refinery in 2021. Saudi Arabia has the Wasit and Al Fadhili sour gas projects in 2018-19 and 2021 respectively and the Jazan refinery in 2019. As mentioned, the Barzan project in Qatar is also due in the 2020 timeframe. Additional volumes from South Pars in Iran and Shah in Abu Dhabi will also add to sulphur supply. Finally, in China, Puguang operating rates are back up, and there will be new production at Yuanba and Chuangdongbei, with phase 2 set for 2021. Refinery start-ups at Yunan and Huichou have added another half a million tonnes of sulphur and one or two more are due by 2022.

Overall, the global sulphur balance remains positive for 2018 and 19, with low prices continuing, but by 2020 the notional 1 million t/a surplus could sink to just 100,000 tonnes, and once stock builds in central Asia and Canada are accounted for this is likely to be a net deficit of up to 400,000 t/a, and the market should be further in deficit during 2021-22.

Changing pricing structures

Brendan Daley of CRU examined the way that pricing has changed in the sulphur market. In the 1970s and 80s and into the mid-1990s, he said, half-yearly contract prices gave way to quarterly pricing, but during the 2000s there was an increased move towards spot pricing, and since the price shock of 2008, when many people

found themselves locked into unrealistic contract prices, either too high or too low, spot prices have come to predominate. This had led to the market becoming much more volatile. The difference between contract and spot pricing is essentially one of predictability vs flexibility, and the rise of monthly price indicators has become something of a halfway house between the two. ADNOC has offered its monthly OSP since 1985, but Qatar and Saudi Aramco joined the move to monthly pricing in 2013. In 2000, Brendan said, contract prices represented around 75% of sulphur trades. By 2010, this had fallen to 60%, and in 2017 it was 50%, but this overall figure disguises regional variations. The US and Brazil have two main buyers, and this tends to be on contract. Likewise Morocco, where there is a single buyer, takes 75-80% of its sulphur on contract, mainly quarterly priced. However, India and China are dominated by spot pricing for solid sulphur (although liquid sulphur in East Asia remains 75% on contract). The continuing ascendancy of the Middle East as a source of sulphur supply is likely to lead to a continuing move towards monthly and spot pricing, he said.

Phosphates

Alexander Derricot of CRU looked at phosphate markets, and especially the price divergence between phosphate rock and phosphate fertilizer prices that has happened since 2016, which remains obvious even when you factor out ammonia and other price factors. Phosphate rock has become one of the worst performing commodities due to oversupply in the market, especially of low grade rock from Egypt and Algeria. However, on the finished

phosphates side, market discipline among the main DAP producers in China meant that production was cut when prices fell below \$300/t, leading to a price rally. The rock market continues to be oversupplied, and new capacity and falling energy prices have led to a lower cost structure. But low prices have also triggered improved non-integrated demand, as has higher fertilizer prices, leading to the potential for a belated recovery in phosphate rock prices.

In DAP markets, OCP has decided to leave its second wave of Jorf Lasfar hubs to 2022. Mosaic has idled Plant City for a year, but Ma'aden is commissioning its new phosphate complex on schedule. India will be the key market for 2018 on the demand side, as DAP producers try to take advantage of the cost disparity between cheap imported rock and high international fertilizer prices. Elsewhere, sales of NPK and NPS have also exceeded expectations, and African demand growth has been exceptional. Chinese environmental policy enforcement has been a fundamental shift in that market, and costs are becoming more important, as China is the marginal DAP producer. Two thirds of Chinese capacity is run by the 'big four', and have lower site costs, so the marginal producers are the smaller operators. Most 'at risk' capacity is in China – up to 3 million t/a of DAP capacity, with another 1.5 million t/a of definite closures, but Ma'aden and OCI are continuing to add capacity, and the DAP market is likely to remain oversupplied for 2018-19, albeit with a tighter market ahead due to Chinese closures and raw material price increases, leading to rising prices over the next five years.

The phosphates paper was followed by a presentation on the new TCO sulphur import consortium in China by David



Transporting sulphur in Abu Dhabi.

PHOTO: ETIHAD RAIL

CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

COVER FEATURE 3

Emissions reduction in sulphuric acid plants

COVER FEATURE 4

Seven deadly sins of tail gas treating

SULPHUR
ISSUE 376
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Wang, TCO's director – this will form part of a longer look at this subject in the next issue of Sulphur (July-August 2018).

Innovation and research

Monday afternoon's session covered new developments in sulphur research and innovation. It began with a paper on innovations in sulphur enhanced fertilizers by Dr Cyrille Alais of Shell Sulphur Solutions. There continues to be a deficiency in soil sulphur around the globe, which can limit plant yields in key areas, and which needs to be tackled if we are to continue feeding the planet's growing population. Dr Alais charted the development of Shell's Thiogro range of micronised sulphur enhanced fertilizers, allowing for faster conversion to plant-usable sulphates, which field trials in the US have shown increases yields by an average of 12% and up to 48%. New developments in Thiogro have been Urea-ES, designed for fluid bed and Rotoform forming machines, and now Special-S, a high sulphur product with up to 75% sulphur. This launched in 2017 and the first licensing agreement, with H-Sulphur, was signed earlier in 2018.

Alberta Sulphur Research's general manager Paul Davis gave an overview of the organisation and its capabilities, and mentioned some of the current research strands at ASRL, including H₂S scavengers, H₂S in shale gas, and partial upgrading of bitumen using coal liquefaction technology and hydrogen.

Dr Saeed Alhassan of the Petroleum Institute Abu Dhabi discussed his team's work on mixing sulphur in polymers. In low density polyethylene (LDPE), mixes of up to 20% sulphur by weight had similar mechanical properties and a higher tensile modulus, but sulphur obviously costs less than polyethylene and hence could potentially be a cheap extender. In HDPE, conversely, sulphur appears to act as a plasticiser, improving elongation up to 50%. In polypropylene, sulphur incorporation decreases PP crystallinity and again shows better elongation. However he admitted that fire behaviour was an issue as obviously SO₂ would be generated.

Finally, two papers looked at sulphur in solar power. Project Pegasus, described by its research coordinator Dennis Thorney of the German Institute of Solar Research (DLR), uses solar energy to irradiate solar 'particles' whose heat is then used to decompose sulphuric acid, yielding sulphur which can be stored and burned when needed to regenerate acid as well as gen-

erate power. Jan-George Wagenfield of the UAE's Masdar research centre is part of a project with DLR, General Atomics and UnerSUL Consulting to develop a solar sulphur cycle for power and fuel production in the Middle East using similar technology.

Technical papers

As well as a round table session on the Tuesday morning which was billed as 'MESPO revisited', and which featured contributions from Martin Taylor of Bechtel, Mohammed Asif of ADNOC's Shah plant, Frank Scheel of Jacobs, Ibrahim Khan of ADNOC Gas Processing and Philip le Grange of Sulphur Exports, Simon Weiland of Optimised Gas Treating looked at a cost study on acid gas enrichment (AGE) as an alternative to fuel gas co-firing to deal with lean acid gas, which is normally used in Abu Dhabi. Depending on the configuration used, AGE improves acid gas quality and SRU operation, but can increase capex and opex. Although elimination of a Claus stage alleviates the cost impact it may not be recommended depending on the tailgas unit operation, but utility prices can be crucial and will be the basis of a further study.

Lorraine Fitzwalter of Petrofac highlighted the importance of providing a sound engineering basis during the pre-FEED and FEED stages of a project as a way of evaluating and screening competing technologies and providing cost-effective alternatives and shorter project schedules without compromising on quality, safety or reliability of mega sour gas projects.

Matt Thundiyil of Transcend Solutions described a case study of large amine unit facing frequent change-outs of its rich amine solution which was solved by a different separation medium configuration which resulted in an 8-15-fold decrease in change-out frequency and a reduction in particulate contamination in the recirculating amine below detection limits.

Staying with the amine section, John Sczensy of MPR Services looked at the amine treater as a source of hydrocarbon carryover into sulphur plant, and its mitigation via a rich amine flash drum, regenerator reflux purging and adsorption onto activated carbon or MPR's HCX media.

Tail gas treatment

Several papers on Tuesday considered Claus plant tail gas treatment. Dr Lydia Singoredjo of Shell Global Solutions show-

ed Shell's SCOT tail gas treatment technology, particularly the SCOT Ultra process with a new highly selective catalyst. Yves Herssens of MECS highlighted the use of Dynawave scrubbers between the incinerator and stack to reduce SO₂ emissions from sulphur recovery units on a small pilot size and relatively low investment cost, while Jan Lambrichts of Dow Chemical presented the results of an evaluation study with the China National Offshore Oil Company (CNOOC) in Huizhou on a new series of Dow solvents for tail gas treatment. UCARSOL TGT1 was shown to be capable of operating at 10-20% lower flow rate than MDEA without any additional H₂S slip.

Rich Huang of Keyon Process presented a case study of revamping of a 50 t/d Claus plant which had previously used a SCOT process with Keyon's S-Plus technology, and Mark van Hoeke of EuroSupport described the benefits of using titania instead of alumina in Claus and tail gas catalysts.

Sulphur handling

The final session on Tuesday looked at sulphur handling. Don Champion of Pentair Thermal Management and Joe Donoghue of Rilco Manufacturing looked at the issue of sulphur pipeline supports, which can be a heat sink for the pipeline and can in extreme cases cause plugging of pipelines. A new thermally insulated design of anchor support designed by Rilco for 6" to 12" sulphur pipelines is an advance in this area which can help minimise disruption.

Mike Smeltink of Jacobs Comprimo Sulphur Solutions showcased a variety of modular liquid sulphur degassing systems to help deal with H₂S emissions from liquid sulphur, above or below ground and in new builds or replacements in existing pits.

Finally, the conference finished with a presentation by Ulrich Nanz of Sandvik Process Systems on the work his company conducted for the huge Dangote refinery at Lekki in Nigeria, which will process 650,000 bbl/d when it comes on-stream at the end of 2018. A Sandvik ProCool system is used to cool liquid sulphur to 125°C to produce the optimum viscosity for pastille forming. Sandvik has installed two 15 t/d Rotoform HS units as well as conveyors and two storage silos each with a capacity of 280 tonnes. It is also supplying an automatic bagging system for 50kg bags with pre-weighers, metal detection and automatic closing.

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CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

COVER FEATURE 3

Emissions reduction in sulphuric acid plants

COVER FEATURE 4

Seven deadly sins of tail gas treating

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Emissions reductions for adjacent acid plants

NORAM is offering a new solution to greatly reduce emissions from sulphuric acid plants during start-up and transient operating conditions. Through the installation of ducting between parallel or tandem plants, emissions can be transferred from a plant undergoing unsteady state operation to a neighbouring plant operating at steady-state, without adversely affecting production of the steady-state plant. In this article, NORAM describes the new emissions reduction process and compares it to current emissions reduction procedures.

Chemical plants around the world are facing more stringent environmental regulations by governing bodies to reduce emissions. Emissions of species such as SO₂, SO₃, H₂SO₄, NO_x, HC, CO, and other pollutants are under close scrutiny. While plants today face continuous "normal" operation regulations, it is becoming more common to see regulations being set for plants in transient and upset states. This specifically includes start-up scenarios, where SO₂ emissions can exceed normal conditions emissions by several orders of magnitude. Plant owners and regulatory authorities are becoming more conscious of these scenarios, and are looking at more comprehensive solutions that can address the emissions throughout the complete operation cycle of chemical plants.

Today, control of emissions of species such as SO₂, SO₃ and H₂SO₄ is generally done through catalyst upgrades, equipment upgrades, and improvements in operation procedures. These strategies can provide cost-effective ways to reduce plant emissions; however, they will not be a bulletproof solution to handling transient conditions, as poor conversion of SO₂ will inevitably cause emission spikes. Installations of tail-gas scrubbing technologies have also proven to abate the release of harmful emissions and are a valid solution to meeting emission regulations during transient conditions and start-up. However, installing and operating tail-gas scrubbing technologies have high capital and operating costs. Adding SO₂ scrubbing units can increase the pressure drop of the plant,



Start-up plume from a sulphuric acid plant.

create unwanted waste by-products, and incur more operating costs through the need to purchase and handle chemicals.

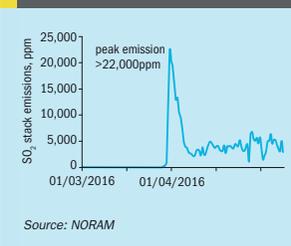
Fig. 1 shows the start-up plume of a sulphuric acid plant. This plume is difficult to avoid, especially when the plant is executing a cold start-up. The tail gas plume often contains SO₂ gas in the range of 1,000 to 10,000 ppm and in some cases can exceed 20,000 ppm. Moreover, the tail gas plume may contain acid mist (formed from SO₃ carryover or H₂SO₄ emissions) that gives an opaque appearance to the gas, or persistent white/bluish smoke as in the photo, which travels with the wind,

and that can be seen for very long distances.

In some situations, depending on the conditions of the surrounding air, an inversion can occur, and the plume can fall onto the ground and affect people. There are some known cases of acid plant plumes causing health and environmental emergencies during plant upsets and plant start-ups.

Fig. 2 contains plant data for a large acid plant during start-up. This figure clearly shows the severity of the emission event that can occur during a plant upset or start-up.

Fig. 2: Plant data from the start-up of a metallurgical acid plant



Types of stack emissions and mitigation technologies

Stack emissions can vary widely depending on the operating mode of the plant.

Steady state emissions

SO₂ gas emissions: Well-designed sulphuric acid plants can achieve emissions of less than 500 ppmv of SO₂ at the stack, with many double absorption plants achieving 200 ppmv SO₂ in the stack. Depending on local environment requirements, it is possible to design for stack SO₂ concentrations as low as 10 ppm using further treatment such as tail gas scrubbing¹. The following should be reviewed in order to minimise the SO₂ emissions of an acid plant²⁻⁶.

- loading of the catalytic converter (catalyst volume);
- design and mechanical conditions of catalytic converter;
- operating conditions of the converter including SO₂ strength and gas inlet temperatures;
- catalyst activity and the catalyst type;
- plant production rate;
- interpass absorption tower efficiency;
- gas exchanger leaks;
- design of the acid cross-flow to prevent SO₂ stripping (Segregated final pump tank);
- use of a tail gas scrubber.

SO₃ gas emissions: The emissions of SO₃ are affected by the final absorption tower load and efficiency. The following should be reviewed to reduce the emissions of SO₃:

- design and mechanical conditions of the final absorption tower, acid distributor and packing;
- operating conditions of the final absorption tower.

H₂SO₄ vapour emissions: The emissions of H₂SO₄ vapour are affected by the final absorption tower operating conditions. The following should be reviewed:

- design of the final absorption tower;
- operating conditions of the final absorption tower.

H₂SO₄ emissions as liquid acid mist droplets: The emissions of acid mist and sprays are determined by:

- design and sizing of the mist eliminators;
- mechanical conditions of the mist eliminators;
- condition of acid seal-cups or loots;
- design of the final absorption tower;
- operating conditions of the final absorption tower.

Other emissions: The emissions of NO_x and other emissions are outside the scope of this article.

Start-up emissions

A number of methods with different levels of maturity exist to meet existing environmental regulations regarding emissions of SO₂, SO₃, H₂SO₄, NO_x, HC, CO and other pollutants. In a sense, most modern sulphuric acid plants utilise some kind of method to reduce start-up emissions. For example, if acid plants start-up at full SO₂ strength with only one catalyst bed in active mode, the SO₂ concentration in the stack could reach 4% SO₂ (40,000+ ppm), which is unacceptable by current standards. For this reason, modern plants follow a strict preheating procedure to minimise the peak SO₂ concentration.

Some methods require small changes to the plant operation and equipment. These can be useful to improve the emission levels of a plant, but alone they tend to offer only incremental reductions in emissions. These methods include¹⁻⁶:

Modifications of procedures for plant operation, start-up and shutdown: Plant start-up procedures can be modified to reduce the total emissions from the plant gas stack. Example modifications include optimisation of preheating sequences, modification of process set-points, operation with lower gas strengths, simultaneous preheating of several catalyst beds and key unit operations, preheating of absorption circuits, and plant gas purging strategies.

Catalyst Improvements: High sulphur dioxide emissions may be a result of inactive catalyst beds, caused by the catalyst operating outside of its optimum operating

temperature. Today, the conventional catalyst formula is vanadium-based, promoted by alkali metals (normally potassium). The minimum ignition temperature for these catalyst formulas is generally around 360°C. Caesium-promoted catalysts are significantly more active than the conventional catalysts, with ignition temperatures around 320°C. Caesium-promoted catalysts are often added to the top of catalyst beds or to the final pass to help reduce emissions during transient conditions or during start-ups. The addition of catalyst with a lower ignition temperature helps to maintain autoignition and reduce the start-up time of the acid plant. Lower ignition temperatures allow for reduced start-up times and therefore offer a potential reduction in the total SO₂ emissions released during a start-up event.

Equipment modifications: Plant equipment can be upgraded to achieve lower emissions. For example, improved preheaters can be used to more quickly achieve ideal process temperatures, and equipment can be upgraded to reduce process inefficiencies such as bypassing. This requires modification of equipment, and offer limited improvement in terms of start-up emissions.

Preheating/purging strategies: It is known that proper gas purging strategies during shut-down can reduce emissions during start-up. The catalyst can store up to 10% of its mass through the absorption of SO₂, SO₃, and O₂ upon solidification of the catalyst salt melt⁷. In order to remove the free sulphur content in the catalyst melt, hot gasses should be blown through the catalytic converter before a planned shut-down. However, keeping the catalyst bed hot during the purging process remains a challenge for operators. Depending on the plant arrangement, the catalyst should be kept above 400°C by utilising by-passes around boilers, superheaters, and gas exchangers. Plants that are equipped with a preheating system should use it to keep the catalyst temperatures high. Improved catalyst management can reduce the start-up time and the peak SO₂⁸. Sulphur burning plants that are not equipped with a preheating system should reduce the dry air flow rate through the sulphur furnace and converter. This effectively helps to maintain the catalyst bed at temperatures above 400°C for longer without adversely affecting catalyst stripping efficiency. Acid preheating can also be used to reduce the emissions of H₂SO₄ from acid towers⁹.

What's in issue 376

COVER FEATURE 1

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COVER FEATURE 2

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The effectiveness of these strategies varies from plant to plant, and more often than not, they are not a surefire method to reduce start-up emissions.

Use of different feedstock: Processes involving combustion of fuels may choose to use low-sulphur content fuels. Such fuels are typically more expensive than high-sulphur content fuels.

Other methods implement tail gas cleaning technologies. However, all these technologies require high capital investment. Examples of such technologies include:

Chemical scrubbing technologies: These technologies remove sulphur species by contacting process gas with a chemical in a scrubber. Such chemicals include liquid caustic solutions or milk of lime to remove sulphur species. These technologies typically produce a liquid or solid waste stream.

Dry and wet scrubbers are well-known examples of chemical scrubbing. Depending on applications, dry and wet scrubbers may operate over a broad temperature range. If the discussed catalyst innovations or purging/preheating strategies do not alleviate the issue of start-up emissions, tail gas scrubbing equipment can be a viable option. SO₂ scrubbers can be installed for normal operation or specifically for start-up scenarios. Tail gas scrubbers that are designed for start-up scenarios often handle gas flow rates that are significantly lower than normal operation. However, the caveats of operating a scrubbing unit primarily include increased pressure drop and costs associated with scrubbing chemicals. Reagents for SO₂ removal can vary depending on the needs of the plant and the type of process.

Absorption/desorption technologies: These technologies remove sulphur species using absorption/desorption columns. These technologies typically use chemical absorbents (e.g. amines), physical absorbents, or adsorbents. SO₂ is separated from the tail gas. These technologies require large capital investments in tall absorption/desorption columns and consume significant amounts of energy to regenerate the absorber.

Mist removal technologies: These technologies remove acid mist using electrostatic precipitation (WESPs), fibre-bed filters (Brownian diffusion candle demisters), or high-intensity direct contact scrubbers (NORAM's Turboscrubber®). Mist removal technologies are only effective in removing acid mist and do not significantly

remove other pollutants such as SO₂, except for the Turboscrubber technology, which can remove acid mist and SO₂ in the same unit¹⁰.

NORAM'S new emissions reduction process for side-by-side plants

NORAM has developed a gas treatment process for reducing tail gas emissions such as SO₂, SO₃, H₂SO₄, NO_x, HC, CO, and other pollutants. The process includes transferring tail gas from at least one source of tail gas (such as an acid plant in start-up mode) to at least one destination sulphuric acid plant (such as acid plants operating in steady-state mode) via a tail gas transfer system, wherein the tail gas replaces or supplements the gas used by the destination sulphuric acid plant. The process described herein may be used to eliminate start-up emissions and convert sulphur-containing species present in tail gas emissions into commercial H₂SO₄. NORAM's process is patent pending worldwide.

Multiple or tandem plants are commonly seen in the sulphuric acid industry. NORAM's new process greatly reduces the start-up or transient conditions emissions by transfer of tail gases of one (source/donor) plant to a neighbouring (destination/receiver) plant. Plants with the ability to control oxygen enrichment and the feed SO₂ strength are well-adapted to treat the off-gas from the source plant. With proper design and operation, the production and emissions of the receiver plant would not be adversely affected.

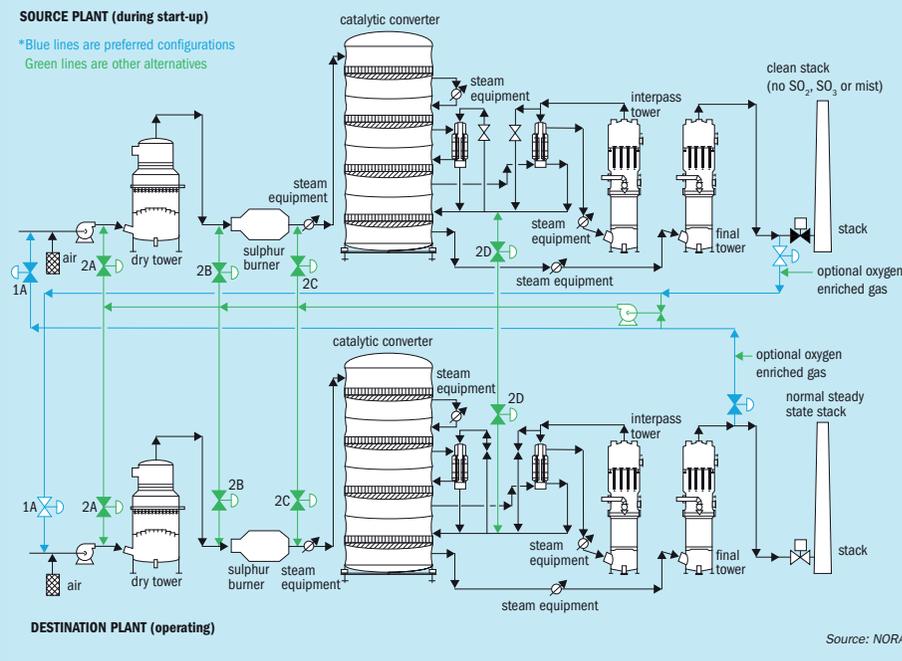
NORAM's process offers to retrofit parallel-plants, which are capable of transferring their off-gas to one another, resulting in the reduction of the emissions associated with transient conditions. Furthermore, the ability to transfer off-gas will result in quicker start-ups and higher overall acid production. Sulphur firing can commence once the first converter bed is above the ignition temperature and the off-gases associated with inefficient conversion can be directed to the receiver plant. The discussion in this article will be limited to two scenarios: parallel sulphur burning plants and metallurgical off-gas treatment plants. Both scenarios have distinct challenges that must be overcome in order to successfully implement tail gas transfer and will be discussed in this article. Other scenarios may be considered for sites with more than two plants, for acid regeneration plants, for wet plants and for acid gas plants.

Sulphur burning plants

An example of parallel sulphur burning plants can be seen in Fig. 3. The configuration of the two plants shows that either is capable of transferring its off-gas to its counterpart in the event of transient conditions or process upsets. The transfer point to the receiver plant can happen in several different locations, depending on the needs of the plant and the plant configurations. Blue lines in Fig. 3 indicate the use of a booster fan is not necessary, as the feed point is upstream of the receiver plant's main blower, and therefore, under negative pressure. Conversely, the green lines indicate that the tail gas will require an increase in pressure to be transferred to the receiver plant, wherein the tail gas replaces or supplements the gas used by the destination sulphur burning requires monitoring the temperature of the sulphur burner. The volumetric gas flow to converter bed 1 must be controlled to minimise the upset on the destination plant. Furthermore, the residual oxygen concentration must be controlled to above 5% (preferably) in order to ensure the reaction kinetics are favourable. The blue lines are preferred configurations.

Table 1 shows the possible configurations and their respective feed point locations in the receiver plant. Configuration 1A is a favourable feed point location as it does not require the installation of a booster fan, lowering the cost of the retrofit. The selection of the feed point depends on plant layout, specific plant configuration and equipment constraints. Furthermore, this may be a viable solution if the off-gas may contain a considerable amount of moisture or SO₃. However, in most circumstances, the off-gas from the donor plant will be dry. The same can be said to configuration 2A, however, this option requires the use of a booster fan. Configurations 2B and 2C bypass the receiver plant's main blower, and therefore, reduce the load placed on it. Moreover, configurations 2B and 2C allow for the independent control of the sulphur furnace temperature, which is beneficial in certain situations. If the sulphur furnace temperature is reduced, more gas can be diverted to bypass the furnace itself. Feed point 2D could be used in some cases to minimise the impact on the destination acid plant in terms of hydraulics and catalyst performance. However, in most situations, Feed point 2D can only be used for a small fraction of the tail gas flow since the gas needs to be heated up to catalytic

Fig. 3: Example of tail gas transfer configurations for parallel sulphur burning sulphuric acid plants*



conditions, and it is preferred not to cool the gas going to bed #4 below its normal operating point. Moreover, feed point 2D, may be considered when the source plant is much larger than the destination plant.

Metallurgical and acid regeneration plants

An example of parallel metallurgical off-gas treatment plants is shown in Fig. 4. Similar to the sulphur burning plants, there are several transfer points that can be chosen, and each option is dependent upon the nature of the gas and configuration of the plant. For all scenarios, the feasibility of the process relies on controlling the volumetric flow, SO₂ strength to the first converter bed, and residual oxygen concentration (~5%) in the receiver plant. Residual O₂ concentrations above 5% indicate favourable reaction kinetics and will help to ensure emissions are held at or below normal operation in the receiver plant. The tail gas transfer process is comparable to diluting the process gas prior to its input to the first converter bed. If a proper control strategy is in place, the receiver plant can

manipulate the composition of the smelter feed gas to accommodate the off-gas. Table 2 shows the possible tail gas configurations and their respective feed point location in the receiver plant. For configurations 1A, 1B, and 1C, the process will not require a booster fan because all locations are upstream of the receiver plant main blower (feed point is under suction). If the tail gas of the donor plant is relatively free of moisture and SO₃, configuration 1A may be a feasible feed point.

This may be a favourable configuration because the handling of the off-gas in the receiver plant is the lowest in this

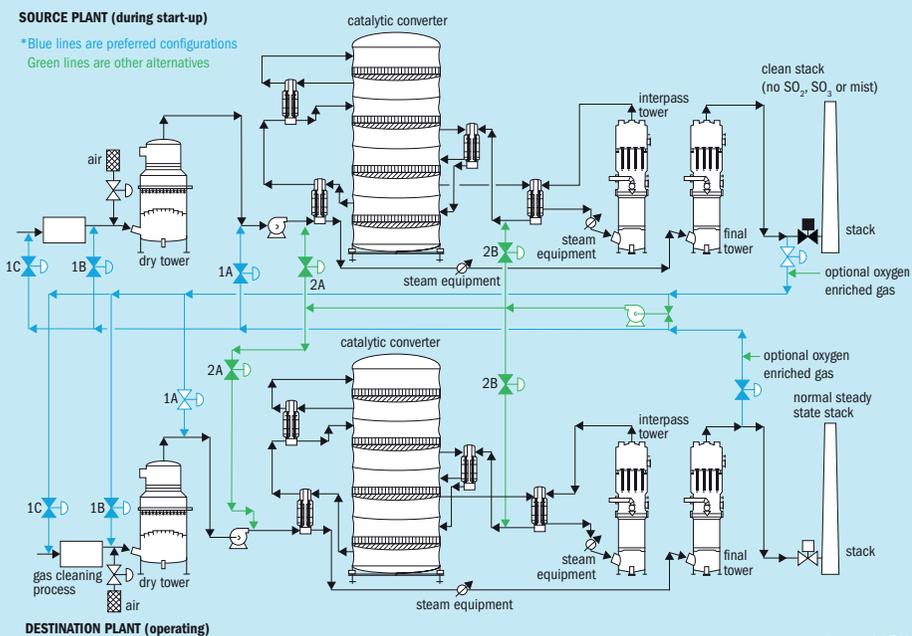
configuration. Configurations 1B and 1C may be required if the tail gas contains a considerable amount of moisture or acid mist. Configurations 2A and 2B require the use of a booster fan as the feed point is downstream of the receiver plant's main blower. Configuration 2A directs the off-gas from the donor plant through the entire catalytic converter, ensuring maximum conversion of the off-gas and limited emissions. Feed point 2B may be used under certain conditions, in combination with other feed points, or in cases where the temperature feed to bed 4 can be maintained above the required temperature.

Table 1: Sulphur burning plant – tail gas transfer feed points

Configuration	Feed point location in receiver plant
1A	upstream of main blower (preferred)
2A	downstream of main blower, upstream of dry tower
2B	downstream of dry tower, upstream of sulphur burner
2C	downstream of sulphur burner, upstream of bed 1
2D	upstream of bed 4

Source: NORAM

Fig. 4: Example of tail gas transfer configurations for parallel metallurgical off-gas treatment plants*



Source: NORAM

NORAM'S new emissions reduction process start-up procedure

NORAM's process has the advantage of reduced start-up time for the source acid plant. The process uses a control system that utilises advanced process control routines that take into account process variables to maximise the combined production rate (such as acid production), minimise the combined gas emissions (in terms of peak stack SO₂ concentration and total SO₂ emissions), minimise start-up time and minimise the total consumption of oxygen-enriched gas (if required, from an oxygen storage tank and/or an oxygen plant) for both the source of tail gas and the destination sulphuric acid plant. The following general start-up procedure is considered:

- Data recording:** Recording the process parameters for both plants for use in advanced process control of both plants.
- Steady state for destination plant:** Operating the destination sulphuric acid plant under steady-state conditions.

Table 2: Metallurgical plant – tail gas transfer feed points

Configuration	Feed point location in receiver plant
1A	upstream of main blower, downstream of dry tower (preferred)
1B	upstream of dry tower, downstream of gas cleaning (preferred)
1C	upstream of gas cleaning (preferred)
2A	upstream of catalytic converter, downstream of main blower
2B	upstream of catalyst bed 4

Source: NORAM

- Pre-start-up:** Performing the initial start-up steps of the source of tail gas as is conventionally done.
- Tail gas transfer:** Transferring tail gas from the source of tail gas to the destination sulphuric acid plant before its catalyst begins to release SO₂ and SO₃ gases while preheating the converter.
- Preheating acid:** Preheating the sulphuric acid inventory used by the absorption towers of the source of tail gas in start-up conditions to minimise acid mist carryover from the acid towers of the source of tail gas. The acid may be preheated

- by adding heat to the source of tail gas and/or by cross-flowing hot sulphuric acid from the acid system of the destination sulphuric acid plant to the acid system of the source of tail gas. Preheating acid is preferable, but not required.
- Preheating bed 1:** Preheating the source of tail gas until bed 1 reaches a desired feed temperature (typically around 380 to 450°C). Only one catalyst bed needs to reach the desired feed temperature to minimise start-up time.
- Start on sulphur or SO₂:** Introducing SO₂ gas to the converter of the source

of tail gas. This may be achieved by feeding feedstock gas rich in SO₂ and/or by adding sulphur-containing species to a sulphur furnace.

- Balance O₂ load if needed:** Adding oxygen-enriched gas to the tail gas of the source of tail gas as needed to balance the oxygen content of the destination sulphuric acid plant. This requires monitoring SO₂ and/or O₂ concentrations and/or monitoring the temperatures of the catalytic converter and/or the thermal stages of the destination sulphuric acid plant. Oxygen enrichment is required if the destination acid plant cannot allow for any SO₂ emissions increases, or capacity changes.
- Ramp-up:** Increasing the source of tail gas production rate by increasing the feedstock SO₂ concentration and/or throughput.
- Monitoring and control:** Monitoring and controlling process parameters to maximise the net production rate, minimise the net gas emissions, minimise start-up time, and minimise the total consumption of oxygen-enriched gas (if required).

The start-up of a plant with tail gas transfer can be comparable to the start-up sequence of a plant with an SO₂ scrubbing unit. The criteria to fire sulphur in the donor plant may be met once the minimum ignition temperature of the first catalyst bed is reached. Any SO₂ that is not oxidised in the donor plant catalytic converter will be directed to the receiver plant and controlled accordingly.

Sulphur burning plants

Sulphur burning plants will need to be preheated according to general practices; heating the sulphur furnace and performing dry blows until the dew point of the gas is reached will still be a requirement. Combustion gasses can directly heat the catalyst beds thereafter. Dampers should be adjusted to direct off-gas from the source plant to the receiver plant. The pre-heating process can proceed with off-gasses being transferred to the receiver plant. The donor plant's main blower should be operated at reduced rates (as low as practicable by the main blower, and typically 30 to 60%) to limit the effects on the receiver plant. Sulphur firing can commence at the donor plant's autothermal limit and the respective off-gas may be directed to the receiver plant accordingly. Similar to the metallurgical receiver plant, controls must be in place to match the receiver plant's gas handling

capacity and designed SO₂ gas strength. Sulphur burning plants may need to be equipped with oxygen enrichment to handle the off-gas from the destination plant, if it is required to maintain the same operating conditions of the destination plant during continuous operations. Sulphur concentrations can gradually be increased in the donor plant until normal catalyst temperatures are sustained. Blinds can be installed and dampers can be changed to direct off-gas back to the atmosphere, until steady-state operation is achieved in both plants.

Metallurgical and acid regeneration plants

Metallurgical and acid regeneration plants that are equipped with a separate preheating system which can heat the catalyst beds as done according to general practices. In addition, the emissions associated with firing hydrocarbons in the preheating furnace can be directed to the atmosphere as previously done. The catalyst beds are indirectly heated by combustion gases. The off-gas from this heating process will contain trace SO₂ and may be directed to the destination plant or to the atmosphere.

Dampers and blinds in the appropriate locations should be adjusted and installed to direct off-gasses to the receiver plant. This is done to make sure any trapped SO_x in the catalyst is released to the receiver plant once the catalyst salts begin to melt. The main blower for the donor plant should be running at approximately minimum rates (typically 30 to 60%). Once the criterion for SO₂ feeding in the source plant is met, the operator may choose to run low concentrations of SO₂ to the catalyst beds. Similar to normal practices, the preheater may need to be utilised to keep downstream beds hot and above the minimum ignition temperature. The feed gas from the smelter may be reduced if needed to accommodate the load from the source plant. Depending on the feed point location, the volumetric flow should be adjusted to match the designed polytropic head of the receiver plant's main blower and SO₂ gas strength. Metallurgical and acid regeneration plants that are equipped with oxygen enrichment have the capability to control the gas strength under the addition of the donor plant's off-gas. Depending on the SO₂ concentration of the feed gas as well as the off-gas, oxygen can be supplied to match the plant's designed gas strength. Doing so will keep all beds at their normal operating temperature and match the designed operation of the gas exchangers. Once the donor plant's cata-

lyst temperatures are close to normal operation, blinds and dampers can be changed to direct off-gas back to the atmosphere. Full SO₂ processing can commence and steady-state operation is returned.

Performance predictions

Two identical metallurgical acid plants with oxygen enrichment have been simulated. The general design parameters for each plant are as follows:

Type:	4 bed, DCDA
Capacity:	2,370 t/d
Volumetric flow:	177,000 Nm ³ /h
Conversion efficiency:	99.85%
Bed 1 inlet gas (dry basis):	
SO ₂	12.8%
SO ₃	trace
H ₂ O	trace
O ₂	11.9%
CO ₂	1.7%
N ₂ /Ar	73.7%
Normal stack emissions:	
SO ₂	~230 ppm
SO ₃ /H ₂ SO ₄	trace

Two start-up cases are considered for the neighbouring plants. The first case can be considered a "conservative" start-up of Plant 1, as the emissions are a primary concern. The second case is an "aggressive" start-up of Plant 1; the criterion to start SO₂ is met when the minimum ignition temperature of bed 1 is reached, neglecting the temperatures of downstream beds. For both cases, the transfer point of the off-gas into Plant 2 (receiver) is simulated to be downstream of the main blower and upstream of the cold exchanger (2A from Fig. 4). Furthermore, it is assumed that the donor plant has pre-heated the circulating acid and operates Brownian diffusion candles in the final absorption tower. Therefore, it is assumed that the tail-gas contains limited SO₃ slippage and trace H₂SO₄ emissions.

Case 1 (conservative/slow)

For case 1, all catalyst beds are considered to be pre-heated to their recommended start-up temperature (400-450°C). Upon the onset of processing SO₂ gas in Plant 1, the off-gas from the smelter is controlled at 7.3% SO₂ (dry basis) at 50% of the plant's designed capacity. The overall conversion of SO₂ in the donor plant is assumed to be at 87.6%. It is understood that this is a dynamic process that undergoes changes in feed concentration and catalyst performance.

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Table 3: Process summary for cases 1 and 2

	Case 1 "conservative/slow" start-up with 4 beds hot		Case 2 "aggressive/fast" start-up with only 1 bed hot	
	Plant 1 (donor)	Plant 2 (receiver)	Plant 1 (donor)	Plant 2 (receiver)
Conversion efficiency, %	87.6	99.85	62.9	99.85
Bed 1 conditions				
SO ₂ (dry basis), %	7.3	12.8	7.3	12.8
O ₂ (dry basis), %	6.8	12.0	6.8	12.0
Total volumetric flow, Nm ³ /h	77,831	177,587	77,831	177,587
Acid production, t/d/rate, %	542/22	2,384/100	376/16	2,384/100
SO ₂ concentration feed to plant 2, ppm	10,000 (1% SO ₂)	N/A	29,000 (2.9% SO ₂)	N/A
SO ₂ concentration to stack (each plant), ppm	0	~230	0	~230

Source: NORAM

Employing a control strategy that increases the SO₂ gas strength from the smelter to meet the designed bed 1 gas strength, the receiver plant can adequately handle the "diluted" off-gas from the donor plant. The feed conditions from the smelter are optimised to meet the designed SO₂ gas strength of the plant based on the addition of the off-gas. Furthermore, if the plant is equipped with oxygen enrichment, the O₂ content can be controlled to adjust for the off-gas and keep the residual oxygen concentration above 5%. The volumetric flow in the receiver plant is adjusted to roughly match the normal steady state operation of the main blower. It can be seen in Table 3 that if these control strategies are employed, the tail gas of the plant starting up can successfully be transferred to its neighbouring plant. The production of the receiver plant is not adversely affected, and the emissions of Plant 2 remain around 230 ppm. There are no emissions for the stack of Plant 1.

Case 2 (aggressive/fast)

For case 2, SO₂ processing commences when the first catalyst bed is above the minimum ignition temperature. Downstream beds may be at or below their minimum ignition temperature due to the pre-heating sequence and this is considered during the simulation. The overall conversion of SO₂ in the donor plant is assumed to be only 63% (with only one bed active). The same strategy is considered as in the first case; the off-gas from the smelter is controlled at 7.3% SO₂ (dry basis) at 50% of the plant's designed capacity. Despite the poor conversion of SO₂ in the donor plant, the receiver plant is capable of adjusting the inlet

SO₂ and O₂ concentration to meet the normal operation gas composition design. When compared against the conservative case, the measures to control the high SO₂ strength off-gas are to slightly decrease the concentration of SO₂ from the smelter. The volumetric flow from the donor plant is the same as Case 1, and therefore, the capacity remains at 50%. Overall, the "aggressive" case is feasible, and the overall emissions between the two plants remains around 230 ppm.

With intermittent and variable strengths of SO₂ from the smelter and from the tail gas, detailed analyses should be carried out to ensure the autothermal limit and water balance limit of the receiver acid plant are met under variable conditions. If the receiving acid plant does not have the ability to control the SO₂ strength of the smelter gas or the oxygen concentration, it may be required to utilise the pre-heating system to maintain adequate temperatures in the plant. Moreover, the use of low ignition temperature catalyst and the optimisation of catalyst temperatures would be required using advanced process control logic.

Technology comparison

NORAM's new process is compared with existing technologies in Table 4:

Process requirements

NORAM's process requires the following equipment: gas ducting (length defined by distance between plants), dampers, valves, instrumentation. In some cases it may require only one major duct and a set of gas dampers. Engineering is required for the control system. ■

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Table 4: Comparison of technologies (colour code: white = preferable)

	No mitigation of start-up emissions	Chemical scrubbing	Absorption-desorption scrubbing	NORAM's new emission reduction process
Plant requirements	None	Tail gas scrubbing plant (new)	Tail gas absorption-desorption plant (new)	Neighbouring plant (existing) – see footnote
Number of plants on site	1 or more	1 or more	1 or more	2 or more
Suitable for single plants	Yes	Yes	Yes	See footnote
Process water consumption	No	High (stack gas is wet)	High (stack gas is wet)	No
Steam consumption	No	No	High (for amine generation)	No
Chemicals consumption	No	Yes (NaOH, H ₂ O ₂ , NH ₃ , etc.)	Yes (amine)	No
Production of byproducts or waste	No	Yes (scrubbing byproducts)	Yes (amine salts)	No
Allows for fast start-up	N/A	Yes, depending on capacity of scrubber	Yes, depending on capacity of scrubber	Yes, depending on control strategy
Equipment familiarity for operators	Familiar	Not familiar	Not familiar	Familiar
Requires O ₂ enrichment	N/A	No	No	To maintain production capacity or emissions level of destination plant, O ₂ is required
Public perception	Poor, high emissions	Visible plume caused by water vapour	Visible plume caused by water vapour	Good, no visible plume, no start-up emissions
Energy consumption	N/A	Increased blower energy cost due to increased plant pressure drop. Electrical power to run pumps.	Increased blower energy cost due to increased plant pressure drop. Electrical power to run pumps. Steam use.	Minimal energy required to transfer gas from one plant to another.
Equipment required	N/A	Scrubber column, circulation pumps, product pumps, reagent pumps, reagent tanks, piping, reagent storage tank, product storage tank, instrumentation.	Pre-scrubber, absorber column, desorber/regenerator column, amine cooler, amine heat exchanger, reboiler, amine purification unit, instrumentation.	Gas ducting (length defined by distance between plants), dampers, valves, instrumentation.
Capital cost	N/A	High	High	Low
Operating cost	N/A	High	High	Low
Tail gas SO ₂ concentration during start-up	1,000 to 20,000 ppm	10 to 100 ppm	10 to 100 ppm	Negligible

Note: NORAM's process can also be utilised for a single acid plant with partial recycle of tail gas to the feed of the same plant, with other benefits during preheating and start-up. It would require oxygen enrichment

Source: NORAM

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Acknowledgement

This article is based on the paper "New emissions reduction process for side-by-side plants", by Andrés Mahecha-Botero*, Kim Nikolaisen, Brad Morrison, C. Guy Cooper, Brian Ferris and Nolan Okrusko of NORAM Engineering and Constructors Ltd, and was presented at the Sulphur 2017 Conference, 6-9 November, Atlanta, USA.

The seven deadly sins of tail gas treating units

Since the start-up of the first SCOT® unit in Alberta, Canada in 1973, sulphur hydrogenation with an amine system for acid gas recycle has become the predominant Claus tail gas treating technology where very high sulphur recovery and very low emissions are required. Despite the maturity of this technology, some facilities do not operate the SRU and TGTU with a proper understanding of the fundamentals of the process integration. In this article, **J. Brindle, G. Bohme** and **B. Spooner** of Sulphur Experts Group of Companies discuss the most common design, operation, and reliability problems encountered in these units that impact emissions compliance or reliability of the unit and guidance for achieving compliant and reliable operation.

Reliable and effective operation of hydrogenation-based tail gas treating units (TGTUs), of which the SCOT® unit is the archetype, has become a critical process for many plants to meet increasingly stringent emissions regulations worldwide.

While process knowledge of the Claus process sulphur recovery units (SRUs) and amine-based gas treating processes in the industry has increased, the TGTU is at the confluence of these technologies and reliable operation of the TGTU requires an understanding of both these technologies as well as the basics of a hydrogenation reactor.

The title of this paper was chosen to match two sister papers: *The Seven Deadly Sins of Sulphur Recovery* and *The Seven Sins of Amine Treating*. For the sake of consistency, the number of sins was fixed at seven, but, depending upon the degree of specificity, one could produce several more "sins" that, if not avoided, would cause grief.

It is, however, the opinion of the authors that these seven sins represent the most common problems encountered in TGTU operation. Each of these seven sins is analysed in detail, with examples of typical bad outcomes discovered through testing or field experience obtained by Sulphur Experts, along with mitigation or prevention of the sin.

Why do we use TGTU technology?

The modified-Claus process used by most SRUs yields sulphur recovery efficiencies of between 94 and 98%, and in many cases, this is insufficient to meet emissions regulations. Hydrogenation with H₂S absorption was the first technology that provided the possibility of sulphur recovery efficiency exceeding 99.9%. While other H₂S absorption technologies exist, amine-based technologies (such as the SCOT process) have dominated this market because of the improved economics of the regenerable solvent as compared to previous technologies.

Where regulations require better than 99.8% sulphur recovery efficiency, the TGTU is the preferred process. In addition to SCOT, there are many other processes of this type that vary the process flow diagram, or the operating conditions, or the solvent; each intended to improve some aspect of the cost or performance of the plant. Fig. 1, shows a generic TGTU process flow diagram.

In recent years, oxidation and SO₂ recovery technologies have appeared, with credible equivalent capability to the TGTU, but so far, these technologies have not had the same market penetration as the hydrogenation and amine TGTU combination.

Fig. 1: Simplified TGTU flowsheet

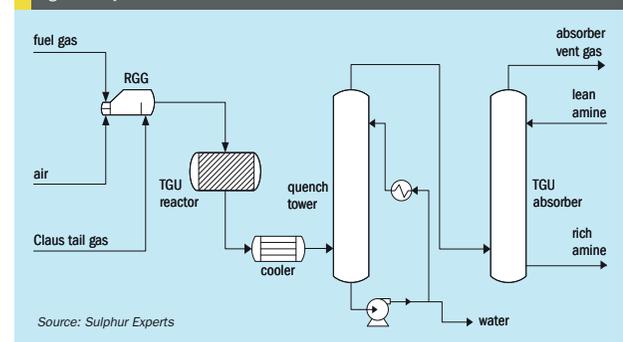


Table 1: TGTU chemical reactions

Desired reactions	Undesired reactions
Hydrogenation reactions: $\text{SO}_2 + 3\text{H}_2 \rightarrow \text{H}_2\text{S} + 2\text{H}_2\text{O}$ $\text{S}_2 + \text{H}_2 \rightarrow 2\text{H}_2\text{S}$ $\text{CH}_3\text{SH} + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{S}$	Sour shift reaction: $\text{CO} + \text{H}_2\text{S} \rightarrow \text{COS} + \text{H}_2$
Hydrolysis reactions: $\text{COS} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{CO}_2$ $\text{CS}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{S} + \text{CO}_2$	Other undesired reactions: $\text{SO}_2 + 3\text{CO} \rightarrow \text{COS} + 2\text{CO}_2$ $\text{S}_2 + 2\text{CO} \rightarrow 2\text{COS}$ $\text{CS}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{SH} + \text{H}_2\text{S}$
Gas-water shift reaction: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	

Source: Sulphur Experts

The wages of sin

Since by tradition "the wages of sin are death", this article focuses on operations that could result in "deadly" outcomes with respect to TGTU performance, reliability, and expense. In this article, only two outcomes are considered deadly: high emissions or SO₂ breakthrough from the TGTU reactor.

Hydrogenation basics

The primary function of the hydrogenation reactor is to catalytically reduce, or hydrogenate, the various sulphur compounds in Claus tail gas to H₂S in the presence of hydrogen. In addition, hydrolysis of carbonyl sulphide (COS) and carbon disulphide (CS₂) occurs over this catalyst. The water-gas shift reaction also occurs in the hydrogenation reactor which allows conversion of

CO to H₂, which is then available for the hydrogenation reactions, and consequently reduces the emission of CO, as this species becomes increasingly important to manage. There are other reactions of concern as well. A list of desired and undesired gas phase reactions is shown in Table 1.

Based on industry experience and research into equilibrium data, all sulphur species except for COS are reacted essentially to completion on active catalyst in the presence of hydrogen and water vapour, however at low temperatures or on catalyst with low activity some mercaptan intermediate product may survive. A typical theoretical equilibrium outlet concentration of sulphur vapour and SO₂ is less than 0.00001 ppm.

Carbonyl sulphide is a more complicated problem because conversion of COS by hydrolysis is thermodynamically limited and at the same time a second reaction, the

sour-shift reaction, creates additional COS by reaction of H₂S with CO. CO is consumed in the water-gas shift reaction, which helps keep COS production low, but at lower temperatures and with higher CO₂ in the acid gas, higher amounts of CO can survive which then further limits net conversion of COS. Because of the more complex set of reactions associated with this species, COS is the most challenging sulphur molecule to manage in the TGTU, as well as being a handy indicator compound for failing catalyst or an inappropriate operating temperature.

TGTU sin no. 1: Low SRU recovery efficiency

The TGTU is intended to clean up after the SRU, so how well the SRU is operating determines how much clean up there is to do. Hence another set of seven sins to be avoided exists for extracting the most from the SRU to minimise this downstream effort. There will be a maximum capacity for a given TGTU to convert sulphur species to H₂S, so an excessive loading of sulphur compounds can increase the likelihood of breakthrough events. A two or three catalytic stage SRU can be expected to deliver a sulphur recovery efficiency of between 96 and 98% (see Fig. 2) to the inlet of the TGTU.

The paper *The Seven Deadly Sins of Sulphur Recovery* provides an essential checklist for ways to ensure the SRU is achieving high recovery, the SRU sins are summarised here:

Fig. 2: Practical recovery capability of SRUs

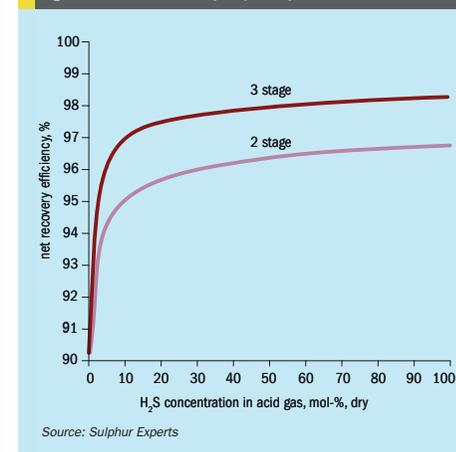
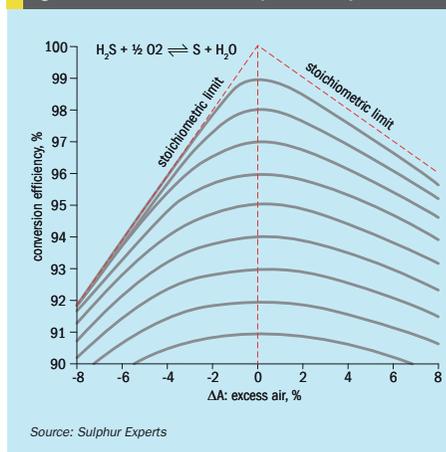


Fig. 3: Effect of excess air on sulphur recovery



CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

COVER FEATURE 3

Emissions reduction in sulphuric acid plants

COVER FEATURE 4

Seven deadly sins of tail gas treating

SULPHUR
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MAY-JUNE 2018

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- **SRU sin no. 1:** poor reaction stoichiometry
- **SRU sin no. 2:** catalyst deactivation
- **SRU sin no. 3:** operating the first converter too cold
- **SRU sin no. 4:** operating the second and third converters too hot
- **SRU sin no. 5:** bypassing gases around conversion stages
- **SRU sin no. 6:** high final condenser temperature
- **SRU sin no. 7:** liquid sulphur entrainment

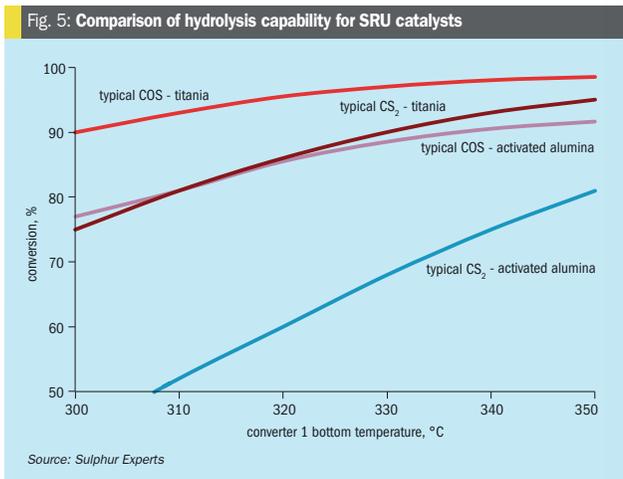
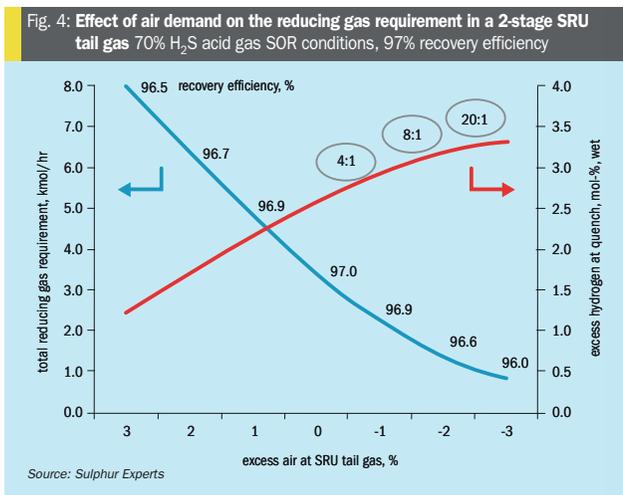
In general, optimising the SRU results in the least potential work for the TGTU, however, there are some additional considerations to address for obtaining the best combined operating efficiency and reliability.

Controlling SO₂ in the TGTU Feed

The amount of SO₂ present is mainly a function of the number of Claus stages and the tail gas ratio. When operating the SRU in the conventional Claus mode, the desired reaction stoichiometry requires an H₂S-to-SO₂ ratio of 2:1 in the Claus tail gas (often expressed as a zero air demand). Under these conditions, the Claus conversion is maximised, as shown in Fig. 3, but does not necessarily minimise the SO₂ load to the TGTU.

One strategy for reducing the SO₂ load is to operate with H₂S-to-SO₂ ratios between 4:1 and 8:1, which corresponds to an air demand set point between -0.5 and -1.0%. As can be seen in Fig. 3, a shift to a -1% air demand set point for an SRU that normally achieves ~98% recovery results in a decline to 97.8% recovery.

Moving to a tail gas ratio of between 4:1 and 8:1 also provides a margin for reliable operation such that a normal range of feed rate or composition changes in the feed to the SRU should not result in high SO₂ entering the TGTU. However, feed deviations outside of the normal range can result in reactor temperature excursions or SO₂ breakthrough. The disadvantage of operating at a higher tail gas ratio is that it will slightly increase the quantity of recycle acid gas and may therefore require more amine circulation to the absorber. Ultimately, it is necessary to find a tail gas ratio that balances reliable prevention of SO₂ breakthrough with an acceptable quantity of recycle acid gas. Operation at higher ratios will reduce the SO₂ conversion work required, with an accompanying decrease in the amount of reducing gases required (see Fig. 4). When the reactor starts with a



higher excess of reducing gases, the probability of SO₂ breakthrough is reduced.

Selecting SRU catalyst for optimum TGTU performance

Where continuous co-firing of natural gas is used in the reaction furnace or high hydrocarbon content is expected in the acid gas, more COS and CS₂ will form in the reaction furnace. In extreme cases, as much as several percent of the feed sulphur is tied up in these species. In an optimised SRU, the first converter operates at a tem-

perature set between favouring hydrolysis of these species to H₂S, which occurs at higher temperatures, and favouring the Claus reaction, which is better at lower temperature. This compromise is needed because COS and CS₂ are not recovered to elemental sulphur on Claus catalysts, so hydrolysis must happen first.

While the hydrogenation catalysts used in TGTUs are active for COS and CS₂ hydrolysis, there are kinetic limitations that make minimising the amounts of these species desirable in the TGTU

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CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

COVER FEATURE 3

Emissions reduction in sulphuric acid plants

COVER FEATURE 4

Seven deadly sins of tail gas treating

SULPHUR ISSUE 376 MAY-JUNE 2018

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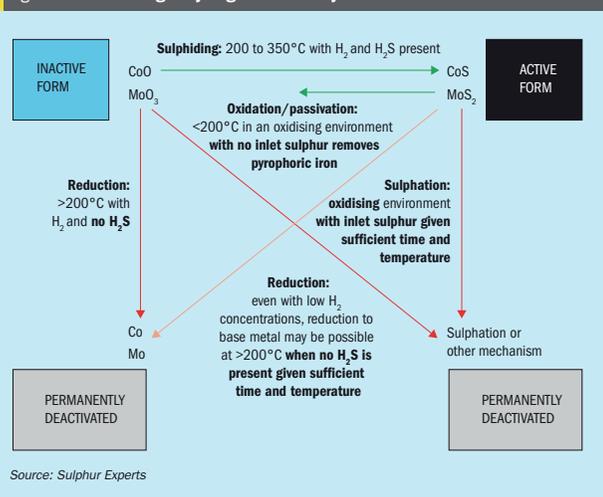
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inlet gas, especially with catalyst that is somewhat deactivated at end-of-run conditions (EOR). When high concentrations of these species are present in the tail gas and the catalyst is kinetically limited by deactivation or low temperature, low hydrolysis rates translate into high emissions. Typical TGTU amines do not have a high affinity for COS, and none for CS₂, so unconverted molecules add directly to emissions. This problem is even more common with low temperature catalysts where, due to the use of steam heaters, inlet temperatures cannot be increased to recover hydrolysis activity at EOR.

While a healthy TGTU can hide many SRU sins, it is wise to always consider the total system and EOR conditions in the selection of the SRU catalysts. Proper selection will help to ensure compliant operation until the next planned turnaround. Fig. 5 shows a comparison of hydrolysis capability of titania vs. alumina catalysts for typical first converter operating temperatures (derived from over 1000 actual plant tests). Where very high sulphur recovery is required but elevated COS and CS₂ formation is expected, a partial load of titania catalyst in the first converter can provide better upstream hydrolysis at reasonable cost. For a plant with a lower COS and CS₂ concentration, it is usually possible to use standard alumina and a hotter Converter 1 temperature to achieve acceptable EOR performance.

Fig. 6: States of tail gas hydrogenation catalysts



Source: Sulphur Experts

TGTU sin no. 2: Low catalyst activity

At the heart of the TGTU is the hydrogenation reactor. The purpose of this reactor is to convert all inlet sulphur compounds into H₂S, which can then be absorbed in the amine contactor and recycled back to the SRU as part of the acid gas feed. Like Claus catalyst, TGTU catalyst is manufactured in the oxide state, but unlike Claus catalysts, TGTU catalysts need to be in a sulphided state to be active. These catalysts are usually cobalt-molybdenum or sometimes nickel-molybdenum on an inactive alumina substrate, and are broadly like those used in naphtha hydrotreaters, but with characteristics that optimise their performance for the TGTU process and for the expected feed compounds.

The first place where catalyst activity may be lost is from inadequate activation procedures. Catalyst is most commonly purchased in the oxide state and activated in-situ using a source of H₂S, however it can also be purchased with post-manufacturing treatments in a partly pre-sulphurised state (e.g. Porocel's actiCAT[®] Maxcel TGS-01/02 products). It is also possible to obtain fully pre-sulphided catalyst that is in a passivated state. (e.g. Eurocat's Totsucat[®] TG).

For pre-sulphurised catalyst, some activation is still required, while for pre-sulphided catalyst, only heating up to operating temperature is required. Regardless of how

the catalyst is activated, it is important to have the correct understanding of the various states for the tail gas catalyst and what operating conditions are required to keep it active, what conditions will passivate the catalyst, and what conditions can result in permanent deactivation (see Fig. 6).

Incomplete or incorrectly executed sulphiding and activation is one of the most common causes of low catalyst activity. The best recommendation is to always follow the vendor's activation procedure.

Most often, the source of H₂S for sulphiding and activation is a slipstream of amine acid gas, and provided this gas is low in hydrocarbons it is probably the best option as compared to using high-ratio tail gas and less complex than using an external source, like DMDS. Key contaminants of concern for activation with acid gas are hydrocarbons, particularly BTEX. Hydrocarbon can crack on the catalyst surface and cause blocking of active sites. This is a permanent deactivation mechanism. A typical guideline is that the total hydrocarbon heavier than C1 should be less than 0.5% and BTEX content should be less than 1,000 ppm. Where high hydrocarbon content, and especially BTEX, is expected and re-activated catalyst is unavailable, it is recommended to use other methods (typically high ratio tail gas) for sulphiding and activation.

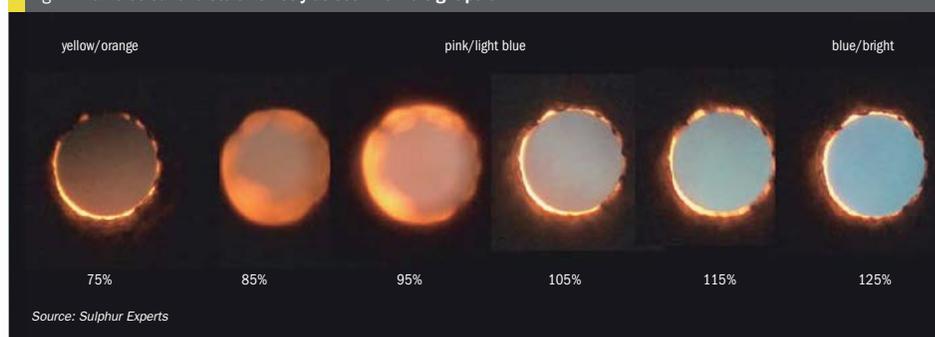
The other common in-situ method of activation is to rely on the reaction furnace and SRU to eliminate the contaminants and to use the Claus tail gas for activation. For this process, it is important that the amount of SO₂ is at a minimum to avoid direct sulphation. This is accomplished by operating the SRU at a tail gas ratio of 8:1 H₂S to SO₂, or higher. Note that performing this procedure on-line with an elevated reactor temperature may rejuvenate low-activity TGTU catalyst.

Hydrogen stripping is another concern in the activation process that may adversely affect the catalyst. This typically occurs if H₂S is not present as the catalyst is heated above 200°C (390°F). Left uncorrected or with very high temperatures this will permanently deactivate the catalyst by reducing it to base metal.

Significant oxygen present during activation of new catalyst may prevent proper activation, or for pre-sulphided catalyst can result in serious fires. Similarly, significant oxygen while the bed is hot during shutdown can cause fires and damage.

While the TGTU is in operation, other deactivation mechanisms exist. For example, the presence of oxygen in the

Fig. 7: Flame colour and stoichiometry as seen from a sight port



Source: Sulphur Experts

hydrogenation reactor feed can cause sulphation (which results in potentially permanent catalyst damage) or initiate the Claus reaction (which can cause pore plugging or plugging, fouling, or corrosion of equipment downstream of the reactor). Eliminating oxygen is normally only problematic in plants using a direct-fired heater as a reducing gas generator (RGG).

To eliminate oxygen when operating an RGG that directly fires natural gas requires operating at or below 90% of combustion stoichiometry. It is good practice to also inject moderating steam to assist in suppressing soot and improving residual oxygen conversion, and improving production of hydrogen and CO. Oxygen slip from the RGG typically happens because of inaccurate flow measurement resulting in firing in an excess air mode.

Sometimes burner damage results in poor mixing allowing oxygen to be present despite operation at substoichiometric conditions, and in some cases, air-purged instruments after the combustion chamber may introduce oxygen. In units with a recycle gas blower or booster blower with a spill back upstream of the reactor, there are known cases where the seal on the blower leaks when the unit is under vacuum and causes air ingress.

As with any other sub-stoichiometric hydrocarbon burner, excessively sub-stoichiometric firing will produce soot.

For well-designed RGGs that are in good condition, this occurs at or below 70% of stoichiometry. Soot is generally less of a deactivation problem and more of a hydraulic plugging problem. Soot from excessively substoichiometric operation or from hydrocarbon contamination of supplemental hydrogen tends to sit on

top of the catalyst rather than attaching to active sites. Unfortunately, there is no equivalent procedure in the TGTU to a sulphur wash in the SRU. In principle, soot could be eliminated by removing, screening and reloading the catalyst, however with severe fouling, it may be impossible to passivate and impractical to process the fouled catalyst on site. In most cases removal under an inert atmosphere and replacement with new catalyst is the most practical choice.

The best means for confirming stoichiometry is to measure the oxygen, hydrogen and CO in the heater effluent. For managing the risks of both soot and oxygen, the RGG should be operated between 70 and 90% burner stoichiometry with injection of 1 unit weight of steam per unit weight of natural gas fuel. Another option is to use hydrogen as the fuel, assuming the burner can operate with this fuel, and that it is hydrocarbon-free. Operating at very low combustion stoichiometry is possible with pure hydrogen. Flame colour can give a coarse indication of stoichiometry, but it takes experience with a given burner and fuel to know how it should appear through the sight port (see Fig. 7). Sampling and analysis of the gas will provide better information and an additional means for correcting the flow ratio. Gas analysis can also detect burner mixing problems and the presence of additional oxygen sources (such as instrument purges).

Eventually all catalyst deactivates by aging, but TGTU hydrogenation catalyst should last ten years or longer if it is well activated and not exposed to various deactivating conditions.

The most common deactivation pathway for TGTU catalyst is exposure to air

(oxygen) while at elevated temperature, a risk which exists during a shutdown. A high-temperature burnout usually does considerable damage to the activity of the catalyst. At elevated temperatures, the CoS and MoS₂ active sites can be destroyed either by sulphation or sintering. This is different than passivation at lower temperatures where only accumulated pyrophoric iron is removed due to the low temperature and controlled oxygen.

Coke formation as witnessed in Claus catalyst is not typically seen in normal TGTU operation and usually relates to activation using poor-quality acid gas. Where BTEX is present in the acid gas, the Claus reactors act somewhat as a guard system for the TGTU and the loss of Claus activity related to BTEX usually requires a shutdown well before the TGTU catalyst is significantly harmed. In refineries, it may be tempting to use hydrogen from units like platformers as a supplement to the RGG, however these hydrogen streams often contain hydrocarbon that will usually form soot, but may also block active sites on the catalyst. Supplemental hydrogen should be free from hydrocarbon.

Finally, there are many stories in the industry of inadvertently water flooding the TGTU reactor, usually due to commissioning the quench without a functioning level instrument. Provided the catalyst was not mechanically damaged by sudden temperature change, water contact for short durations has not typically caused the death of the catalyst. While the substrate for TGTU catalyst is alumina oxide, it is a stronger, less porous version than used for Claus catalyst. Some vendors will even provide a procedure for this situation, but in general,

CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

COVER FEATURE 3

Emissions reduction in sulphuric acid plants

COVER FEATURE 4

Seven deadly sins of tail gas treating

SULPHUR
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MAY-JUNE 2018

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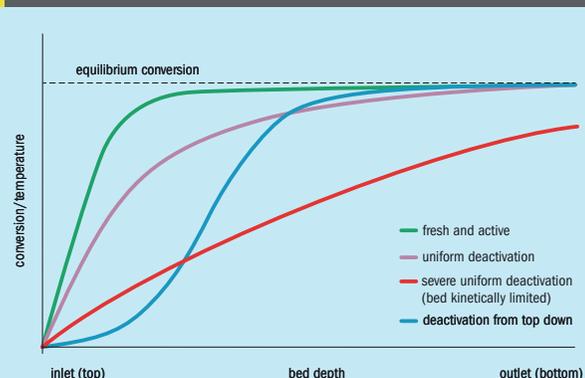
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Table 2: Analytical troubleshooting results: Example 1

Parameter	Before temperature increase		After temperature increase	
	277 (530)	277 (530)	292 (557)	292 (557)
Inlet temperature, °C (°F)	277 (530)	277 (530)	292 (557)	292 (557)
Outlet temperature, °C (°F)	307 (584)	302 (576)	320 (608)	318 (605)
Temperature rise, °C (°F)	30 (54)	26 (46)	28 (51)	27 (48)
TGTU reactor outlet residuals	Gas analysis	Predicted	Gas analysis	Predicted
SO ₂ , ppmv wet	not detected	<1	not detected	<1
COS, ppmv wet	129	3	28	4
CS ₂ , ppmv wet	3	<1	not detected	<1
CO, ppmv wet	2,693	130	1,236	357

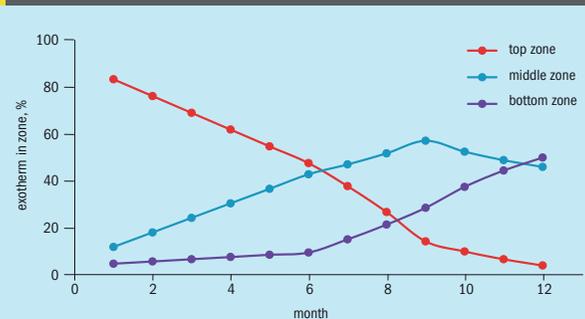
Source: Sulphur Experts

Fig. 8: Reactor temperature profiles



Source: Sulphur Experts

Fig. 9: Reactor exotherm by zone



Source: Sulphur Experts

after draining all the water from the vessel, the catalyst can be put back in service with a simple controlled heating to evaporate the remaining water.

Since catalyst activity is so very important, the TGTU operator or engineer is well advised to have a monitoring plan in place to keep track of the health of the reactor. One typical approach is to plot the temperature data on a trend to show the temperature profile at a given point in time. Example trends are shown in Fig. 8. This method gives an excellent “snapshot” of the distribution of the catalyst activity.

Another option is to create a trend that looks at the fraction of the total temperature rise in each zone of the catalyst bed. This technique is useful for trending changes in performance over time. The example in Fig. 9 illustrates a rapid decline in bed activity.

The final and best monitoring technique is periodic gas sampling and analysis and doing a mass balance to determine directly the performance of the reactor, especially with respect to CO and COS. Table 2 shows an example of analytical results associated with a troubleshooting test, noting the clear improvement in COS residual resulting from tuning the reactor inlet temperature.

To summarise:

- ensure catalyst is properly activated;
- for in-situ activation, high quality acid gas is the best option;
- follow the activation procedure from the vendor;
- control the RGG burn stoichiometry;
- monitor the reactor temperature profile;
- when in doubt, gas analysis is the answer.

TGTU sin no. 3: Insufficient hydrogen or reactor overloading

No matter how active the catalyst is, there must be excess hydrogen for the reactor to convert SO₂ and elemental sulphur to H₂S. Converting these species is less vital from an emissions perspective than from a reliability perspective as unconverted SO₂ acidifies the quench water and makes sulphur formation in the quench water possible, and unconverted sulphur will become suspended sulphur solids. To understand hydrogen deficiency, it is necessary to understand where hydrogen is produced in the SRU and TGTU.

For most TGTUs the main source of hydrogen is the SRU reaction furnace. The amount of hydrogen produced is influenced by the temperature of the reaction furnace, a higher temperature favours more hydrogen production. In general, it requires a significant excess air upset condition to produce so much SO₂ that the hydrogen available from the reaction furnace is insufficient to meet the hydrogenation needs of the reactor. Such an upset occurs most frequently due to either a sudden reduction in SRU feed rate or because of intermittent hydrocarbon contamination of one or more acid gas streams.

In the case of variable hydrocarbon content, the deviation occurs when the hydrocarbon content suddenly decreases leaving an excess of air as compared to the requirements for good Claus operation. Unless there is a feed forward analyser on the SRU feed, the air demand analyser, (ADA) may take several minutes to catch and correct the deviation. Good SRU control and stable SRU feed quality are therefore key to avoiding this cause of hydrogen deficiency.

While the kinetics for conversion of sulphur in a hydrogenation reactor are very fast, it is possible that a large enough liquid carryover of sulphur could result in running out of hydrogen. This would be most likely in a Claus plant where the final condenser rundown becomes blocked.

Finally, while the reaction furnace does in most cases produce sufficient hydrogen, additional hydrogen is sometimes needed to guarantee against upset cases. For this reason, the TGTU is equipped either with a substoichiometric direct-fired heater or a supplemental hydrogen supply, or in some cases, both. For those equipped with a fired heater, to generate useful quantities of hydrogen, the burner must be operated substoichiometrically, as discussed in sin no. 2.

Preventing hydrogen shortfalls requires proactive monitoring and control of the conditions. A hydrogen analyser, preferably after the quench tower, is a key element for monitoring the concentration of hydrogen. There should be alarms on the measured value to ensure it is not below a practical minimum of 1.5%, nor is there any need to run above a practical maximum of 5%. Essentially, excess hydrogen is insurance against upsets. If a closed loop control is possible on the hydrogen supply, this may decrease response time to a deviation, and is generally advised, while numerous plants rely only on the alarm. It is inadvisable to use the pH analyser on the quench column as a back-up; by the time the quench water pH goes down, potentially fatal trouble has already begun. See sin no. 5.

While it is possible to mount the analyser on the ground with a properly heat-traced sample line or a sample conditioning system for dealing with any water, this is not the preferred configuration as it adds more process lag time, potentially more complexity, and more risk of plugging. The most reliable configuration has proven to be mounting the analyser close to and above the process pipe. This ensures the sample line is both short and self-draining in event of condensation.

In response to a low-hydrogen alarm, the operators should respond by investigating the Claus plants to determine if one or more units are high in SO₂ and act accordingly and/or increasing the amount of hydrogen available. For Claus operation, see sin no. 1.

Plants with chronic issues of insufficient hydrogen also tend to have quench water problems and it is worth investigating upstream of the SRU through the amine and sour water units as required to determine what reliability, control, and feed composition issues may be contributing to the cause of the reactor breakthrough.

In some plants, the reactor may exceed the maximum allowable temperature before the hydrogen runs out due to the exotherm from excessive amounts of SO₂ conversion. This might result in equipment damage, unapproved flaring, etc., even if the hydrogen has not been depleted. In these cases, the alarm setpoint or trip point may be too conservative in assessing the temperature, pressure, and duration of events.

To summarise:

- always have a working hydrogen analyser;

- always ensure there is excess hydrogen;
- if there is low or no excess hydrogen
 - check for upstream problems that are causing high tail gas SO₂ or sulphur carry over
 - add or make more hydrogen;
- act quickly or sin no. 3 will beget sin no. 5.

TGTU sin no. 4: Operating the reactor too cold

Regardless of whether low-temperature or high-temperature catalyst is used, a higher TGTU reactor temperature generally favours higher conversion (within the design constraints of the equipment). In many cases, catalyst that is somewhat deactivated can be brought back to acceptable performance through an increase in the inlet temperature. This has been an issue with low-temperature catalysts in the past but is less of an issue with newer generations of low-temperature catalysts.

Despite a favourable equilibrium for COS at low temperature, there are more potential issues with COS and CO at low temperatures due to kinetic limitations. For most TGTU operators, the quantity of COS and CS₂ is not measured by an on-line analyser or these species are converted to H₂S by the analyser prior to measurement, so poor conversion of these species is not directly detected.

Some H₂S analysers can also measure these species separately at the outlet of the absorber. For plants without separate measurement of these species sampling and analysis of the gases is the only measurement option. Plant operators should always maintain the inlet to the reactor hot enough for the catalyst in use and the current feed composition to ensure good overall conversion.

In addition, with low temperatures and low activity it is possible to form mercaptans in the TGTU reactor. As mercaptans are not absorbed by amine, this may cause an incremental loss of sulphur and increased emissions.

Increasing the reactor temperature will reduce the formation of these undesirable components. In the analytical test shown in Table 2, the COS was significantly improved by changing the reactor temperature. In Table 3, total emissions were marginally acceptable and the client was looking for improvements. The plant was equipped with a steam heater, so the

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CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

COVER FEATURE 3

Emissions reduction in sulphuric acid plants

COVER FEATURE 4

Seven deadly sins of tail gas treating

SULPHUR
ISSUE 376
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Table 3: Analytical troubleshooting results: Example 2

Parameter	Test 1		Test 2		Test 3	
Reactor inlet temperature, °C (°F)	239 (463)		249 (480)		257 (494)	
Temperature rise, °C (°F)	25 (45)		23 (42)		23 (42)	
Component	Reactor outlet	Absorber outlet	Reactor outlet	Absorber outlet	Reactor outlet	Absorber outlet
CO, ppmv dry	1.783	1.963	1.512	1.723	1.213	1.330
COS, ppmv dry	39	43	28	37	31	28
CS ₂ , ppmv dry	1	1	1	0	1	0
RxSH, ppmv dry	11	12	4	6	4	3
Total TRS as S ₂ , ppmv dry	5	56	33	43	36	31

Source: Sulphur Experts

maximum reactor inlet temperature was quite low. By testing the reactor at higher temperatures, it was possible to show improvement in COS conversion and a decrease in mercaptans.

While these were small improvements, when a plant is at end of run and near emissions limits, small reductions can be critical.

To summarise:

- if emissions are up but the H₂S still appears normal from the absorber, the issue may be poor conversion of COS, formation of additional COS, and formation of RxSH;
- increasing the reactor inlet temperature will aid in destruction of these sulphur compounds;
- for COS, also ensure the first Claus converter has been optimised for COS/CS₂ hydrolysis, see sin no. 1;
- if there is an absorber outlet H₂S analyser, investigate if it can also measure COS and CS₂.

TGTU sin no. 5: Poor quench water quality

The quench section of the TGTU serves three purposes: to cool the gas sufficiently so that it can be contacted with the amine, to reduce the water content of the gas prior to contacting the amine, and to prevent SO₂, sulphur, and solids contamination of the amine during breakthrough events. There may or may not be a cooler in between the hydrogenation reactor and the quench section to assist with the cooling function. Aside from an effluent cooler, there are two main variations on the quench column: the traditional single-

stage column and the two-stage column. In the single-stage column, all the process functions are conducted simultaneously, whereas in the two-stage column, the lower section (the desuperheater) is primarily tasked with cleaning the gas and initial cooling, while the upper section (contact condenser) removes water and provides final cooling. External to the column are heat exchangers for cooling the water, usually air coolers, pumps for moving the water, and filtration to remove solids.

The pH of the quench water must be continuously monitored. Despite the maturity of TGTU technology, poor and unreliable quench water pH measurement is a recurring theme. The quench pH analyser and sample system needs to be selected for the harsh conditions that may exist during upsets (solids, suspended sulphur, pH variability), and with consideration for dissolved H₂S and ammonia. Therefore, select an analyser designed for harsh sour water conditions. Redundancy is also a worthwhile consideration.

For the single-stage column, the whole column will have a "natural" pH because circulating water will constantly absorb small quantities of H₂S, CO₂, and, in the case of refineries, NH₃ from the process gas. These weak acid and base species will equilibrate since the condensed water will remove them as it is purged from the system.

In plants where there is no continuous chemical addition, the "natural" pH falls between 6.0 and 8.0, with the lower pHs usually associated with gas plants with a high CO₂ content in the acid gas feed to the SRU, and the latter in refineries with low CO₂ content in the acid gas, combined with residual ammonia in the Claus tail gas.

This range of pH is acceptable for

typical carbon steel grades that are used for piping, vessels and heat exchangers in this service. If upgraded metallurgy is employed, tolerance for pH deviations should increase so the expense of stainless steel can be off-set by less corrosion and less risk of fouling by iron sulphide solids causing an unplanned shutdown. One client with a reactor problem managed to operate a quench system made entirely of stainless steel at a pH of between 2 and 5 for several weeks before accumulation of sulphur compounds ultimately plugged a downstream water treatment unit. While the unit still failed, the more robust materials of construction allowed time to plan for the outage.

What is important to understand about the "natural" pH is that without intervention, the pH will always revert to this value as condensed water and absorbed gases replace the circulating water in the column. This means that trying to maintain any pH other than the "natural" value will require constant addition of caustic or ammonia and typically, these chemical additions are expensive and often unnecessary. Over-zealous pH control has caused a great deal of trouble for many TGTU operators due to corrosion associated with high pH, or by causing FeS scale to become mobile resulting in more frequent filter changes and associated tower fouling.

For two-stage quench columns, the bottom section can more easily be maintained at an "artificial" pH as in theory, water is neither condensed nor evaporated in the bottom section, however there would still be an accumulation of any species that can be absorbed at the pH of this section. Typical "artificial" pH set points are between 7.5 and 8.5, with highs of

11+. Note that the "artificial" pH will also change if the bottom section temperature is not at the water dewpoint and trying to maintain a very high "artificial" pH will likely still require constant chemical addition; usually expensive and unnecessary.

When SO₂ escapes from the TGTU reactor unconverted, it is captured in the quench water. Absorption of this SO₂ will result in extremely low pH values and high rates of corrosion in the column. Excessive corrosion will result in leaks and ultimately a shutdown. In addition to reducing wall thickness, low pH tends to create or release solids in the tower that plug or foul the system, limiting the function or capacity of the quench tower. These solids (usually iron sulphides and sulphur) are generally not successfully removed by on-line cleaning methods and so unplanned downtime for mechanical cleaning is a frequent outcome when there is a significant breakthrough event. Because mitigating the fouling is vital to keeping the quench system healthy, it is necessary to have adequate filtration, and it is well advised to use full stream filtration for any packed column in this service. Filters also need to be designed and situated such that they can be serviced quickly and repeatedly. Fouled quench towers furthermore result in contaminated, potentially acidic quench water carryover into the amine absorber, causing foaming and heat stable salt formation.

During SO₂ breakthrough, the pH is typically managed by injection of caustic soda, ammonia (gas or aqueous), soda ash, etc. During an event, these chemicals are needed immediately, so the system that delivers them should be within the control of the TGTU unit. Many TGTU operators with adequate supplies of clean make-up water preferentially dump the fouled tower water instead of chemical addition in upsets. This method is usually as effective as chemical dosing for managing the pH and has the advantage of controlling the speed of the change in pH which can reduce corrosion, particularly around chemical injection points. If water supplies are more limited it is still preferable to dump and make-up as much as possible and to use the chemical dosing as a back-up system.

To summarise:

- quench water should be clean
 - the system requires adequate filtration capacity
 - full flow filtration is preferred

Table 4: Effects of lean amine temperature and H₂S loading

Lean amine loading (moles H ₂ S/mole of MDEA)	Lean amine temperature		
	35°C (95°F)	45°C (113°F)	55°C (131°F)
0.0005	21 ppm	35 ppm	65 ppm
0.001	45 ppm	77 ppm	127 ppm
0.002	90 ppm	150 ppm	276 ppm
0.005	252 ppm	417 ppm	771 ppm

37.8wt% MDEA; absorber inlet gas composition 1.751 mol-% (dry) H₂S; 7.758 mol-% (dry) CO₂

Source: Sulphur Experts

- filters must be serviceable quickly – or the tower will become the filter;
- the water pH must be monitored continuously;
- except for the de-superheating section of two stage quench systems, artificial pH targets are usually unwise;
- pH control by water dumping and make up is usually preferable to dosing with caustic, ammonia or soda ash;
- when dosing chemicals are required, they need to be available without delay.

TGTU sin no. 6: poor amine operation

If the amine does not absorb the H₂S, then everything that was done to the SRU tail gas in the upstream reactor and quench water system has been for nothing. The amine has two jobs, first to capture enough of the H₂S such that what is left is compliant with the operating requirements of the plant, and second to recover the H₂S (but as little CO₂ as possible) as a recycle acid gas stream to the SRU. For amine quality, the parameters that are normally of most concern to ensure the treated gas are lean amine loading and lean amine temperature.

In the TGTU, the gas leaving the absorber has low pressure overall; typically, either very slight positive pressure or sometimes a slight negative pressure caused by the draught of the incinerator. Because the absolute pressure of the gas leaving the absorber is very low, the partial pressure of H₂S is also very low. Since the equilibrium between the partial pressure of the H₂S over the amine and the H₂S dissolved in the amine determines the residual H₂S, a low residual H₂S content in the lean solvent, known as "lean loading", is critical to ensuring emissions compliance.

Where a typical refinery or gas plant absorber in hydrocarbon treating service

can meet 5 to 15 ppm H₂S specifications using typical lean loadings and temperatures, in a TGTU with conventional unmodified MDEA solvent, we expect several tens to even hundreds of ppm of H₂S in the overhead gas. This means for most TGTU operators, the lean loading must be lower than the typical values used in other services so as to ensure acceptable residual H₂S in the absorber outlet to meet the emissions requirements. In some cases, additives, such as phosphoric acid, or even leaving a reasonable accumulation of heat stable salts assist with achieving lower lean loadings and better H₂S capture, however excessive amounts of acid, especially if SO₂ breaks through all the way to the amine, will make solvent inactive for H₂S absorption. Heat stable salts and additive content should be monitored regularly to ensure deviations from adequate solvent quality are detected and corrected. For plants that use the same amine for both the TGTU and other absorbers, all of the lean amine must meet the TGTU lean loading specification, or a more complex scheme using either partially loaded or partially regenerated amines (often called semi-rich or semi-lean) for bulk absorption must be used in order to minimise the amount of amine that gets stripped to the limit.

As with other amine absorbers, feeding the lean amine at too high a temperature in absolute terms into the absorber increases the residual H₂S in the outlet gas. This is especially a problem during summer operation when many plants find themselves lacking in lean amine cooling duty. The inability to cool the lean amine to a reasonable temperature (<49°C/120°F) can make the difference between meeting and failure to meet specification. The cooler the lean amine temperature, the greater the capacity for H₂S removal and loading of the solvent,

Table 5: Impact of amine circulation on H₂S in absorber outlet gas

Parameter	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
SRU conversion, %	98.45	98.53	98.74	98.66	98.58	-
SRU recovery, %	97.63	97.38	97.58	97.82	97.41	97.54
TGU recovery, %	99.98	99.98	99.98	99.99	99.98	99.99
TGU amine circulation (usgpm)	135	135	120	100	90	95
TGU Residual H ₂ S (ppm)	323	344	379	218	259	222

Source: Sulphur Experts

but temperature is often the less important parameter as compared to the lean loading. Table 4 provides a case study showing the effects of key operating parameters on the absorber outlet H₂S concentration.

In upstream amine units in gas plants or refineries there is generally a concern about hydrocarbon condensation in the absorber, for TGTU operation we must unlearn this rule. Instead of a 5-10°C margin above the inlet gas temperature, in the TGTU case the lean amine temperature is ideally within +/-2°C (3°F) of the quench column overhead temperature. The reason for this is ensuring a reasonable water balance on the amine. Higher amine temperature relative to the quench water overhead will lead to net water loss, lower amine temperature compared to the quench overhead will lead to net water gain into the amine solvent. For most TGTU amine systems, set the quench column temperature and the lean amine temperature together to a suitably low temperature to meet the H₂S specifications and very close to the same value. Excessive water condensation into the amine may make the solution become too dilute resulting in excessive circulation of water which increases total duty required from the reboiler and other heat exchangers such that lean loading and lean amine temperature cannot be met, also excessive water will lead to increased CO₂ absorption leading to even higher energy duty requirement from the reboiler.

Despite the importance of achieving a sufficiently low lean amine temperature to achieve treated gas specification, in many facilities, it is not always possible to achieve the required temperature, especially in summer months. Lean amine coolers need to be monitored and cleaned at appropriate intervals to ensure treated gas specification can be met at the most challenging summer conditions.

For almost every TGTU CO₂ slip is a concern as there are many energy and cost advantages to minimising the recycling of this non-sulphur bearing species. Excessive circulation rates increase the quantity of CO₂ removal, it could result in additional energy demand from the reboiler and failure to meet lean loading requirements to meet the required H₂S residual in the gas leaving the absorber. Table 5 shows the results from an analytical troubleshooting test of a TGTU that had excessive amine circulation. Removing CO₂ unnecessarily also lowers the quality of the recycle acid gas which may impact Claus unit operation.

Where ultralow H₂S levels (e.g. below 10 ppmv) are required, specialty amines products with additives or specialty solvents like ExxonMobil's Flexsorb® may be required. In general, these solvents have the same key operating parameters regarding minimising circulation and optimising lean loading, lean solvent temperature and additives and salts.

To summarise:

- the most important parameter for the TGTU amine is lean loading to ensure circulation of water which meets the requirement
 - keep the solution at the right strength
 - minimise CO₂ co-absorption;
- the lean amine must be sufficiently cool and close in temperature to the gas
 - monitor the lean amine cooler
 - there is no need for a gas to amine temperature difference to prevent condensation of hydrocarbon
 - the lean amine temperature and quench tower overhead temperature should be nearly the same to manage water balance;
- monitor concentrations of heat stable salts and additives to detect and correct deviations from acceptable solvent quality.

TGTU sin no. 7: Bypassing

Probably the least considered but sometimes worst of the deadly sins is the intentional or unintentional bypassing of sulphur species around one or more conversion stages in a TGTU. Fig. 10 shows locations where bypassing can occur. In general, any gas that does not go through the TGTU catalyst bed will have a negative impact on efficiency. In bypassing cases, there are no typical values, however some worst-case examples for each form of bypass are discussed as anecdotes below.

Tail gas bypass valves, and TGTU inlet/outlet valves

Wherever there is a valve, there is also the possibility that the valve does not shut tightly. There is more than one case in the industry of a leaking bypass valve shutting down a unit. If there is no absorber outlet analyser, this problem can be very hard to diagnose online as often there can be other sources of sulphur like pit and tank sweeps or degassers that also may contribute to emissions.

Passing inlet valves can also be a big problem for managing safe start-ups and shutdowns, and may contribute to premature deactivation of catalyst and other unplanned events.

In addition to leaking valves, poorly located inlet and bypass valves may accumulate condensed sulphur vapour or solidified sulphur on the upstream side of the valve. A build-up of liquid sulphur on the bypass valve usually results in a large emissions event but really has no effect on the TGTU operation. On the inlet side of a TGTU, a large build-up of liquid sulphur can result in overwhelming the reactor and plugging the quench, resulting in an unplanned shutdown.

Bypassing valves can usually be found with a pressure hold test before start-up. An option may be to inject a radioactive tracing agent while online to find the source of the leak.

Multiple converters in one shell

In smaller plants, having multiple converters in one shell is generally a good option to save on capital cost. The integrity of the partitions must be inspected, or ideally pressure-tested, at turnarounds if possible as leaks do occur between sections. While leaks between Claus converters are a "bypassing sin" in the SRU, bypassing below the catalyst bed into the TGTU will

quickly result in sin no. 5. Depending on which Claus stage is adjacent, there may also be abnormal amounts of COS and CS₂ that will directly affect emissions, as well as potentially excessive H₂S for the absorber to process.

A similar bypassing mechanism can exist in units using a gas-gas heat exchanger as part of the reactor inlet heating/outlet cooling scheme.

Internal bypassing

Internal failures and incorrect installations of internals can result in creating paths by which the tail gas can get through the reactor without fully contacting the catalyst. The two worst cases that the author is aware of involved a screen design that encapsulated the catalyst. The shell-to-head joints of the reactor had no catalyst and offered no resistance to the gas flow with the result of very little activity from the reactor catalyst. In the other instance, the reactor inlet gas deflector failed and the gas flow pushed a path through the catalyst under the inlet pipe resulting in poor conversion, and

consequently all the problems cited in sin no. 5.

Note that internal bypassing can sometimes be detected using the same technology used to scan distillation columns. The first case described was not a suitable candidate, but the case with the failed inlet device is similar to a number of Claus converters that were successfully scanned.

In summary:

- locate TGTU valves correctly to prevent corrosion and sulphur accumulation;
- leak check inlet, outlet and bypass valves before start-up;
- if you suspect bypassing in a vessel, try a vessel scan
- if you suspect bypassing in of a valve, radioactive tracing agents may help. ■

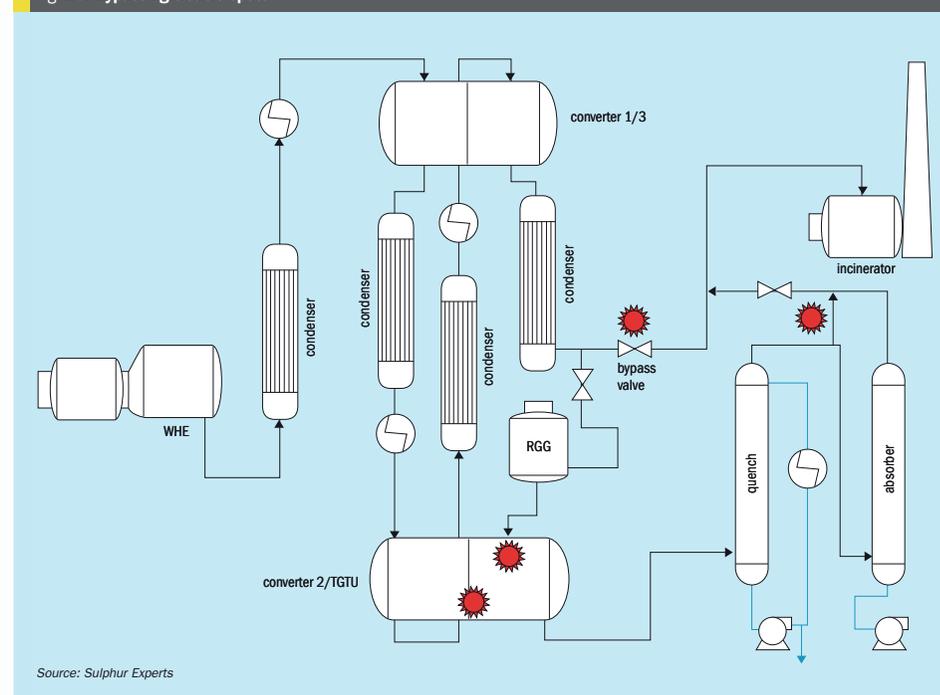
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Fig. 10: Bypassing trouble spots



Source: Sulphur Experts

CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

COVER FEATURE 3

Emissions reduction in sulphuric acid plants

COVER FEATURE 4

Seven deadly sins of tail gas treating

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Ensuring low emissions with technical services

Besides advanced catalysts, good technical services can be a valuable tool to achieve better sulphuric acid plant performance and meet stricter emission limits. In this article **M. Grantho** of Topsoe reports on the effective use of technical services for catalyst loading design, optimisation of plant operation and plant debottlenecking and troubleshooting.

Table 1: Relative catalyst loading required to achieve maximum 100 ppm emission at three different gas conditions

	S burner	Zn roaster	Cu smelter
Gas, SO ₂ /O ₂	10.5/10.5	7.0/9.0	15.0/13.9
Relative loading, %	100	133	80
Emission, ppm	125	80	195
Production, t/d	1,000	1,000	1,000

Source: Topsoe

Air pollution is, or is becoming, a significant issue in big cities and highly industrialised regions across the globe. As a consequence, emissions from all sources attract more and more attention from the public and legislators. This increased attention has affected the sulphuric acid industry through a tightening of the maximum permissible limits for a number of pollutants, such as sulphur dioxide (SO₂) and acid mist. The tightened limits can be met with more advanced catalyst, where the most advanced solutions, employing VK69 and LEAP5 catalyst, can help plants originally designed for emission levels of around 300 ppm to achieve levels below 100 ppm. Revamped or new plants could even achieve levels down to 20 ppm at reasonable gas strength.

With increasing ambitions for lower emissions, there is less room for sub-optimal operation of the plant. For instance, minor stripping of 50 ppm SO₂ in the final absorption tower due to a shared acid pump tank might not be critical when trying to achieve an emission of 300 ppm, a small amount of extra catalyst or slightly lower load might correct that. If trying to meet a limit of 50 ppm it is another issue altogether, no catalyst or load change will

be sufficient. Although plant operators can take many steps to optimise the plant, good technical services can be a valuable tool to achieve better performance without excessive requirements on plant owners.

The effective use of technical services can be divided into three categories; catalyst loading design, optimisation of plant operation and plant debottlenecking and troubleshooting.

Catalyst loading design

To meet new, very low, emission limits, it is not sufficient to use general loading guidelines to design the catalyst loading. To be on the safe side, replacing more or less all catalyst with fresh catalyst of the most advanced types at every turnaround will work, but it is hardly very cost effective. If, on the other hand, a plant seeks to meet low emission limits with the most cost effective solution, detailed simulation models and knowhow is necessary. By using models and knowledge, tailor-made loadings for the specific plant can be prepared, meaning that the new limits can be achieved safely by replacing a minimum amount of catalyst. Table 1 shows different loadings requirements for different

scenarios for plants based on zinc roasting and copper smelting off-gases.

As seen in Table 1, the loading size and catalyst distribution is very different depending on the scenario. General guidelines will do a poor job of capturing this difference, resulting in either too big, or too small catalyst loading.

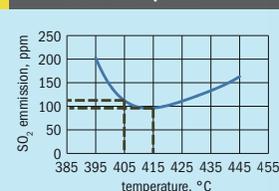
Optimisation of plant operation

Optimising inlet temperatures

To maximise the performance of the plant, in addition to having the right equipment and catalyst loading, it is also important to operate it in the best way. As an example, relatively small mismatches in bed temperatures can have a significant impact on the emissions of the plant (see Fig. 1).

The graph in Fig. 1 illustrates that a plant with a catalyst loading designed for a SO₂ emission of 100 ppm with optimised inlet temperatures will have an emission of close to 115 ppm if the inlet temperature is 10°C too low. This not only shows the importance of continuously optimising the

Fig. 1: Effect on SO₂ emissions of operating the last bed 10°C lower than optimal



Source: Topsoe

inlet temperature to the catalyst bed, but also the importance of accurate and representative temperature measurements.

Optimising inlet temperatures can be done, to a large degree, by trial and error by the plant operator. However, for beds 2 and 3, where the temperature increases are small and no on-line outlet SO₂ measurement is available, accurate SO₂ measurements at the inlet and outlet of each bed is often necessary to fully optimise the beds. Furthermore, more often than not, the outlet temperature measurements turn out to be less accurate than expected. Table 2 provides an example of a plant where a TOPGUN study revealed a total mismatch of 37°C between the measured and the correct temperature increases.

From Table 2 it becomes apparent that not only is there a mismatch in the total measured and theoretical temperature increases, but the mismatch is also unevenly distributed across the beds. The effect of these mismatches is that the operator in question will not be able to optimise the catalyst bed temperatures effectively based on temperature measurements alone.

Optimising gas composition

Optimising operating conditions is not limited to inlet temperatures to the catalyst beds, the feed gas composition may also be tuned to maximise plant performance. Although plant operators can try different gas compositions, with all other parameters that also need to be re-adjusted, doing so will be very time consuming. Using simulations, preferably together with a TOPGUN gas analysis or catalyst activity analysis, will allow many different conditions to be tested simultaneously, to find the optimum operating conditions given the constraints of the specific plant in question. Additionally, simulations allow other catalyst solutions to be used in different scenarios, or future gas compositions to be evaluated.

Table 2: Comparison between measured temperature increases, and theoretical temperature increases based on SO₂ measurements for an industrial sulphuric acid plant

Bed No	ΔT measured	ΔT based on SO ₂ measurement
1	155	177
2	59	91
3	21	53
4	31	4
Total	266	303

Source: Topsoe

Optimising quench and cooling options

In case the capacity of the main blower is fully utilised and the plant uses air quench cooling in one or more locations, optimising the distribution of air between the furnace and the cooling points can have a significant impact on emissions. As with the previous example, trying different combinations can be done by the plant operator, however it will be time consuming and there will likely be some emission spikes.

As gas flow measurements are often inaccurate, having the option to do gas analysis can also be critical to optimise the quench cooling.

Troubleshooting and plant debottlenecking

Having the possibility to combine gas analysis and catalyst activity analysis with advanced simulation models and skilled engineers is a powerful tool to detect issues that may be holding a plant back from performing optimally. It may be possible to detect some issues based on the plant data and simulations alone, but other issues or limitations may require further data. Issues can be anything from leaks in heat exchangers, to uneven flow distribution or the aforementioned SO₂ stripping in the final absorption tower. The following three examples from the industry show how technical services have helped acid plant operators to overcome performance obstacles.

High SO₂ emission with new converter

One customer had operated its sulphur burning plant with VK69 in the final bed for a long time and had enjoyed good stable performance for close to a decade. The converter, on the other hand, was in rather poor shape and the customer decided it needed to be replaced. They opted on having the

converter designed by a well-respected international designer, but contracted a local fabricator themselves. As is common, the operator decided to replace a significant portion of the catalyst when replacing the converter. The performance with the new converter and catalyst was good when they started up again, but a few months later, it gradually became worse than what they were used to with the old converter and catalyst. As the situation appeared to get worse, something needed to be done.

A TOPGUN study showed that the conversion over bed 4 was significantly worse than expected, based on the amount of new VK69 installed. During a short shutdown, samples of the catalyst were taken and analysed. The results indicated that the VK69 had 100% activity, somewhat contradicting the result of the TOPGUN study.

After extensive discussion and thorough studies by the designer of the converter, two locations were identified where leaks would explain the results, in the internal heat exchanger and in the division plate between beds 4 and 3. The operator was unsure what to believe, was the issue a result of poor catalyst performance, or a leak in the brand new converter?

It was agreed to shut down the plant for inspection, and to have fresh VK69 on hand, should no leaks be found. As the plant cooled down, tensions were high, what if no leak was found and replacing the catalyst did not help? When the converter was cool enough to be entered, a large crack was found between the wall and the division plate separating bed 4 from bed 3. It turned out that the local contractor had not done a good enough job when welding the converter. The crack was repaired, the plant started back up and the performance was good once again."

Plant performance held back by uneven flow distribution

A sulphur burning plant in Europe was struggling to achieve the predicted conversion over the first catalyst bed. A full replacement did not remedy the issue, which indicated that poor catalyst performance was not the root cause. During the turnaround, the operator decided to replace the outlet thermocouple with one that could measure the temperature at multiple locations radially. Once these data had been evaluated and compared with the results of a TOPGUN study, it was concluded that the average outlet temperature corresponded well to the SO₂ concentration measured on the outlet of the bed. Interestingly, the multiple temperature measurements

CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

COVER FEATURE 3

Emissions reduction in sulphuric acid plants

COVER FEATURE 4

Seven deadly sins of tail gas treating

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Fig. 2: Temperature gradient at the outlet of bed 1 due to uneven flow distribution

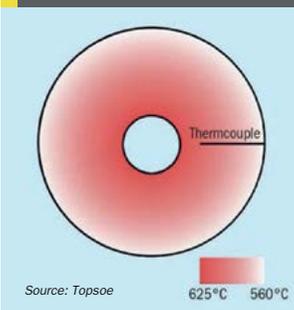


Table 3: Radial temperature distribution at the outlet of Bed 1 in and industrial sulphuric acid plant

Sample point	Temperature at 80% load (°C)	Temperature at full load (°C)
1 (closest to outer wall)	580.0	560.5
2	616.5	612.5
3	618.9	618.3
4	619.8	622.3
5	620.4	622.8
6	620.5	623.2
7 (closest to central column)	620.6	622.9

Source: Topsoe

Table 4: SO₂ concentration downstream of bed 5, showing SO₂ stripping in the final absorption tower

Sample set	Bed 5 outlet	FAT inlet	FAT outlet
1	440 ppm	420 ppm	817 ppm
2	335 ppm	270 ppm	550 ppm
3	586 ppm	575 ppm	949 ppm

Source: Topsoe

also revealed that there was a significant difference between the different measurement points, and that the difference decreased as the load was reduced (see Table 3).

To better visualise the temperature distribution over the outlet of bed 1, see Fig. 2.

When an average is corrected for the different diameters at the different measurement points, it matches the measured SO₂ concentration and duct temperature measurement well. Simulation of the different measurements reveals that the central part of the bed operates at equilibrium, while the outer part operates far from equilibrium. The effect of the uneven outlet temperature is that only a very small part of the bed, some

20% from the wall, operates at an optimal temperature, while the capacity of most of the bed is not utilised properly. Theoretical simulations based on the TOPGUN study and temperature data show that the uneven outlet temperature would explain the lower than expected performance.

Knowing that uneven outlet temperature was the most likely reason for the lower than expected performance enabled the operator to start planning how to resolve the issue at the next turnaround.

High emission turned out to be SO₂ stripping

Finding the root cause of high SO₂ emissions can be difficult and sometimes hard to pinpoint for a plant operator. Poor

Fig. 3: Floor of bed 1 which collapsed due to high pressure drop; taken during MMF2010



PHOTO: TOPSOE

catalyst performance might first spring to mind, but leaking heat exchangers or other mechanical related issues may be just as likely. An operator of an acid plant based on metallurgical off-gases could not meet the expected emission level and was at a loss as to what was the cause. A TOPGUN study was carried out to shed some light on the issue. The TOPGUN study revealed the SO₂ trend downstream of bed 5 (see Table 4).

As can be seen in Table 4, the concentrations at the outlet of bed 5 and the inlet of the final absorption tower are similar, suggesting that the gas at the outlet of bed 5 is fairly well mixed and that there are no leaks in the heat exchangers between bed 5 and the final absorption tower. At the outlet of the final absorption tower, the concentration was, however, significantly higher, showing that the explanation for the higher emission is probably SO₂ stripping in the final absorption tower. Although rectifying SO₂ stripping requires more substantial changes to the plant, without it, the plant will never achieve an emission below about 500 ppm at full load, even with the most advanced catalyst solutions.

Southern Peru's Ilo Smelter meeting SO₂ emission requirements at high Load

In 2007, Southern Peru Copper Corporation commissioned a 3,740 t/d sulphuric acid plant (AP2) in Ilo, Peru. This was done in connection with a complete modernisation of the smelter unit.

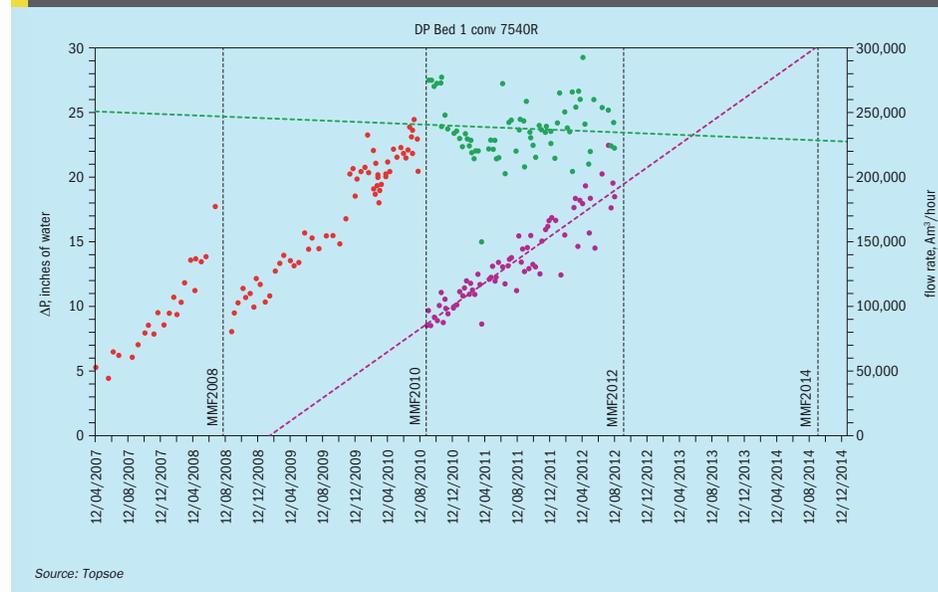
At the end of 2009, a catalyst optimisation study was performed together with Topsoe. The aim of this study was to obtain operation at design capacity as well as reduce the SO₂ emission.

The TOPGUN measurements confirmed the low performance of all beds, resulting in conversion below the design of 99.85%. It was also verified that no leaks existed in the heat exchangers, but measurements around bed 4 showed an increase in the SO₂ concentration, indicating a leak, most likely from either the start-up line or structural damage in the top of the converter.

The TOPGUN results were confirmed by activity testing of spent catalyst samples. A reduced catalyst activity was found, mainly in the samples from bed 1 and bed 4.

Based on the output of the catalyst study, a custom-made catalyst loading was designed, including installation of fresh caesium-promoted VK59 catalyst in the first bed in order to accommodate up to 13% SO₂ in the feed gas. The VK59 will

Fig. 4: Pressure profile of bed 1 between major maintenance of smelter (MMF)



Source: Topsoe

also improve the operational flexibility of the plant, which is critical to AP2 due to the variation in the inlet gas conditions. In bed 3, a partial replacement of the catalyst was made, and in bed 4 the high activity caesium-promoted VK69 catalyst was installed in the top of the bed in order to improve the conversion to 99.85%.

The catalyst was installed in AP2 during the 2010 shutdown. During the shutdown, it was discovered that the floor of bed 1 had collapsed in several locations (see Fig. 3), probably due to high pressure drop.

The high pressure observed in bed 1 is believed to be related to the unstable operation in the first year of operation. Fig. 4 shows how the rate of pressure drop build-up has been reduced from 2010 compared with the previous operation periods. By comparing the change in pressure drops between shutdowns, it is found that the pressure drop increase is around 25% slower after the 2010 shutdown.

In August 2012, a new TOPGUN analysis was performed in AP2. The TOPGUN measurements confirmed that the modifications carried out during the shutdown in 2010 significantly improved the performance of AP2. In particular, conversion across the beds having undergone

partial change of catalyst back in 2010 had increased, which could be observed directly as a significant increase in overall conversion of the plant (see Fig. 5 for 2010 and 2012 TOPGUN results).

Based on the TOPGUN measurements, it is possible to estimate the overall conversion at 100% production, and the calculated conversion of 99.81% is just short of the predicted value back in 2010 of 99.85%. However, the TOPGUN analysis also revealed the presence of a bypass, resulting in around 2% of the unconverted feed gas being shortcut to bed 4. If the contribution from the bypass is removed in the simulation, the overall conversion of the plant reaches 99.89%, slightly above the 2010 prediction. The simulated values with and without the bypass are presented in Fig. 2.

The catalyst loading from 2010 resulted in a significant reduction of SO₂ emissions. Since 2010, the plant has been operating with both improved pressure drop and significant reduction in SO₂ emission. The second TOPGUN analysis in 2012 showed that the plant was operating at a conversion rate of above 99.80%, however, even higher conversion is achievable if leaks are identified and repaired.

CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

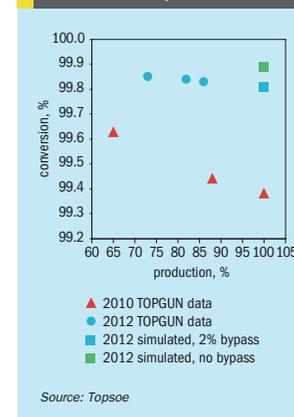
COVER FEATURE 3

Emissions reduction in sulphuric acid plants

COVER FEATURE 4

Seven deadly sins of tail gas treating

Fig. 5: SO₂ conversion in AP2 before and after the 2010 shutdown at various production rates



Source: Topsoe

Reference

- Jurado K. and Vognsen M.: "Southern Peru's Ilo Smelter meeting SO₂ emission requirements at high load", Sulphur 2012 Conference, Berlin (Oct 2012)

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Next issue: July/August 2018

- Sulphur forming project listing
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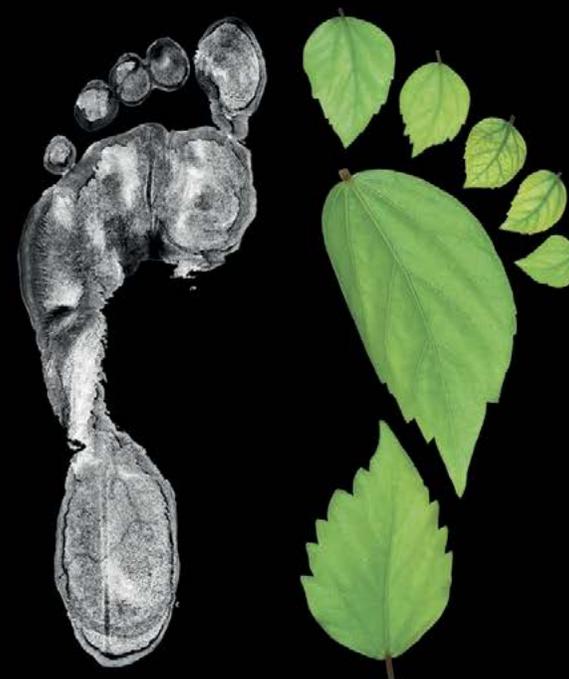
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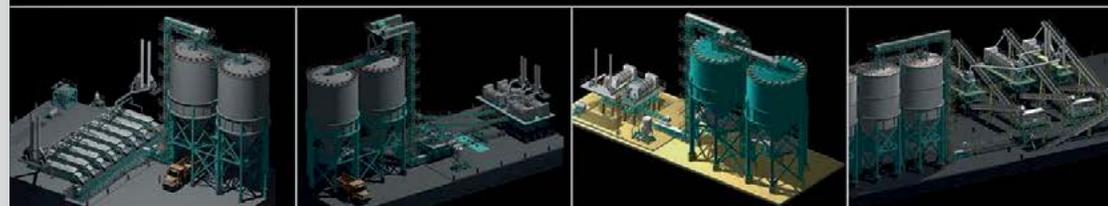
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CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper
in Southeast Asia

COVER FEATURE 2

New Asian refining
capacity

COVER FEATURE 3

Emissions
reduction in
sulphuric acid
plants

COVER FEATURE 4

Seven deadly sins
of tail gas treating

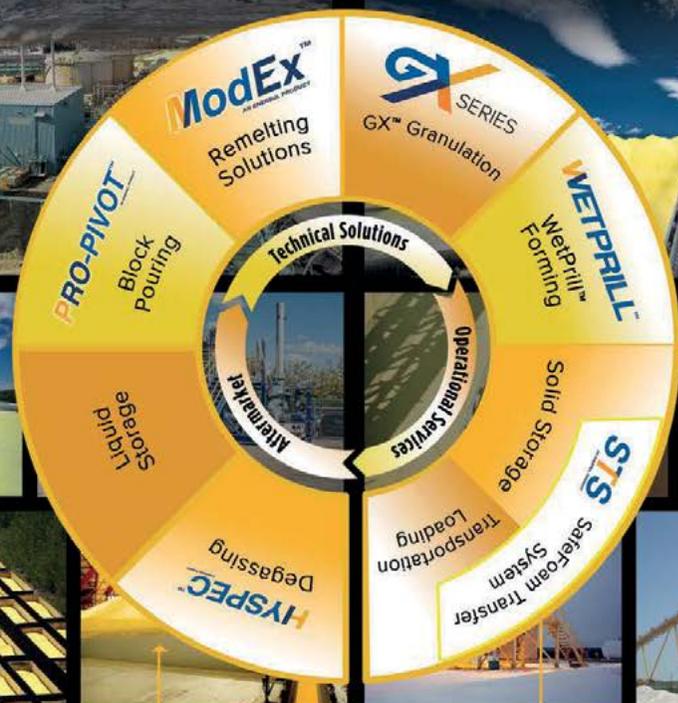
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CONTENTS

What's in issue 376

COVER FEATURE 1

Nickel and copper in Southeast Asia

COVER FEATURE 2

New Asian refining capacity

COVER FEATURE 3

Emissions reduction in sulphuric acid plants

COVER FEATURE 4

Seven deadly sins of tail gas treating

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ISSUE 376
MAY-JUNE 2018

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