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Number 371

July | August 2017

SULPHUR

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Sulphur market overview

China's sulphuric acid industry

Acid catalyst upgrades

Improving performance with simulation

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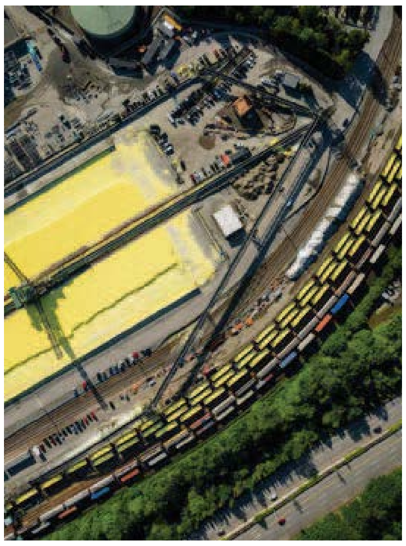
NUMBER 371 JULY | AUGUST 2017



Cover: *Sulphur awaiting shipment, Vancouver, Canada. Overflightstock Ltd/Alamy Stock Photo*

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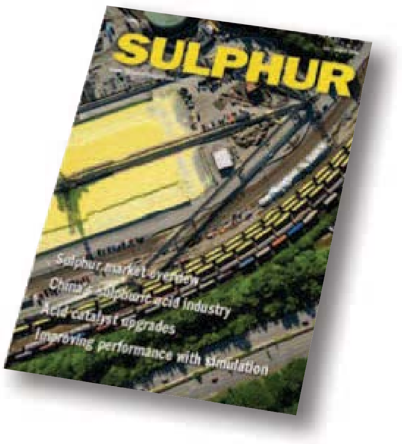

An age-old problem

On April 26th, Port Manatee in Florida suffered its second sulphur fire in ten days. The first fire, on April 17th, reportedly was due to a fire in a truck spreading to three small piles of sulphur nearby, and lead to the temporary closure of the nearby Highway 41 while the fires were dealt with. The second, on April 26th, was said to be caused by an electrical spark from some cleaning apparatus accidentally striking a piece of metal, igniting sulphur dust, and the subsequent fire led to the hospitalisation of five workers due to inhalation of sulphur dioxide. The sulphur handling area, owned by Logistec Gulf Coast, imports sulphur mainly for use by Mosaic at its nearby phosphate facility, and has now been shut down for a sprinkler system to be installed.

> **"An entire city ended up burned to the ground because of a sulphur fire.**

The fact that these kinds of incidents continue to happen, sometimes with far more serious consequences that the relatively minor fires at Port Manatee, are a result of the perennial issue of sulphur's flammability, especially sulphur dust, often produced when granules have been crushed by the wheels of low loaders, or rough handling in transport and storage. This is not, of course, a new problem, but rather an age-old problem which the industry must still contend with on a daily basis. However, just how old a problem it truly is was brought home to me recently by a friend's historical researches. This report which she found, from an Italian eyewitness account of the siege of the German city of Magdeburg in the late stages of the Thirty Years War, comes from 1640. Here an entire city ended up burned to the ground because of a sulphur fire in an apothecary's shop resulting from a carelessly unattended match:

"the Citie was in short time sacked and burnt to ashes: which hapned by the carelesenesse of a Souldier, who throwing aside his Musket with the Match lighted, to get up the stairs in a Drugsters house, the Match set fire on a barrel of Brimstone, and this taking hold of other cumbustable matters, the fire did so dilate it selfe, as the houses being built of wood all was destroyed."

The two incidents, although they are separated by a gap of over 375 years, show that for all of the advances we have made in the intervening centuries, on occasion we may still have things to learn about the safe storage and handling of sulphur, and for that reason it's worth reminding ourselves now and again of the hazards it can engender, and ways in which those can be minimised. Perhaps the best starting point is the US National Fire Prevention Association (NFPA) standard, NFPA 655, 'Standard for Prevention of Sulfur Fires and Explosions', which "establishes requirements to eliminate or reduce explosion and fire hazards encountered in the crushing, grinding, and pulverizing of bulk and liquid sulfur, and to the safe handling of sulfur in any form". It can be consulted online at www.nfpa.org, and provides a wealth of useful advice on handling sulphur in all forms, as well as particularly stressing the importance of good housekeeping in preventing fires which can quickly get out of control. It is not the most thrilling read, to be sure, but nevertheless it is of vital importance to anyone involved in the routine handling of sulphur.

Sulphur is generally a relatively inert, harmless substance, and it is easy for familiarity to breed contempt when dealing with it. However, the occasional cautionary tale ought to be cause to remember that sulphur fires can be devastating, and it must always be treated with respect.

Richard Hands, Editor

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Price trends

MARKET INSIGHT

Meena Chauhan, Research Manager, Integer Research (in partnership with ICIS) assesses price trends and the market outlook for sulphur.

SULPHUR

Market support

The downturn in the sulphur market during the second quarter stalled on the back of unexpectedly tight regional supply and the return of spot interest in China in June. One of the main issues on whether the firmer footing will be sustained is the downstream processed phosphates market, which has taken a softer turn. The short term view is for firm to stable sulphur prices, with downward pressure likely to re-emerge as the third quarter progresses, particularly if phosphate prices remain subdued. One of the market bears for the final quarter of 2017 is the start-up of sulphur exports from the Kashagan project in Kazakhstan. The first cargo is expected to be available in September. Meanwhile, the other major project on the horizon – the RasGas Barzan project in Qatar – is not likely to start up until 2018.

Producer prices in the Middle East in June reflected the more stable turn in sentiment. In the UAE Adnoc announced its Official Selling Price (OSP) at $82/t f.o.b. – rolling over its May posting for liftings to India. Aramco Trading also rolled over its price at $80/t f.o.b. Jubail in Saudi Arabia. In Qatar, the price was posted at an increase of $2/t, to $78/t f.o.b. Ras Laffan. Early third quarter prices are expected to be rolled over or see slight firming, likely followed by decreases – due to regional supply issues normalising and ongoing challenges in the downstream markets.

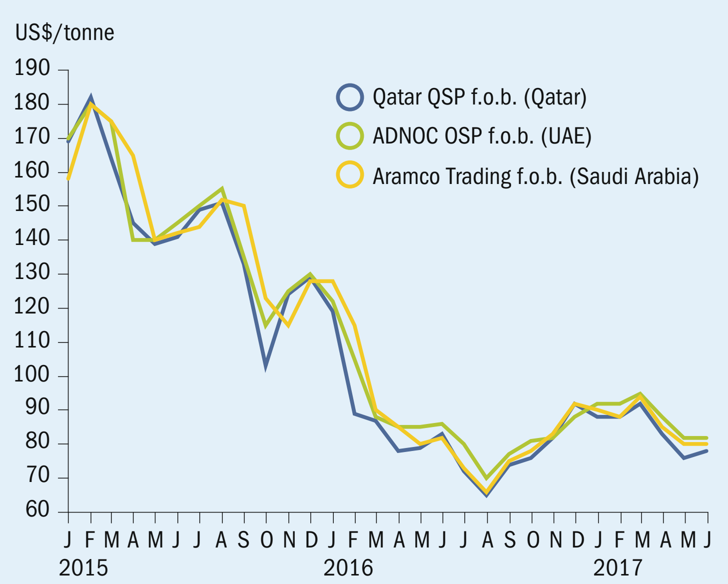
Refinery run rates in China and at gas plants were below expectations in recent weeks, leading to increased interest for imported volumes and local stock erosion. Buyers have been looking to restock ahead of the fertilizer season, boosting recent demand. As a result, China spot prices in June moved back to the mid-$90s/t c.fr to the low $100s/t c.fr in trade from key supply sources – up from the low end of the range at $90/t c.fr in May. Year on year, prices are around 27% higher overall in China, while average prices are similar to those achieved at the start of 2017. Total sulphur inventory at the nine major ports in China dropped down to 1.2 million tonnes but this was expected to stabilise due to the spate of purchasing. Imports to China in January – April show a drop year on year, down by 8% to 3.8 million tonnes, with the weaker sentiment weighing on trade. This is expected see a shift in more recent import levels, with June likely to reflect a boost. For 4M 2017 there has been a slight drop in volumes from Saudi Arabia, down by 1% as well as liquid trade from South Korea (down 4%). Meanwhile, trade from the UAE continues to climb – growing by 36% to over 600,000 tonnes. Canadian sulphur is also rising this year in China, with market share at 11% so far, up from 8% and 4% in 2016 and 2015 respectively.

Indian uptake was slower in June, although prices ticked up on the high end of the range into the high $90s/t c.fr – driven by international developments. As some major buyers were covered for the month of June through private deals, this kept fresh spot interest muted compared to China. Pricing is expected to remain in the $90s/t c.fr in India until there is a round of interest in the spot market. Rising sulphuric acid prices in Asia could motivate some Indian buyers to the sulphur market instead, which in turn would likely lead to an upward price trend.

The focus in Europe has been around the run up to the third quarter contract negotiations, with no firm indications of price points in mid-June. However, market consensus remained that the balance did not warrant any major changes to pricing up or down, with stability the key word across both supply and demand. The approach to the summer season can see a seasonal slowdown in activity in the market, likely to emerge in July.

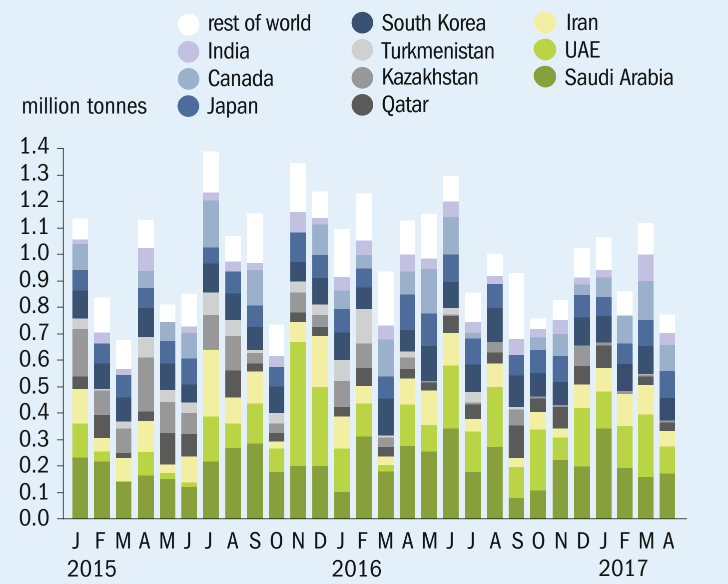
Over in Latin America, Brazilian sulphur imports continue to support spot pricing, with the improvement on 2016 levels showing no signs of abating. In January – May 2017, trade was up by 18% compared with a year earlier and 7% above the period in 2015. The notable boost in volumes has come from suppliers other than the US, the leading supplier to the country. Instead, we

Fig 1: **Middle East sulphur prices, Jan 2015 to Jun 2017**



Source: Integer, ICIS

Fig 2: **China monthly sulphur imports, Jan 2015 to Apr 2017**



Source: Integer, GTIS

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see trade from Kazakhstan and the UAE up by 59% and 64% respectively. Russian and Canadian volumes also continue to rise. The market share of volumes from the US have dipped to 38% in 5M 2017, this compares with 46% a year earlier. The healthy soybean and sugar crop has contributed to the improved demand this year, as well as a general recovery on the downstream markets downturn in 2016.

For the year ahead, the development of the Kashagan project's exports from Kazakhstan will be a major consideration for fresh supply in the market. With the first shipment set to be available for export in September, and around 17% of the full capacity likely to become available in the latter part of the year, this points to the potential for a softer market going into 2018. In 2018, sulphur from the project is forecast at 900,000 tonnes.

SULPHURIC ACID

Firm footing

The global sulphuric acid market continued on its firmer footing through May and June, with prices across major benchmarks creeping up as supply remained stretched. In Europe, export prices for spot reached a height of $25/t f.o.b. in June, on the back of fresh business into Latin America. Single digit prices were no longer achievable from Europe by the second half of June. While the European smelter turnaround schedule this year is quieter than in 2016, a handful of turnarounds has added to the more buoyant sentiment in the market. Atlantic Copper's turnaround in Spain led to a contraction of acid exports from the port of Huelva in May and early June. Boliden is also still scheduled to undergo its maintenance schedule. The supply/demand balance in the European market continues to support pricing, as well as smelter inventories.

The situation in Chile has remained a talking point for pricing, but this is likely to normalise as supply in Latin America returns to more usual levels. The spate of spot purchases in May and into June led to prices rising to the mid-$80s/t c.fr. The expectation is for a softer tone in the second half of the year, particularly in the fourth quarter as annual contracts for 2018 will be under discussion. From July onwards we expect to see stability in supply in Chile and its supply sources, with a downward correction likely for any fresh business.

The firmer sulphur import market to date in 2017 into Brazil has also been seen for sulphuric acid. In the first five months of the year, acid imports were up 16% to almost 250,000 tonnes – above 2016 and 2015 levels in the same period. Shipments from Spain have surged by 36% and remains the leading supply source. Acid from Belgium has also seen significant leaps, up by over 78% to 53,000 tonnes. The drop in trade from Mexico highlights the reduced competition from this export market, also adding to the more bullish tone in the market.

The Northeast Asian market has remained tight – with the market balance pushing prices higher. Availability of spot volumes from Japan and South Korea are expected to remain stretched through the second half of the year, supporting firm pricing for the short term. Interest is noted from end users in Asia for September due to availability concerns but deals have yet to conclude. Japanese acid exports in January – April 2017 were down 14% year on year, at below 900,000 tonnes. The main dip in trade has been to the Philippines and India. At the same time, shipments to Thailand, Chile and China have gained ground. Acid exports from Japan are expected to recover in 2018, likely to lead to softer pricing in the outlook.

Acid shipments to OCP in Morocco are set to see a significant drop in June, despite January – April trade strength. The buyer was heard taking elemental sulphur instead of acid cargoes in the month of June. However, trade is likely to improve in the second half of the year, or when prices ease. In 4M 2017, acid trade to Morocco was up by 50% on a year earlier. May acid arrivals were pegged at around 82,000 tonnes and June is estimated much lower.

Price indications

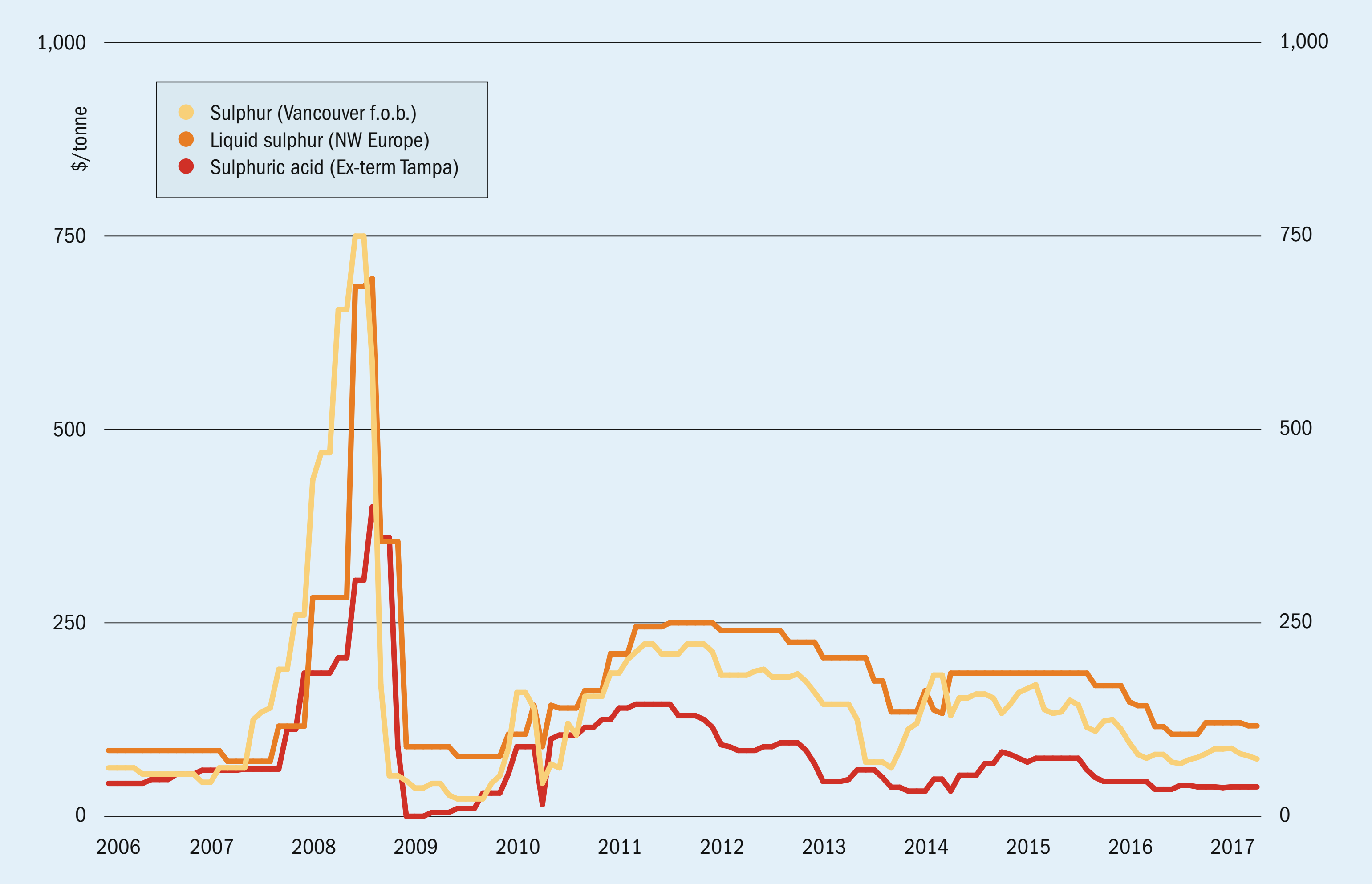
Table 1: **Recent sulphur prices, major markets**

Cash equivalent	January	February	March	April	May
Sulphur, bulk ($/t)					
Vancouver f.o.b. spot	86	88	81	78	74
Adnoc monthly contract	92	95	95	88	82
China c.fr. spot	98	103	98	91	91
Liquid sulphur ($/t)					
Tampa f.o.b. contract	75	75	75	70	70
NW Europe c.fr.	121	121	121	117	117
Sulphuric acid ($/t)					
US Gulf spot	38	38	38	38	38

Source: various

Market outlook

Historical price trends $/tonne



Source: BCInsight

SULPHUR

- Developments at the Kashagan project in Kazakhstan remain a crucial tipping point for length in the market during Q4 2017. We expect to see some impact in the latter part of the year, but 2018 is estimated to see around 900,000 tonnes from the project and capacity rates from 2019.
- China's domestic sulphur production is expected to improve in the coming months but sulphur imports are expected to see improvement in June/July due to restocking and local supply tightness, supporting prices in the short term.
- Middle East producer pricing will set the tone for the start of Q3 – led by demand from China and other key regions. However, a downward correction may ensue later in the quarter unless there is a meaningful recovery in processed phosphates prices.
- Africa and the Middle East are the regions due to grow most significantly in 2017/2018 for sulphur demand – as further processed phosphates capacity is added in Saudi Arabia and Morocco. Meanwhile markets such as China are expected to see very limited growth in the fertilizer sector, slowing compared with the past decade.
- **Outlook:** Firmer pricing is likely to remain the short term, with stability in some regional contracts expected for Q3. However, as we progress through the next quarter, we expect to see the weaker phosphates market weighing on sulphur market, potentially to a downward correction in pricing. The delay of the Barzan project in Qatar provides a temporary reprieve for the Middle East balance. However, other projects such as South Pars in Iran and the Clean Fuels Project in Kuwait will tip the balance in the outlook.

SULPHURIC ACID

- The absence of OCP in the market for June and reduction of acid shipments in May has raised questions over the volume likely to be imported in the second half of the year. Market consensus remains that imports will be in the region of around 900,000 – 1 million tonnes.
- The lack of availability from Northeast Asia will support the market through the rest of 2017, with prices likely to remain strong as Asian demand has been healthy.
- Chinese imports have seen a 5% dip in January – April and this would usually prove a slight market bear. However, due to the tight market balance in Asia, this is unlikely to emerge. Exports from China have been strong to date in 2017 but this may remain firm for destinations in the Asian market due to the limited availability from other producers.
- In North America, turnarounds at smelters in the region led to pockets of regional tightness. Kennecott Utah Copper entered a month long turnaround in May. However, the producer was heard offline at points during June, with production returning to normal later in the month.
- **Outlook:** The acid market is expected to remain firm in the coming months due to healthy demand in Latin America and tight supply in Northeast Asia. Potential weak spots remain China and Morocco, as monthly imports have waned recently.

Sulphur Industry News

GERMANY

Using sulphur to store solar energy

Researchers of Karlsruhe Institute of Technology (KIT) and their partners plan to develop an innovative sulphur-based storage system for solar power. Large-scale chemical storage of solar power will be achieved by means of a closed sulphur-sulphuric acid cycle which, the Institute says, in the longer term might be the basis of an economically efficient renewable energy source capable of providing base-load power. Pre-development work under the auspices of the PEGASUS project will be funded by the EU to the tune of €4.7 million.

The long-term goal of PEGASUS is the development and demonstration of an innovative solar power tower facility. A solar absorber is combined with a thermochemical solar power storage system based on elementary sulphur and sulphuric acid. Compared to previous concepts, this promises to reduce costs significantly. The technology will be tested under real conditions at the Jülich Solar Power Tower Facility (STJ) in Germany. PEGASUS is coordinated by the Institute of Solar Research of the German Aerospace Center DLR. It is planned to develop a lab-scale sulphur burner for stable combustion in the range from 10-50 kilowatts at high power densities under atmospheric conditions and temperatures higher than 1,400°C. Power density in particular allows for the effective use of sulphur as a fuel for electricity production.

"Solar power plants effectively capture process heat and sulphur might be a suitable storage material to use this power for base-load electricity production," professor Dimosthenis Trimis of KIT's Engler-Bunte Institute says. "Although combustion often is associated with fossil technologies, we want to show that it also is an important element in the context of the energy transition."

Elementary sulphur is produced by the conversion of sulphur dioxide into sulphur and sulphuric acid. The focused sunlight of the solar power plant supplies the process heat with the energy and temperature required to close the sulphur cycle and to convert sulphuric acid back into sulphur dioxide in the presence of suitable catalysts.

The current feasibility study will include drafting a detailed flowsheet, and scaling the optimised integrated process up to a 5 MW thermal power level, with development of prototypes of the key components, such as the solar absorber, sulphuric acid evaporator, sulphur trioxide decomposer, and sulphur burner and testing of them at the solar power tower facility. In addition, the materials required for heat absorption, transfer, and storage and for the catalysts of the chemical reactions are planned to be tested for efficiency and long-term stability.

Shell and Sandvil launch sulphur enhanced urea

Shell and Sandvik have launched a granulated urea variant incorporating elemental sulphur fertilizer produced with Shell *Urea-ES* technology, using Sandvik's Rotoform granulation system. The combined technology was tested during a series of continuous plant trials at Sandvik's productivity centre in Fellbach (Germany). Shell's unique technology and the versatility of the Sandvik equipment enables the production of Shell *Urea-ES* granules containing up to 70% of finely dispersed elemental sulphur in a urea matrix. The homogeneous Shell *Urea-ES* emulsion is fed to the Sandvik Rotoform unit and deposited in the form of drops (diameter of 2-4 mm) across a steel belt cooler. Water is sprayed against the underside of the solid steel belt, ensuring no cross-contamination either to product or to water. As the product moves along the steel belt, the liquid droplets are converted into solid pastilles. The final solid product is collected at the end of the belt and sent to the downstream handling system (conveying, storage silo, bagging, etc.).

"We are pleased to collaborate with Sandvik to granulate our new Shell Urea-ES technology products on their robust Rotoform equipment. With this success, more and more fertilizer producers can granulate our urea + elemental sulphur fertilizer to potentially unlock better crop yields and improve soil health," said Michael Lumley, vice president of Shell Sulphur Solutions.

Shell has collaborated with key players in granulation technologies in order to develop solutions for owners of small to medium-sized granulation plants and believes Sandvik's standalone Rotoform granulation equipment provides a fully fit for purpose system to undertake product diversification at fertilizer production sites.

"We believe specialty fertilizers are the future, as they promise not only a win-win situation for both farmers and fertilizer producers, but also contribute to a better environment through effective fertilizer applications. Sandvik offers versatile Rotoform system to manage various formulations. Our collaboration with Shell for the Urea Elemental Sulphur has been a rewarding partnership," said Johan Sjögren, managing director of Sandvik Process Systems.

CANADA

Suncor looking to new oil sands projects

Suncor Energy, Canada's largest oil and gas producer, says that it will make a regulatory application this year to move ahead with a new oil sands project. The Lewis project, 25km northeast of Fort McMurray, Alberta, would most likely be based on steam assisted gravity drainage (SAGD) with co-generation of electricity, and could begin construction in 2021, with first production in 2027. Suncor says that it is targeting 160,000 bbl/d of bitumen production at Lewis. The move is a sign that in spite of some high-profile withdrawals from Canadian oil sands production, there is still an appetite for new projects among the remaining, mainly domestic producers, and confidence in the long-term viability of oil sands production, presumably via an expectation of a longer term rise in oil prices. Suncor, which took a majority stake in Syncrude last year, has also applied for regulatory approval for its 40,000 bbl/d Meadow Creek West project, and recently received approval for the neighbouring 80,000 bbl/d Meadow Creek East project. Shell's exit from the oil sands patch has led to its assets being acquired by Canadian Natural Resources Ltd (CNRL), while ConocoPhillips sold up to Cenovus Energy. Chevron, BP and Total are also rumoured to be looking for a way out of the relatively high cost oil sands business.

Report highlights need for new pipeline capacity

In line with expectations of increased oil sands bitumen production, with Western Canada potentially seeing a 1 million bbl/d increase in supply by 2020, a recent

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report by IHS Markit says that there will be increased pressure on an already constrained pipeline system that has struggled with delays in bringing incremental pipeline capacity online. The report examines the relationship between pipelines and prices, the implication of delay in new pipeline capacity that has occurred in western Canada and the current outlook for the industry. Absent new pipeline takeaway capacity, Canadian crudes will face limitations from the existing pipeline infrastructure as Western Canadian volumes continue to build, the report says. Capacity constraints in the past have contributed to price volatility, a rise of crude-by-rail shipments and a loss of economic value for Western Canadian producers.

A survey of recent major pipeline proposals by the report finds that the length of the pipeline review process (from first application through the end of 2016) has averaged more than five years per project, creating uncertainty for project proponents and western Canadian producers alike. Although the recent approvals of Keystone XL by the Trump Administration and Trans Mountain Expansion by the Government of Canada have returned a level of optimism for pipeline projects, potential for additional delays exists, the report says. If four major pipeline projects (Alberta Clipper Expansion, Energy East, Keystone XL and TransMountain Expansion) advance as currently proposed, they could add 2.9 million bbl/d of new capacity between 2019 and 2022, enough to move Western Canadian pipeline takeaway capacity from shortage to surplus.

Although the United States (the Gulf Coast in particular) remains the most likely market for growing Canadian heavy production due to the regions pre-existing refinery capacity capable of processing heavier crudes, lessons from the timing of Keystone XL and concerns over a possible resurgence of US protectionism have also highlighted the importance of market diversification. As none of the currently proposed pipeline would come online prior to 2019, a resurgence of crude-by-rail shipments out of Western Canada is likely to occur through the end of the decade, the report concludes.

Government to help develop clean oil sands technologies

The provincial governments of Albert, in conjunction with the Canadian federal government and industry partners, are funding three clean technology projects with a combined budget of C$70 million. Government funding of C$26.2 million will be added to $43.3 million from the three companies; Cenovus Energy Inc., Field Upgrading Ltd. and MEG Energy Corp.

The Cenovus project will test a new technology that uses a steam-solvent mix to more efficiently extract oil from a steam-assisted gravity drainage well. The new process will rely largely on the solvent (50-95% of the mixture by weight) and aims to reduce the amount of water required in conventional SAGD. The company says the project could lower the steam-to-oil ratio and reduce energy and water treatment costs.

Field Upgrading plans to carry out a front end engineering design (FEED) study that will serve as a building block for a new demonstration plant. The company is developing a technology known as Desulphurisation & Upgrading (DSU) that removes sulphur and metals from heavy oils and refinery bottoms to produce marine fuel. Using a modular design, the plant would be capable of producing 2,500 barrels per day using less energy than conventional technologies.

The final project also focuses on mproving oilsands bitumen recovery while using less steam. In place of steam, MEG Energy's *eMVAPEX* process uses a light hydrocarbon for injection after the initial SAGD process has been started and bitumen recovery reaches 20-30%. The company estimates the new method could increase production by 70% using the same amount of steam while reducing overall greenhouse gas emissions by as much as 43%.

Bunker fuel desulphurisation technology

Calgary-based Genoil Inc., has signed a licensing agreement with bunker fuel supplier Bomin Group to provide low sulphur fuel oil (LSFO) for ships in anticipation of the MARPOL Annex VI regulations in 2020 which will cap sulphur content of marine fuels at 0.5% worldwide. Genoil's contribution will be its Genoil Hydroconversion Upgrader (GHU), the nucleus of which uses a patented fixed bed reactor which improve the hydroconversion processes, yielding 75% more efficiency than comparable fixed bed reactor technology via better saturation of hydrogen and carbon molecules in the GHU reactor, creating a more stable molecular bond and a better reaction. Genoil says that installation costs are around $30-80 million at existing bunkering installations and can process 1 million t/a of heavy fuel oil into emissions compliant <0.5% sulphur fuel, and claims that this can provide a return on investment in as little as three months with current market spreads. The shipping industry currently consumes over 320 million tonnes of bunker fuel per annum.

The GHU also has a lower footprint than a full refinery unit, measuring as little as 50m x 80m, allowing it to be installed wherever adequate existing infrastructure exists, such as in major bunkering hubs worldwide, receiving terminals, pipelines and ports.

"Shipping continues to face significant financial and liquidity challenges, which is why Genoil is offering its low cost GHU solution for the industry," said Bruce Abbott, president and COO, Genoil Inc. "We have received a high level of interest throughout the industry from many large players who realise that the 2020 deadline is looming, and that they need to develop a cost-effective strategy."

MOROCCO

FLSmidth wins operations contract in Morocco

FLSmidth has won a five-year contract from OCP to operate port equipment for handling phosphate rock, fertilizers, and sulphur. The contract is for the port of Jorf Lasfar, near El Jadida, 100 km south of Casablanca, and will be the company's first operation and maintenance contract in Morocco. FLSmidth was awarded the contract as part of OCP's 'ecosystem' initiative to benefit the local economy by bringing external know-how while hiring local workers.

"We are extremely proud to be awarded this contract. It marks the culmination of a long-standing partnership between OCP and FLSmidth and is an important step in materials handling equipment operations in Morocco. We will deliver productivity enhancement to OCP by operating and maintaining the equipment we have supplied ourselves," said Claus Christian Torbøl, senior vice president, FLSmidth Operation & Maintenance.

GHANA

Fuel sulphur content to drop from 3,000 ppm to 50 ppm

Ghanaian vice president Alhaji Dr Mahamudu Bawumia has announced that, as from July 1st this year, the permissible sulphur content in petroleum products in

Ghana is to be reduced from the current 3,000 parts per million (ppm) to 50ppm in line with a new government policy to help reduce respiratory diseases triggered by sulphur dioxide. Nigeria is also moving to a 50 ppm (‘Euro-IV’) limit to prevent what several West African governments have called dumping of ‘dirty diesel’ from Europe and elsewhere on African markets.

INDIA

New refinery SRUs commissioning

Prasad K Panicker, executive director of the BPCL-Kochi Refinery, says that the refinery’s Integrated Refinery Expansion Project (IREP) which began in 2013 is now mechanically complete, and that five of the nine process units are now commissioned. This includes a new crude distillation unit of 10.5 million t/a capacity, a diesel hydrotreater unit and a vacuum gas oil hydrotreating unit to remove sulphur from diesel and petrol. The delayed coker unit which will recover value-added products from refinery residue steams, fluid catalytic cracker and sulphur recovery unit are “under commissioning”, he said. The refinery’s overall capacity has already risen from 9.5 million t/a to 14 million t/a and will ultimately reach 15.5 million t/a, at a total investment cost of $2.64 billion.

EGYPT

ERC refinery nearing completion

Egypt’s Qalaa Holdings says that it has completed 92% of the works in the Egyptian Refining Company’s (ERC) new refinery project, with investments worth $3.6 billion. The refinery, the largest in Egypt, aims to decrease the country’s diesel import needs by 50%, improving Egypt’s balance of payments, as well as lowering SO_2 emissions by one third. Qalaa plans to complete works and inaugurate the project by the end of 2017, according to managing director Karim Sadek.

IRAN

Progress on refinery upgrades

Feasibility studies on upgrading the Tehran and Bandar Abbas refineries have been completed, according to the deputy head of National Iranian Oil Refining and Distribution Company. Projects to reduce production of residual fuel oil and lower sulphur content of fuels are now awaiting funding and the award of EPC contracts, he told local media. Khosravani said that talks are underway with various potential foreign partners, including Italy’s Tecnimont, China’s Sinopec, Japan’s Marubeni, JGC Corporation and JX Nippon Oil & Energy, as well as South Korea’s Daelim to fund the venture. Iran signed a memorandum of understanding with two Marubeni and Chiyoda last year to lower resid output in Bandar Abbas Refinery in the Hormozgan province, which will see sulphur content of fuels fall to less than 1%. Bandar Abbas accounts for 22% of Iran’s total crude refining capacity, which stands at 1.6 million bbl/d. China’s CNPC is also conducting upgrade work at Abadan Refinery, Iran’s oldest crude oil processing unit, badly damaged during the initial stages of the 1980-88 Iraq-Iran war. SK Group is carrying out a feasibility study on the upgrade of the Tabriz refinery. Iran also finalised a $2 billion agreement with Daelim Corp for the upgrade of the Isfahan Oil Refinery in January to renovate and expand the unit. President Hassan Rouhani has earmarked $14 billion to recondition and improve Iran’s major refining facilities.

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 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56

Sulphuric Acid News

CHINA

Contract awarded for large new acid plant

Yidu Xingfa Chemical Co. Ltd. (Xingfa) has awarded DuPont the contract for the engineering and technology license of a 3,600 t/d sulphuric acid plant. This project will make the Xingfa sulphuric acid plant one of the largest in China. Xingfa is expanding its existing site in Hubei province near Yichang city, with the aim of roughly doubling phosphate fertilizer capacity. The new acid plant will process 1.2 million t/a of sulphuric acid and support the production of an extra 400,000 t/a of phosphoric acid, 400,000 t/a of DAP and 35,000 t/a of potassium phosphate. It will also enable the Xingfa site to meet or exceed the Chinese Ministry of Environmental Protection's emission requirements in the sensitive Yangtze river basin area.

"DuPont Clean Technologies is very pleased to be providing its proprietary *MECS® MAX3™* technology for Xingfa's expansion project to enable the company to become one of the most efficient fertilizer producers in China. This… is not only a significant step for both DuPont and Xingfa, but also for the sulphuric acid industry," said Eli Ben-Shoshan, president of DuPont Clean Technologies.

The acid plant will have both high pressure and intermediate pressure steam generation that will be used to produce electricity and provide heat to the plant. It combines a suite of technologies, including two recent technology breakthroughs – *SolvR®* and *Stea-Max™* heat recovery – in a simplified flow scheme which will produce more than 1.5 tonnes of high pressure steam per tonne of acid; an increase of more than 25% over conventional technologies. ■

Conditional approval for Dow-DuPont merger

China's Ministry of Commerce (MOFCOM) has granted conditional regulatory approval of Dow and DuPont's proposed merger of equals. The is conditional on DuPont and Dow fulfilling commitments given to MOFCOM in connection with the clearance, and continues the progress the companies have made to secure regulatory clearances around the world for their merger. As part of earning European Commission approval, the companies will divest parts of DuPont's crop protection portfolio and research and development pipeline and organisation, as well as Dow's global ethylene acrylic acid copolymers and ionomers business. In addition, Dow and DuPont have made commitments related to the supply and distribution in China of herbicide and insecticide ingredients and formulations for rice crops for five years after the closing of the proposed merger. The companies say that they expect closure of the merger to happen between August 1st and September 1st 2017, with the intended spin-offs to happen within 18 months. The first step of the intended separation process will be the spin-off of the Materials Science Company.

MOROCCO

Focus on Africa at IFA conference

The Moroccan Secretary of State to the Minister of Agriculture, Hammou Ouhelli, opened this year's Annual Conference of the International Fertilizer Association with an emphasis on the important role of nutrients for sustainable agricultural development. Speaking to an audience of over 1,300 representatives of companies throughout the fertilizer value chain and other groups from over 75 countries, he referring to the AAA initiative (Adapting African Agriculture) as a concrete and innovative response to the challenges of climate change, and praised the industry by saying: "with your presence, here today, in Marrakech, you are contributing to the vision of a world without hunger."

His remarks were followed by keynote speeches from Sunny Verghese (CEO of Olam), Christian Witt (senior program officer on Soil Health at the Bill & Melinda Gates Foundation), Rebbie Harawa (Head of Soil and Fertilizer Systems at AGRA) and Dyborn Chibonga (executive director at the National Farmers' Association of Malawi), who addressed the opportunities and challenges for ensuring greater access to fertilizers for African farmers, and the need to ensure more crop- and site specific, balanced and sustainable fertilizer application.

According to the UN FAO, sub-Saharan Africa (SSA) alone is expected to experience a population growth of 180% until 2050, which will require an estimated 170% increase in food production. With an average fertilizer application rate of approximately only 12 kg/ha in 2016 (compared to 110 kg/ha in the rest of the world), there is a vast opportunity to grow the market. Indeed, IFADATA shows that SSA is the region with the fastest growing fertilizer demand: 17-18 kg/ha are expected to be reached in 2021, with regional demand expected to reach over 4.8 million t/a by 2021 (including South Africa) compared to 3.3 million t/a in 2015. Although this would bring the application rate to 17 kg/ha within the next two years, it is still far below the 50 kg/ha recommended by the Abuja Conference in 2006: soil mining, large yield gaps and wide-spread hunger remain key problems for the continent.

The fertilizer industry, committed to doing its part towards the implementation of the Sustainable Development Goals, focuses in particular on bringing the goals of food security and climate change together with market development objectives. "While infrastructure, availability and access are key prerequisites to drive fertilizer consumption in SSA," said Charlotte Hebebrand, Director General of IFA, increased fertilizer application must entail "the efficient and effective use of nutrient inputs and be combined with good agronomic practices to assure that higher yields are not increasing environmental impact and greenhouse gas emissions."

This was also the key message of Ibrahim Thiaw, deputy executive director and assistant secretary general at UN Environment, who, speaking to IFA members in a video address, recognized the critical role of fertilizers for the future of our planet, but does not shy away from a strong call for action on environmental stewardship. Mr Thiaw acknowledged explicitly the already existing good cooperation between IFA and UN Environment and invited also IFA members to reach out directly to UNEP.

INDIA

Titanium dioxide plant ordered shut down

India's Central Pollution Control Board (CPCB) has ordered Travancore Titanium Products Limited (TTPL) to shut down, citing the absence of an effective effluent treatment plant. The sulphuric-acid-based titanium dioxide plant, sited at Vettukad in the state capital, has facing criticism and protests from locals for some time for discharging sulphuric acid effluent into the sea. The order was reportedly issued based on a surprise inspection of the plant earlier this year.

TTPL says that the waste treatment plant is now operational, following a dispute with the contractor over the system's ability to maintain levels of by-products and pH. The effluent should have a near-neutral pH of 7, but had been found to be as acidic as pH1-2. The plant extracts titanium dioxide from ilmenite ore, to be used in the manufacture of various products, including paints, ink, flooring material and other products, generating more than 100 t/d of effluent.

NEW ZEALAND

Chatham to reapply for offshore mining license

Chatham Rock Phosphate, which holds a mining licence for a phosphate-rich area off the coast of New Zealand, is set to reapply for a mining license for the area. The New Zealand Environmental Protection Agency (EPA) refused to give Chatham consent to mine in 2015. The company was seeking to recover up to 1.5 million tonnes of phosphate from deep seabed deposits. However, the seizure of a 55,000 tonne phosphate shipment from Morocco to New Zealand over a sovereignty dispute (see below) has raised concerns over the supply of phosphate to the country, which consumes 1 million t/a of phosphate and has no domestic source, and Chatham believes that this may make the need for its domestically mined phosphate more acute. Chatham also argues that it would reduce New Zealand's carbon footprint and avoid high transport and foreign exchange costs.

PANAMA

Second phosphate carrier held over Western Sahara dispute

Panamanian authorities have detained a Moroccan phosphate shipment because of a legal rotest by the Polisario Front, which seeks independence for the Western Sahara region, currently part of Morocco, where the shipment originated. The shipment, mined at Boucra by Moroccan state phosphate producer OCP, had originated from the port of Laayoune in Western Sahara and was bound for Vancouver, for use by Canada's Agrium at its Redwater, Alberta plant in fertilizer manufacture. Panama detained the Danish-flagged *Ultra Innovation*, chartered by Ultrabulk, because of a legal challenge by the Polisario Front, which claims that the cargo has been transported illegally as the Polisario Front and its self-declared Sahrawi Arab Democratic Republic, had not authorised the shipment. This is the second cargo ship detained – the first, the *NM Cherry Blossom*, was detained at Port Elizabeth in South Africa a couple of weeks previously on its way to New Zealand on the same premise.

The move is a new tactic by Polisario in its long-running campaign against the Moroccan government, and follows a ruling by the European Court of Justice in December 2016 that Moroccan exports to the European Union (EU) from Western Sahara could not benefit from the trade agreements signed by Morocco and the EU. Morocco says that the Western Sahara is legally part of its territory.

Agrium said in a statement that it was aware of the detained phosphate rock shipment in Panama, but did not anticipate any production interruptions at Redwater. ■

People

The Sulphur Institute (TSI) has announced that **Mike Lumley**, general manager, sulphur and ventures for Shell Sulphur Solutions has been elected as TSI's chairman of the board. During the meeting of the Institute's board of directors in Dublin, Ireland, **Jack Cohn**, of Savage Sulphur Services was also named as vice chair.

"We seek to be a unified voice for the sulphur and sulphuric acid industry for all aspects of the businesses impacting our license to operate," said Lumley. The Sulphur Institute is dedicated to its more than 60 members with programs specific to Transportation Regulations, Environment Health and Safety, Information and Advocacy and one committed solely to Sulphuric Acid. Under Lumley's leadership the group plans to demonstrate its value to members, not only in North America, but further developing its interests for its European members and expanding into Central Asia, the Middle East and North Africa.

Mike Lumley

At its most recent annual conference in Marrakesh, the International Fertilizer Industry Association (IFA) elected **Rakesh Kapur** as its new chairman. Mr Kapur is joint managing director of the Indian Farmers Fertilizer Cooperative (IFFCO), one of the largest fertilizer cooperatives in the world, and currently celebrating its 50 year anniversary of continuous support to Indian farmers. Mr Kapur is also currently completing his term as chairman of the Fertilizer Association of India (FAI), and sits on a number of international boards. An ex-Indian Revenue Service officer, he has held various senior positions in government, including as director of the Ministry of Chemicals & Fertilizers, the Telecommunications Regulatory Authority of India and, prior to joining IFFCO, as additional assessor and collector at Municipal Corporation of India. Rakesh Kapur has previously served as chairman of IFA's Production and International Trade Committee, and joined IFA's Executive Board in 2015, when he was also elected as vice chairman and chairman of IFA's Finance Committee.

In his speech to the conference, Mr Kapur said: "I am honoured and delighted to assume IFA's Presidency and will continue to further advance and expand IFA's strategic role in promoting product and nutrient stewardship initiatives around the world and delivering added value through its programs on statistics and market analysis. Under his leadership, my predecessor, Dr Jawahery, has already accomplished major advances in driving the industry's commitment to the Sustainable Development Goals. I pledge to continue this engagement in my new role, and ensure that IFA supports the industry to contribute to the important Agenda 2030 Goals. I am also delighted to oversee the development of a strategic, future oriented outlook for plant nutrition and our industry during my two year Chairmanship."

Mostafa Terrab, CEO of OCP, Morocco, and long-standing Executive Board Member of IFA, haa been nominated as vice-chair.

Oil services group Petrofac has suspended its chief operating officer (COO) **Marwan Chedid** "until further notice" due to an investigation being conducted by the UK Serious Fraud Office (SFO). Chedid has also resigned from the Petrofac board. Chief executive Ayman Asfari, who owns 18% of Petrofac, will remain in post but will be excluded from all matters connected to the investigation. The SFO said on 12 May that it was investigating the company, its employees and agents for suspected bribery, corruption and money laundering. The company's shares fell nearly 30% as a result, from £6.15 to £4.30, wiping £600 million ($775 million) off the company's value. The probe is linked to an investigation of Unaoil, a Monaco-based firm which has been accused of corruptly securing contracts for multinationals.

Calendar 2017/18

OCTOBER

2-6

Phosphate Fertiliser Production Technology, MARRAKECH, Morocco
Contact: International Fertiliser Society, PO Box 12220, Colchester, CO1 9PR, UK.
Tel: +44 1206 851819
Email: secretary@fertiliser-society.org

9-11

MESPON, ABU DHABI, UAE
Contact: UniverSUL Consulting, PO Box 109760, Abu Dhabi, UAE.
Tel: +971 2 645 0141
Fax: +971 2 645 0142
Email: info@universulphur.com

NOVEMBER

6-9

Sulphur 2017, ATLANTA, Georgia, USA
Contact: CRU Events
Tel: +44 20 7903 2167
Email: conferences@crugroup.com

13-15

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

FEBRUARY 2018

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

11-13

AFPM Annual Meeting, NEW ORLEANS, Louisiana, 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

12-14

Phosphates 2017, MARRAKECH, Morocco
Contact: CRU Events
Tel: +44 20 7903 2167
Email: conferences@crugroup.com

26-30

SOGAT 2018, ABU DHABI, UAE
Contact: Dr Nick Coles, Dome Exhibitions
Tel: +971 2 674 4040
Email: nick@domeexhibitions.com

PHOTO: GAZPROM

Sulphur: market stability in 2017

Fiona Boyd and **Freda Gordon**, directors at consultancy Acuity Commodities, take a look at the major developments affecting the sulphur market this year.

Above: Sulphur stockpiles – the way of the future?

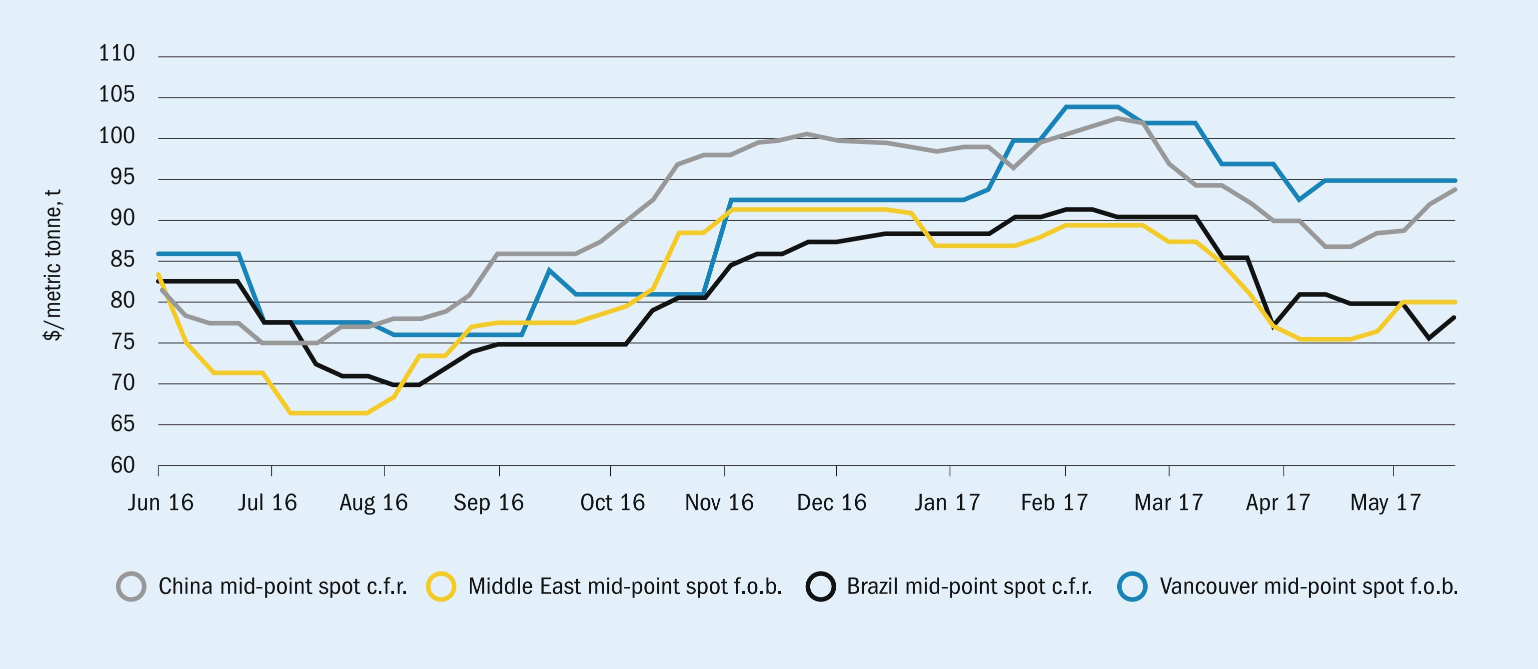
During the first half of 2017, the theme of stability overhung the global sulphur market. This stability is indicative of the global market being relatively balanced following some price volatility in recent years because of tighter supply availability. This article will review the state of the market over the last several months and what the key developments to watch moving forward are.

China

We will look first at China, the world's largest importer of elemental sulphur. As an indication, China imported just under 12 million tonnes of sulphur in 2016 out of the approximately 62.5 million tonnes which Acuity estimates were produced worldwide last year, accounting for 19% of global demand. Because of its significance in the market, price direction there shapes price ideas in most other markets in terms of exports as well as imports. What has been notable since late 2016 is the relative stability of the spot sulphur price in China. As Figure 1 shows, since the beginning of January through early June 2017, the spot price in China has hovered in a $15/t range, spanning $87-102/t c.fr over that five-month window.

In Acuity's view, this stability is indicative of more supply being available on a global basis as new supply has entered the market, and there has been a concerted effort by producers to sell under long-term contracts to reduce exposure to the spot market. As an indication, in order to deal with increasing production from the UAE as a result of the Shah gas project coming on stream in 2015, Adnoc sold more sulphur directly to fertilizer major OCP in Morocco. This meant that China, which buys mainly

Fig 1: **Sulphur prices over the past 12 months**



on a spot basis, benefited from a boost in availability as evident by price direction.

In 1Q 2017 alone, the price in China moved in a narrow $8/t range. This relative price stability is unusual in China and can be further attributed to higher domestic sulphur output from the Puguang gas field. For instance, Puguang was recovering around 5,000 t/d in 1Q17, compared with around 3,500 t/d for the most of 2016 and 2Q17. China's increasing reliance on domestic production has contributed to a new trend for pricing – the import spot price is increasingly influenced by domestic prices at river ports.

There are two other major developments in China which are expected to impact buying behaviour there. First, at the start of 2017 three of the country's largest phosphate fertilizer producers formed the China Phosphate Producer Sulphur Procurement Consortium (CPPSPC). Sulphur purchases for the consumers, Guizhou Kailin, Wengfu Group and Yuntianhua, will be the responsibility of TGO, a company now owned by the three. The purpose of the CPPSPC is to streamline the sulphur procurement process and increase purchasing power. By having one party to negotiate prices with sellers, the chance of the three companies outbidding each other will be eliminated. The management of inventory among the three will also become more flexible going forward. The estimated consumption of the three players is up to 5 million t/a, or about 42% of the volume China imported last year. In the long run, direct contracts with producers will be what CPPSPC wants the most, as this will ensure stable supply at a reasonable price. China is essentially a spot market, as most contracts are quantity-based. To switch from that to potentially quarterly pricing will require some trust building between the buying and selling sides. Time will tell if this can be achieved in the near future.

Outside of the formation of the consortium and its impact, the market is closely watching for any phosphate fertilizer production capacity rationalisation in China. This has long been expected and ultimately could see its sulphur consumption and imports decrease. As an indication, US-based fertilizer major Mosaic said it expects Chinese exports of the leading phosphate products to decline to 7-8 million tonnes this year following a 2.1 million t/a drop in 2016 after record exports were reached in 2015. The primary drivers for the decline, in its view, are environmental pressures on demand for improved air and water quality, as well as its report that 70% of Chinese producers lost money in 2016.

Phosphates

The overall state of the phosphate fertilizer industry is always in focus for sulphur market participants as it is the largest-sulphur consuming sector. However, that focus has intensified this year on the expectations that production could be lowered in China while growth in other regions continues.

In Saudi Arabia, the Waad Al Shamal project is expected to ramp up during the balance of the year, increasing Saudi's domestic sulphur consumption, but also increasing availability of phosphates for the export market. At the same time, OCP in Morocco is continuing its impressive expansion efforts. Its Jorf Phosphate Hub (JPH) project includes up to 10 fertilizer production units, each with a capacity of 1 million t/a of DAP/MAP, to be brought online in two phases. Four complexes are planned for phase one, which is ongoing, with the JPH III under commissioning at present and the granulating and sulphuric acid units already online. JPH III should be fully commissioned in June. As for JPH IV, expectations are for commissioning to begin between the end of 2017 and early 2018. When phase one is operating at normal capacity, OCP's sulphur consumption will grow to 6-6.5 million t/a, growing from an expected 5.5 million tonnes for this year.

While the entry of the new phosphate supply from Morocco and Saudi Arabia should be more readily absorbed if production in China is cut, there are concerns about the amount of supply and competition there will be in the global phosphate market. If this results in downward price pressure, it will certainly influence price ideas for raw materials, including sulphur and ammonia.

Mergers and acquisitions

Meanwhile, there are a few notable mergers and acquisition deals, as well as some potential divestments in the fertilizer sector which could further impact sulphur procurement, both in terms of volume and overall process. First, Mosaic is expected to close on the acquisition of Vale's phosphate fertilizer assets in Brazil this year. If achieved, it will result in Mosaic becoming the largest sulphur buyer in North America and Brazil. Strategic changes as a result of the merger are unknown but with it and Mosaic's 25% stake in the new production capacity in Saudi Arabia, the future of its production assets in the US should be followed.

Also in North America, Agrium and PotashCorp (PCS) are preparing for a merger of equals, also expected to close this year. One of the synergies identified as part of this deal is a potential closure of some phosphoric acid production capacity in Alberta, Canada, which implies reduced sulphur consumption. This is being closely watched in case it results in the need to increase offshore exports from Vancouver. Finally, there have been unconfirmed reports that Pemex in Mexico is looking to divest the Fertinal fertilizer assets it acquired last year, and Petrobras in Brazil is also heard to be considering divesting its assets.

We have also seen some merger activity in the chemical sector, although more of an impact for the sulphuric acid market. One that has significance to the sulphur industry is Mitsui's recent acquisition of Chemtrade Aglobis, finalised in late May. The deal means Mitsui, which owns several molten sulphur vessels including the *Sulphur Genesis* that operates in Europe, has taken over the terminals, trucks and rail car fleets owned by Chemtrade Aglobis in northwest Europe. With an anticipated drop in molten sulphur production as well as consumption in certain countries, there will be major changes in trade flow within Europe in the coming years. With a heavy presence in European sulphur logistics, the new entity will be in an interesting position going forward.

> **Also key to watch is Reliance's petcoke gasification project at Jamnagar in India.**

The potential for further production rationalisation in the industrial chemical sector should also be watched. In some regions, such as Europe, the growth in production from lower-cost regions has caused some market disruption. Take caprolactam as an example; European producers are embracing difficult years ahead with new capacity growing significantly in China, where the price of the end product is highly competitive. One European producer confirms it has been tailoring its caprolactam output according to demand, starting this year. This can result in a reduction of sulphur consumption.

In summary, on the demand side, the most significant factor to watch is merger and acquisition activity as well as production rationalisation in the phosphate fertilizer sector. At present, Acuity has forecast global sulphur demand to grow to 66.6 million t/a in 2021, up around 10% from our 2016 consumption estimate.

Supply

On the supply side, production is forecast to continue to grow, with output from natural gas processing and crude refining continuing to represent the largest sectors of supply, with growth rates for both about equal. This is attributable to an increase in production throughout Asia (central, south, and east), east Europe, the Middle East and some growth in Latin America. Moving forward, production in Africa and North America will remain mostly flat compared with 2016 levels, while production declines will be seen in the Oceania and European regions.

The most notable projects we are watching on the supply side include the Kashagan project in Kazakhstan, which is forecast to ultimately produce around 1.1 million t/a of sulphur. This project came back online this year after a failed start up in 2013, although no sulphur production associated with it had hit the market at the time of writing. The growth in production will increase export availability from the east European region, which had been constrained by no new production in Kazakhstan and the depletion of inventory, as well as supply availability issues from Russia earlier in 2017. Also key to watch is Reliance's petcoke gasification project at Jamnagar in India. The project, expected to start up before the end of the year, has potential to add over 1 million t/a of supply, depending on utilisation rates. India's largest source of supply is the Middle East. Therefore, any drop in import requirements in India would put pressure on Middle East suppliers to seek alternative markets. New domestic production from other refineries in India has also seen Indian buyers relying less on imports since the start of 2017.

Potential for growth is limited in Latin America because of constraints with Brazil, Mexico and Venezuela. In the case of Brazil, corruption at Petrobras is limiting investment ability, while in Venezuela, the domestic political situation is constraining growth despite the country's significant natural resources. Sulphur production has been declining in Mexico since the second half of 2015 and expectations for it to rebound notably in the medium-term are low.

There also constraints in the Middle East, specifically with Iran and Iraq, because of sanctions and the general situation in that part of the world. As June commenced, news that could impact conditions in Qatar emerged; eight countries (Bahrain, Egypt, Libya, the Maldives, Mauritius, Saudi Arabia, the UAE and Yemen) cut diplomatic ties with Qatar on allegations that the country is supporting extremism. While the impact on the sulphur market was being analysed at time of writing, the most notable impact is on land, air and sea contacts between these countries. This is expected to limit the ability to combine sulphur shipments from the region as well putting pressure on freight rates to move up.

At present, Acuity has forecast global supply to reach just over 70 million t/a by 2021, growing about 12% from estimated 2016 production. Because growth in supply has begun to outstrip demand growth, the sulphur market was in a surplus last year after being in a deficit since 2009, reflected by the price stability. The annual surplus is forecast to peak at around 3.5 million t/a in the 2019 through 2021 period, compared with an estimated surplus of 1.9 million tonnes in 2016. It should be noted that while a surplus has been long awaited and forecast, the ramp up and utilisation of new capacity will dictate the actual realisation of new supply. The market will continue to watch producers' ability to accumulate inventory in times of market oversupply. However, if production does reach 70.1 million t/a by 2021 as forecast, the surplus would only represent around 5% of global supply. In addition, when the amount of sulphur in transit or being held in inventory, outside of blocks, or at consumers' sites is considered, the need for significant blocking on a global basis despite the forecast surplus is not anticipated. ■

The future of Chinese sulphuric acid supply

As China continues to produce additional volumes of acid from copper smelting, will the country become a net acid exporter, or will domestic sulphur burning capacity be displaced instead?

Above: The smelter complex at China Tongling Nonferrous Copper in Anhui.

Sulphur consumption in China is dominated by sulphuric acid production from sulphur-burning acid plants, mainly destined for phosphate processing, but China's sulphuric acid production is supplemented by smelter acid, supply of which has been growing rapidly, and there is also still some production from pyrite roasting. While pyrite roasting has been in long term decline for many years, the relative standing of smelter acid vs sulphur-based acid will determine whether China becomes a long-term net exporter of sulphuric acid.

Acid demand

Chinese acid demand is mainly for phosphate fertilizer and other phosphate processing (>60%), but the rapidly growing industrial sector consumes the remainder. Di-ammonium and mono-ammonium phosphates (DAP/MAP) are the two most important phosphate fertilizers, and Chinese DAP production has had a major growth spurt, reaching 17.4 million t/a (product basis) in 2015, a rise of 6 million t/a over the 2010-2015 period. Chinese MAP and DAP production combined totalled 13.5 million t/a P_2O_5 in 2015. However, 2016 saw that figure fall to below 13 million t/a, for a variety of reasons, but mainly because DAP prices fell by 25% during the year, due to a glut of product on the market. China has overbuilt DAP capacity, and has turned into a major exporter to try and deal with the excess capacity within China, and this in turn – coupled with large new capacity additions in Morocco and the Middle East – has brought down global prices and made many Chinese producers unprofitable. In 4Q 2016 DAP prices fell below \$300/t f.o.b. China for the first time since 2009. The upshot has been production curtailments in China, and some permanent closures. This in turn has helped shake out less productive capacity and raised operating rates, but in essence Chinese phosphate production is set to plateau, with consumption being capped from 2020.

With phosphate consumption plateauing, new acid demand is likely to come

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instead from the industrial sector. While in other sulphuric acid consuming industries like caprolactam, China is also struggling with overcapacity, China's continuing industrial expansion, albeit at a lower rate than during its rapid industrialisation of the early 21st century, should still create fresh acid demand over the coming years.

Sulphur imports

The rapid growth in Chinese sulphur-burning acid capacity has led to a rapid ramp-up in sulphur imports over the past two decades, reaching 12.2 million t/a last year, representing over one third of all global traded sulphur. The figure for 1Q 2017 was 3.1 million tonnes, indicating that imports remain at high levels.

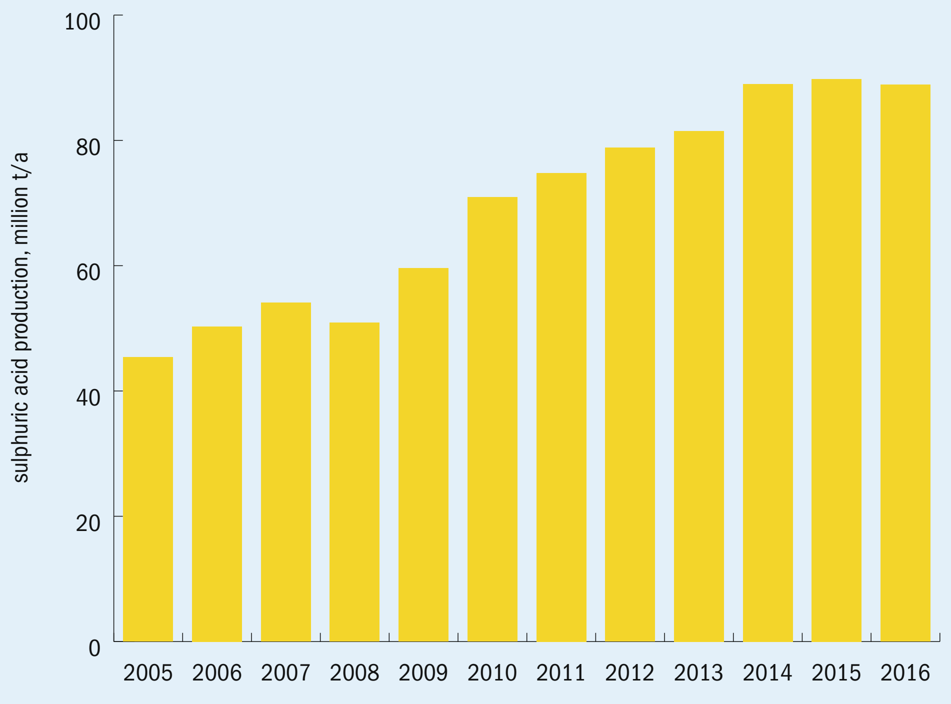
One recent development, prompted by the collapse in DAP prices and industry rationalisation, is the formation of a sulphur-buying consortium by three of the 'big four' largest phosphate producers; Yuntianhua Group (with a 45% stake in the new purchasing company), Guizhou Kailin (40%), and Wengfu Group (15%). The strategic cooperation agreement, signed in February 2017, formed a sulphur purchasing consortium called Tianji Resources. According to the companies, this is a necessary counterbalance to rising sulphur prices at a time of falling fertiliser prices, since the cost of sulphur accounts for about 30% of their total production costs. The three enterprises are responsible for one third of China's sulphur demand. There are indications that the purchasing consortium has already led to c.fr sulphur prices in China falling.

Sulphur production

However, set against this rise in imports is a rise in Chinese domestic sulphur production. Sulphur production from sour gas has been rising, as discussed elsewhere in this issue. The latest news about Chevron's joint venture with CNPC at Chuandongbei Phase II is that it will come on-stream during the third quarter of this year, boosting Chinese sulphur production by around 400,000 t/a. China is also boosting refinery capacity. China's total refining capacity will increase 4.6% to 15.8 million bbl/d in 2017 and net crude oil imports will rise 5.3% to 6.8 million bbl/d, according to China National Petroleum Corporation (CNPC) forecasts. However, China processed only 10.8 million bbl/d of oil in 2016 according to the National Bureau of Statistics, meaning that one third of China's refining capacity is effectively surplus. About 4.5 million bbl/d of capacity is made up by small, independent refineries, also known as 'teapots'. Government policy is evolving on this, as it has in many areas. In 2015 China seemed to be moving to support teapots, which typically run at low utilisation rates, allowing them to import crude and export refined products, and their utilisation rates moved from 30-40% to 60%. Now however the government seems to be changing tack, worried about environmental issues and tax evasion by teapot refiners, and it is trying to squeeze excess capacity out of refining by cracking down on them.

Either way, sulphur recovery is expected to see a boost over the comping years, reaching over 9 million t/a by 2020. Integer Research puts Chinese sulphur recovery up 70% over the coming five years from its present figure of around 7.5 million t/a. At the same time that consumption from the phosphate industry is plateauing, this should lead to a steady fall in Chinese sulphur imports.

Fig 1: **China's sulphuric acid production, million t/a**



Source: National Bureau of Statistics of China

Acid production

Chinese sulphuric acid production was 88.9 million t/a in 2016, actually a fall of 0.8% on the figure for 2015. This means that China now represents 36% of the world's sulphuric acid output. As Figure 1 shows, between 2005 and 2012 production increased rapidly, by nearly 9% year on year, in line with Chinese industrial growth. Much of this fast pace of growth was due to the rapid expansion of non-ferrous metal smelting, although in order to support increased production of phosphate fertilizers, as well as to provide extra electricity generation, a number of large-scale sulphur-burning acid plants were also built. Something like 10 million t/a of sulphur burning acid capacity was constructed over the past five years. In 2014, 45% of China's sulphuric acid production came from sulphur burning acid plants, 30% from smelter acid, and still a surprisingly high 25% from pyrite roasting. While pyrite roasting remains in relative decline in the long term, credits from the iron component of iron pyrites, with the metal slag being sold into the steel industry, have kept it afloat through times of lower acid prices.

Geographically, much of China's sulphuric acid output is concentrated in Hubei and Yunnan provinces, with 7.8 million t/a and 14.2 million t/a of production respectively in 2016, according to the Chinese Natinoal Bureau of Statistics. Guizhou, Sichuan, Shandong and Anhui also produce 6-7 million t/a each of acid. Yunnan, Hubei, Guizhou and Sichuan are major fertilizer producing regions and capacity there is dominated by sulphur burning plants, while Shandong is a coastal chemical producing region, and Anhui has a lot of smelter capacity. In spite of some consolidation in recent years, the industry remains relatively fragmented; there are over 420 producers of sulphuric acid in China.

Smelter acid

Smelter acid capacity has come to occupy an ever-greater share of China's acid production. China's insatiable demand for copper for a variety of industrial uses has been the source of about 75% of this smelter capacity, and the acid has often gone into a myriad of other industrial processes (such as caprolactam manufacture for fibres) as well as fertilizer. According to the International Copper Study Group (ICSG), China has four out of the five largest copper smelters, and nine of the 20 largest. The five largest alone collectively represent 3.15 million t/a of copper smelting capacity, or about 12% of global copper capacity. As can be seen from Table 1, these nine smelters between them represent 4.65 million t/a of copper capacity, or a potential sulphuric acid output of 14 million t/a. Chinese copper production from smelters reached 7 million t/a in 2015, representing 21 million t/a of sulphuric acid production.

China's copper demand rose rapidly during the years of its breakneck industrialisation, with copper going into wiring for large scale electrification programmes, consumer goods, industrial production etc. China has come to represent 47% of all refined copper consumption. However, Chinese copper production is one of the few areas where domestic refined production has lagged behind demand, and China has had to make up the remainder with imports.

Chinese copper demand is continuing to increase, and the government projects in the current Five Year Plan that it will rise from 11.5 million tonnes in 2015 to 13.5 million tonnes in 2020 – an annual growth rate of 3.3%. While this is considerably down on historical trends of around 9% year on year from 2010-15, it nevertheless has provided a much-needed boost to the global copper market, which had been languishing at low prices. The global copper market is expected to begin rising again from 2017-18, as overcapacity in mines is gradually taken up by new demand in China.

> **"Chinese copper demand is continuing to increase.**

The most recent figures available show that Chinese apparent consumption of copper actually fell by 6.5% in Q1 2017, according to ICSG figures. However, this masks an increase in its production of refined copper by 7% over the same period, and imports as a consequence fell by 35%. China is thus still in a programme of import substitution with its copper smelter capacity, and hence it is continuing to build new copper smelters even though the pace of Chinese industrialisation has slowed considerably and copper consumption has plateaued for the time being.

Chinese smelter acid capacity has increased by a tremendous amount over the 2010-15 period – an estimated 4 million t/a of copper or 12 million t/a of acid. A further 5-10 million t/a is expected to come on-stream over the 2016-2020 period. Something like 70% of all new smelter acid capacity is being added in China over the next few years.

Table 1: **China's largest copper smelters**

Producer	Location	Copper capacity
Jiangxi Copper Corp	Guixi, Jiangxi	900,000 t/a
Jinchuan Non Ferrous Co.	Fengchengang, Guangxi	650,000 t/a
Daye Non-Ferrous Metals Co.	Daye, Hubei	600,000 t/a
Yunnan Copper Industry Group.	Qingyuan, Guangdong	500,000 t/a
Baiyin Nonferrous Metals	Baiyin, Gansu	400,000 t/a
Tongling Non-Ferrous Metals Group	Tongling, Anhui	400,000 t/a
Jinlong Tongdu	Tongling, Anhui	400,000 t/a
Xiangguang Copper	Shifo, Yanggu	400,000 t/a
Shandong Fangyuan	Dongying, Shandong	400,000 t/a
Total		**4,650,000 t/a**

Source: ICSG

Effect on imports

Smelter acid production is involuntary; smelter operation tends to depend only on the copper market and not the acid market. For this reason, smelter acid is produced as long as the smelter is running and must find a home somewhere. Pyrite and sulphur burning acid capacity is not voluntary, and if acid prices fall too low relative to the price of sulphur, then there are obviously incentives for sulphur burners to switch to buying acid rather than producing it. During 2013-14, high global sulphur prices and low international acid prices encouraged a degree of substitution by producers. In 2017, sulphuric acid prices are back at their lowest levels for three years, but sulphur prices are much lower now than they were in 2014 on the back of new capacity from sour gas, and so the incentive for substitution is much lower.

China has maintained net imports of sulphuric acid for many years, though these have fallen over the past two decades as new acid capacity additions in China have kept pace with increasing demand. In the early years of the century acid imports sometimes ran as high as 6 million t/a, but these have declined to around 1 million t/a, with a slight pick up in the past couple of years; Chinese acid imports were 1.2 million tonnes in 2015 and 1.5 million tonnes in 2016. However, this is forecast to be lower in 2017 as smelter acid production increases.

Looking to the medium term future, this increase in smelter acid production is projected to lead the Chinese acid market into surplus by 2020, and by 2025 Integer Research is forecasting a 1.5 million t/a acid surplus for China in spite of potential pressure on pyrites and sulphur-burning capacity to switch. This is likely to considerably reshape the acid market in East Asia. The decline in acid imports into China has already pushed Japanese, Korean and Taiwanese acid into other markets, from Chile to the Philippines, but if China becomes an increasingly significant exporter of acid, this will force producers to look ever further afield for markets. ■

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 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56

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 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56

Sour gas project update

Sulphur production from sour natural gas will continue to be the largest slice of new sulphur capacity over the next few years.

Sulphur from processing sour natural gas – initially in western Canada and the US – was responsible for the sea change in sulphur production, moving from on-purpose Frasch mining from underground sulphur deposits to involuntary production from recovered sulphur. While Canada's fields have declined over the past couple of decades, as fields mature and cheap US shale gas undercuts more expensive sour gas production, expertise gained from these wells has now moved to other regions of the world.

Sour gas production is now concentrated in three main regions. In the Middle East, gas demand for power generation for rising populations and fast-growing cities is leading rapidly rising consumption in e.g. Saudi Arabia and the UAE, while much domestic gas production in the region is from associated gas, and hence constrained by OPEC oil quotas. Non-associated gas fields are mainly sour in Saudi Arabia, Abu Dhabi and Oman, and this is driving increased production of sour gas.

In Central Asia, the impetus has come mainly from oil and condensate production, where sour gas extraction is mainly from associated gas fields, and hence the sour gas processing is in many ways incidental to the oil production that is driving it.

The third main region is China, where as in the Middle East gas demand far outstrips supply, and so China is turning to unconventional gas of all types to try and meet the gap, including shale gas, tight gas, and coal-bed methane, but also sour gas production. Additionally, sulphur extracted from sour gas assists with China's growing domestic sulphur deficit for fertilizer production.

Middle East

Much of the Arabian Gulf has offshore highly sour or moderately sour gas reserves, in areas claimed by Saudi Arabia, Iran, Qatar and Abu Dhabi, but the gas fields extend under most of the western United Arab Emirates (UAE) and across into Oman in the east. Ample supply of gas from sweeter sources meant that most of these fields were left untapped for many years, but pressure of demand from rapidly expanding economies in Saudi Arabia and the UAE is now starting to lead to widespread exploitation of these sour gas resources. Foremost among the developers of these projects has been the Emirate of Abu Dhabi.

Habshan

Habshan is the home of Abu Dhabi's Integrated Gas Development, which processes offshore gas from Umm Shaif/Das Island, as well as the Bab onshore oil field and non-associated sour gas from the Habshan fields. The Habshan V processing plant started up in 2013, adding a further 5,200 t/d of sulphur capacity, taking the site to just over 10,000 t/d in total.

Shah

Shah is a $10 billion joint venture between Adnoc (60%) and Occidental (40%) for an onshore sour gas field 210km southwest of Abu Dhabi city, deep in the desert. The reservoir at Shah is approximately 20-30 tcf, with an H_2S content of 23% (and 10% CO_2). Shah came on – stream in 2015, at capacity produces 540 million scf/d (5.2 bcm/year) of sales gas, requiring it to process almost 1 bcf/d of sour gas from the wells. Sulphur production capacity is >9,200 t/d (3.1 million t/a).

The success of Shah has led to plans for an expansion at the site. Current plans are that capacity will be expanded by 50% to 2021, taking total gas processed to 1.5 bcf/d, and a similar sized expansion by circa 2026, taking gas processed to 2.0 bcf/d. This will of course increase sulphur output to 4.5 million t/a and 6 million t/a respectively. Design work on the first stage is currently being conducted by Amec Foster Wheeler.

Bab

Bab is an onshore field 120km SW of Abu Dhabi. It was originally conceived as a mirror of the Shah project, with Shell as the joint venture partner instead of Occidental. However, since Shell's withdrawal in January 2016, Bab's development seems to have gone to the back burner, with the Shah expansion taking precedence. Bab has a CO_2 content of 15% and H_2S content between 15-50%. The gas here is also rich in condensate, which it was hoped would offset the high costs of production.

Hail/Ghasha

The Hail and Ghasha fields are offshore, 100km to the west of Abu Dhabi city Target production here is 1 bcf/d gas with 15% H_2S content, yielding around 400-600 million scf/d of sales gas. Costs of development are higher than for Shah because the field is offshore, albeit in shallow water only 15m deep, but H_2S levels are lower. Al Hosn Gas has been appointed by Adnoc to appraise and develop the project, and a FEED tender was issued November 2016.

South Pars

South Pars is the Iranian side of the massive North Field which sits astride the Arabian Gulf; at 1,500 tcf the largest gas field in the world. In spite of delays caused by international sanctions, Iran has been steadily progressing through the 29 project phases, all of which involve gas and condensate recovery and many of which involve sulphur production. The H_2S content of the South Pars field is only 0.5-1.0%, but the large volumes of gas being processed mean that sulphur production could still be considerable. In 2016 Iranian sulphur production from sour gas from all sources was estimated at 1.3 million t/a, and by 2019 this is expected to rise to 1.8 million t/a.

North Field

On the Qatari side of the field, gas is brought ashore to the massive complex at Ras Laffan, on the northern tip of the Qatar peninsula. Gas is processed for LNG export, export via the Dolphin pipeline to the UAE, and for use in the massive Pearl and Oryx gas to liquids plants at the site.

Rasgas and Qatargas between them export 77 million t/a of LNG, making Qatar the largest LNG producer in the world. Sulphur recovered from all of these facilities is sent to the Common Sulphur Facility where it is formed and exported. Sulphur recovery and forming capacity is approximately 4 million t/a in total, with actual production in 2015 being 2.2 million t/a. Qatar had blocked new gas developments for several years in an attempt to manage its gas supplies until the development of the $10.4 billion Barzan LNG project.

Barzan is owned and operated by state producer Rasgas, and its 6 LNG trains will be fed by 1.7 billion scf/d of gas and condensate in the first phase, rising to 2.5 bcf/d of natural gas by the third and final phase. Start-up at Barzan was delayed by pipeline leaks into 2017, and it is not yet clear what impact there may be from the current sanctions being imposed on Qatar by Saudi Arabia, Kuwait, Bahrain and the UAE. An additional 800,000 t/a of sulphur will be recovered at capacity from the gas destined for Barzan, taking output at Ras Laffan to 3 million t/a.

Wasit

The Wasit gas plant in neighbouring Saudi Arabia was built to process gas from the offshore Arabiyah and Hasbah sour non-associated gas fields. Total gas processing capacity is 2.5 billion scf/d to produce 1.7 billion scf/d of sales gas. H_2S content averages 4-8%, and the sulphur recovery section includes a total capacity of 4,800 t/d of sulphur (1.6 million t/a). Start-up began in 2016, reaching full production in July 2016.

Fadhili

Fadhili is another sour gas processing plant, designed to process additional gas from the Kursaniyah and Hasbah sour gas fields. Target production has been increased to 2.5 billion scf/d, with start-up now pushed back to the end of 2019. Sulphur production will be 4,000 t/d at capacity (1.3 million t/a).

There is also another Saudi gas plant starting up this year, at Midyan, but this will be processing sweet gas with no targeted no sulphur output.

Oman

Oman has two major sour gas processing projects. The first, Yibal Khuff Sudair, is operated by Petroleum Development Oman, a company majority owned (60%) by the Government of Oman, with additional participation from Shell (34%), Total (4%) and Partex (2%). Khuff is a deep oil and associated sour gas deposit beneath an existing field, with an H_2S content for the gas of 3%. An 85,000 t/a sulphur recovery plant is due for completion this year, and commissioning of the gas project is expected in 2019.

The other project is the Rabab Harweel Integrated Project, a joint venture between PDO and Petrofac. Again gas is 2-3% H_2S with start-up expected in 2019. In the first phase, sour gas from the Rabab gas field will be injected into the Harweel oil reservoir for enhanced oil recovery, and no sulphur production is projected.

Central Asia

The area of sour gas exploitation in Central Asia is mostly around the Caspian Sea region, in Russia to its west, Kazakhstan to its north and east, and the zone of sour oil and gas reserves extends further south east into Turkmenistan and Uzbekistan. Onshore deposits in Russia and Kazakhstan are the longest standing and most mature, with discoveries going back to the 1960s and exploitation to the 1980s, while new exploration has focused on offshore reserves in the North Caspian and onshore reserves into Turkmenistan.

Asktrakhan and Orenburg

Russia already has two major sour gas processing plants. The first is at Astrakhan on the west side of the Caspian Sea, which processes highly sour (up to 25%) gas from the Krasnoyarsky gas/condensate field, operated by Gazprom. Sulphur output here averages around 4.8 million t/a, and represents most of Gazprom's output, mainly destined for export. The second is at Orenburg, a Soviet era gas processing plant which also processes production from across the Kazakhstan border at Karachaganak, which is run by KPO, a consortium consisting of ChevronTexaco, Agip, BG, Lukoil and KazMunaiGaz. Total sales gas production at Orenburg is 1.5 bcf/d, and H2S content averages 2-6%. Sulphur production of 1.1 million t/d is mainly for domestic use within Russia. Sour gas is also reinjected, and the Karachaganak Phase 3 project, currently scheduled to be on-stream in 2022, will mostly involve sour gas reinjection.

Tengiz

Tengiz in Kazakhstan, on the northeast side of the Caspian Sea, processes associated gas from oil production at the Tengiz field, both offshore and onshore. The operating company here is the TengizChevroil (TCO) joint venture, in which Chevron has a 50% stake, ExxonMobil 25%, KazMunaiGaz 20%, and Russia's Lukoil 5%. The H_2S content of the gas has varied considerably, but has settled at around 16% H_2S. Some sour gas is reinjected to boost oil production, but sulphur output is running at about 2.4 million t/a. TCO had produced large stockpiles of sulphur but these have been mostly drawn down now. An expansion project will lift oil output from 600,000 bbl/d to 850,000 bbl/d by 2022 but the aim is to reinject the sour gas into the reservoir, so again there is unlikely to be extra sulphur production.

Kashagan

The greatest variable among the Central Asian sour gas processing plants is Kashagan. Kashagan is a very large offshore oilfield with a very deep (4.2km) high pressure reservoir and very sour (17%) H_2S associated gas. Difficult conditions such as winter ice and the high partial pressure of H_2S have posed problems for the North Caspian Operating Company (NCOC) which is developing the project, a consortium of ExxonMobil, Shell, Total, KazMunaiGaz, Inpex, CNPC (which bought out Chevron's stake), and led by Italy's Eni. The massively expensive ($46 billion at last estimate) and long-delayed project finally came on-stream in late 2013, but sour gas leaks and pipe corrosion have forced the replacement of the entire double pipe system which brings sour gas from the artificial island where the wells are to the onshore processing plant. Oil production began again in late 2016, but the acid gas has so far been flared. Start-up of the sulphur recovery section is expected in September 2017, with 1.1 million t/a of additional sulphur production at capacity.

South Yolotan

Meanwhile, in Turkmenistan, there is another large reservoir (700 tcf according to some estimates, making it the world's second largest gas field, though not all is recoverable) at South Yolotan, and other, smaller nearby fields like Dauletabad and Shatlyk. The Galkynysh processing plant came on-stream in September 2013 and is expected to be recovering 1.8 million t/a from 3 billion scf/d of gas with an H_2S content of 6%, once full capacity is achieved.

At last report production had reached 50% of capacity at Galkynysh.

China

China's sour gas fields are mostly in the southern province of Sichuan. Most of the fields were discovered in the late 1990s, and exploration and discovery continued throughout the 2000s, with China's rapidly rising demand for natural gas driving large scale exploitation in the past few years. The move is likely to change China's sulphur picture dramatically.

Puguang

China's first sour gas field to be exploited was Puguang, where there are 410 bcm of reserves with an H_2S content of around 15-17%. The Puguang sour gas processing plant, operated solely by Sinopec, became operational in 2011, and has a maximum gas processing capacity of 1.2 bcf/d, at which point sulphur output would be 3.3 million t/a. Last reports put sulphur output at Puguang at 2 million t/a.

Yuanba

Another field operated only by Sinopec, Yuanba is of similar size to Puguang – estimates say 210 bcm – but extremely deep; the field is over 7.5 km down in places, and averages 6.7km deep. The H_2S content at Yuanba is lower than Puguang, at 5%, but the high pressure makes the demands upon the equipment just as severe. There are two phases to the Yuanba development, each of which will process 1.7 bcm/year of gas. The first phase began operations at the very end of 2014, and the second phase in late 2015. Total sulphur output from both phases is expected to be 300,000 t/a.

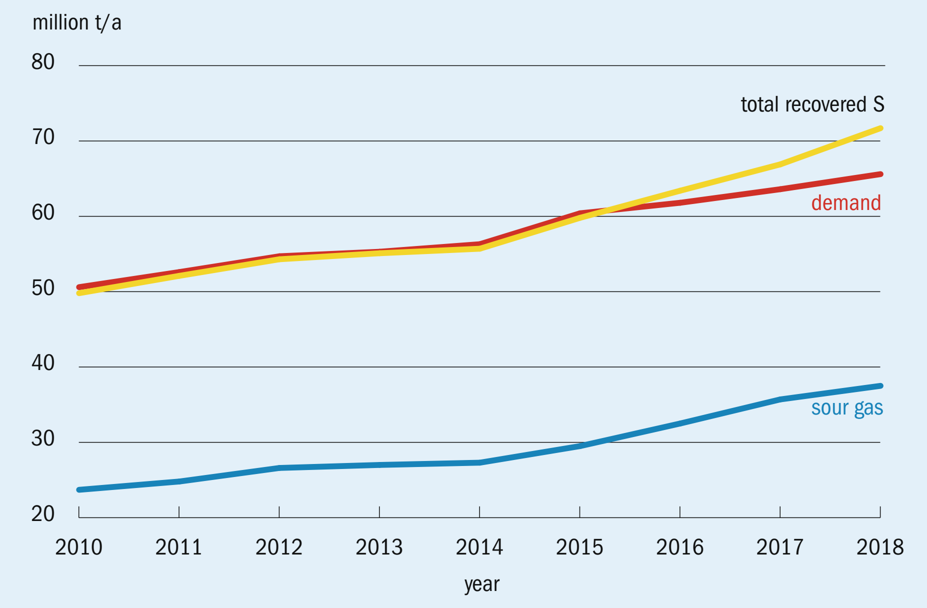
Chuandongbei

Chuandongbei is one of the few sour gas projects in China with foreign participation, in this case Chevron, who have a 49% stake in the project against China National Petroleum Corp's 51%. Total proved reserves at Chuandongbei are put at 6.3 tcf, with H_2S content between 7-11%. Development of Chuandongbei is in three phases, with gas arriving from the Luojiazhai and Gunziping fields in phase 1, and later the Tieshanpo and Dukhouhe-Quilibei fields. The first phase, with 260 million scf/d of processing capacity, reached capacity in April 2016, with the second phase starting late this year, and the third to follow in 2018-19. Sulphur output will be ca. 400,000 t/a in each phase.

Table 1: **New sour gas projects**

Project	Country	Sulphur output at capacity	On-stream date
Middle East			
Shah Expansion	Abu Dhabi	+1.6 million t/a	2021
Hail/Ghasha	Abu Dhabi	2.0 million t/a?	2022?
South Pars	Iran	+0.5 million t/a	2019
Ras Laffan	Qatar	+0.5 million t/a	2017
Wasit	Saudi Arabia	1.6 million t/a	2016
Fadhili	Saudi Arabia	1.3 million t/a?	2019
Khuff/RHIP	Oman	0.1 million t/a	2019
Central Asia			
Kashagan	Kazakhstan	1.1 million t/a	2017
South Yolotan	Turkmenistan	+0.9 million t/a	2020?
China			
Puguang	Sichuan	+1.3 million t/a	2019?
Chuandongbei	Sichuan	1.2 million t/a	2016-2019
Canada			
Various	Alberta/BC	- 0.5 million t/a	2016-2021

Fig 1: **Sour gas as a proportion of total recovered sulphur**



Total recovered sulphur

Table 1 shows all of these projects and their projected recovered sulphur production at capacity. In theory this could result in an extra 11 million t/a of recovered sulphur from these sour gas projects alone over the next few years, even taking into account some decline from western Canada. Figure 1 shows the effect of this against projected sulphur recovery from refineries and other sources, and demand from fertilizer production and industrial uses. While the time taken for projects to come on-stream can vary considerably, and Kashagan is an indication of how long delays can become, there is still a projected overcapacity in sulphur production over the next few years, and this will probably lead to some moving to storage in areas more logistically constrained, such as northern Alberta and Central Asia.

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 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56

TSI Sulphur World Symposium 2017

The Sulphur Institute's (TSI's) annual Sulphur World Symposium came to Dublin in April.

PHOTO: DORAM/ISTOCKPHOTO.COM

The Ha'penny Bridge, Dublin.

TSI convened its annual conference at the Gresham Hotel on Dublin's historic O'Connell Street in late April, with 125 delegates attending from across the world. There was a market focus to papers this year, and the opening paper was a global economic outlook presented by **Rodolphe Blavy** of the International Monetary Fund (IMF). The long-awaited recovery is gaining traction, he said but the medium term outlook remains subdued, with risks still skewed towards the downside. Global growth is at a turning point. The risks of deflation are receding, leading to a renormalisation of monetary policy and a sense of market optimism. The IMF has revised global growth projections upwards for the coming year, moving up from 3.5% in 2017 to 3.6% next year. India is projected to go from 7.2% growth this year to 7.7% next, and while China is slowing from 6.6% in 2017 to 6.2% in 2018, this is still relatively strong growth in global terms. Getting the right policy mix is crucial, Rodolphe said. In the US there is optimism and an expansionary fiscal policy, but there are also risks of protectionism under the new Trump government, while a reversal of financial regulation could lead to greater financial risks.

Oliver Kenter of Shell continued with a short overview of current energy market trends, followed by Shell's perspective on the International Maritime Organization's decision to significantly reduce the sulphur content of the fuel oil used by ships by 2020. Up to 3 million barrels/day of high sulphur fuel oil (HSFO) could be displaced, he said, leading to it being discounted steeply. As far as installation of scrubbers went, only 346 vessels had so far been converted. Another 102 are running on LNG and 10 on methanol, but compared to the overall number of ships in service this is still tiny, and up to 10-30% non-compliance has been predicted once 2020 comes around – some owners may prefer to pay the fines rather than buy fuels that have suddenly become very expensive. Domestic bunkering is not part of the IMO regulation, so there could still be room for HSFO use in the Philippines or Indonesia, and there will probably be a focus on the most polluting ships – 30% of vessels consume 70% of all bunker fuel. There could also be some restoration of HSFO demand in the longer term as scrubbing technology becomes taken up more widely.

Freight markets

The cost of transporting sulphur is very much determined by seaborne dry bulk freight markets, and these markets have been through several years of huge overcapacity. **Marc Pauchet** of Maersk examined whether that situation was likely to change. Coal and iron ore shipping continues to dominate the dry bulk market, with sulphur a very minor component, so it remains very much at the mercy of developments in other markets. Freight rates of $80,000 per day were seen for handysize vessels in 2008, but since 2012 this has been below $10,000/day. However, there has been an uptick in 2017, as demand for steel has also picked up, and India is looking towards more coal for power generation. Nevertheless, CAGR for dry bulk commodities is forecast to average just over 2% for 2016-2021, below the 5% CAGR experienced from 2001-16, as China moves to a 'new normal' of lower industrial growth. Meanwhile, in spite of increased scrapping, there remains a glut of capacity in shipping markets, and even though new demand will outpace supply, the market is likely to remain low until at least 2019-20. The sub-Panamax fleet however is likely to see a recovery more quickly than Panamax and larger vessels.

Sulphur editor **Richard Hands** gave an update on sour gas projects. A full version of this can be found elsewhere in this issue, from pages 24 to 26.

Fertilizer markets

The fertilizer sector continues to be the main driver of sulphur and sulphuric acid demand. In a session which looked at both sulphur's use as a fertilizer as well as in the phosphate market, CRU's **Peter Harrison** began with a look at the potential for further demand from sulphur as a fertilizer. He rehearsed the driver's for sulphur's increased use as a fertilizer – its key role in the construction of amino acids and proteins, especially in crops such as canola. At the same time, tightening regulations on sulphur dioxide emissions are lowering levels of sulphur deposition to soils, and the use of fertilizers such as DAP and urea in preference to SSP and ammonium sulphate have also lowered sulphur application levels. The upshot is a deficit in soil sulphur levels which means that the addition of sulphur can more than double the yield of eg canola when applied at the right time in the growing cycle. At present AS and SSP still represent most of sulphur deliberately added to soils, but there has been considerable growth in recent years in 'NPS' (nitrogen-phosphate-sulphur) fertilizers, especially in India, sub-Saharan Africa, Brazil and North America. There are also increasing numbers of new sulphur formulated fertilizers such as sulphur containing urea coming to the market. The prospects seem bright for further sulphur demand for speciality fertilizers.

Mike Nash of Argus Media examined key changes in the global phosphates market and their implications for the sulphur market. The first changes he drew attention to were on the supply side, where there has been an ongoing process of industry consolidation. In China, the four largest producers now account for around one third of DAP production. Permitting of phosphate rock mining has tightened, there has been more focus on environmental concerns, and encouragement of vertical integration. This has allowed more discipline into the DAP market, with less efficient capacity closing and higher utilisation rates and lower exports from existing players. In the US, declining phosphate rock reserves and environmental constraints mean that the past decade or more has seen some players exit the market, such as US Chem, PhosChem and Agrifos. There have been closures, such as of Mosaic's Green Bay plant, and PCS at White Springs, and there have been mergers and acquisitions which have seen Mosaic buy CF Industries' phosphate assets, and PCS now merging with Agrium. US DAP production has fallen from 12.1 million t/a to 9.9 million t/a over the same period, and is now completely owned by PCS and Mosaic.

In Brazil, demand for MAP has risen, reaching 2.7 million t/a in 2016. A more competitive market environment has seen Chinese imports squeezed out and OCP and Mosaic coming to dominate. Global players have been moving into the Brazilian market, with Yara buying Bunge and a 60% stake in Galvani, Mosaic acquiring ADM and in January 2017 Vale's phosphate business, and OCP taking a 10% stake in Heringer. The Brazilian fertilizer sector is now mostly in the hands of Yara, Mosaic, Heringer and Fertipar.

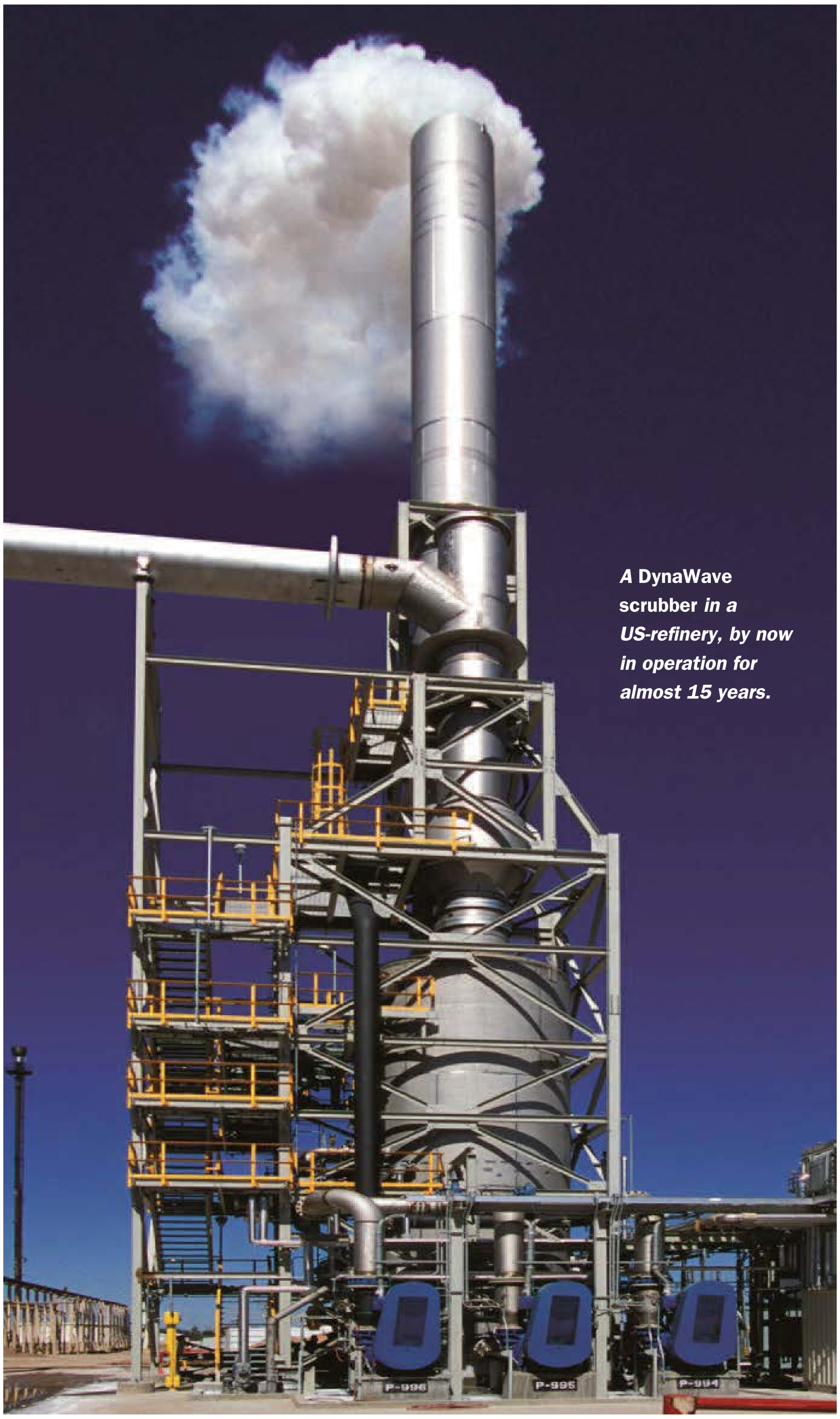
Indian imports have not grown, but the source of those imports has gradually shifted, with China now providing more than half of them, and Saudi Arabia much of the rest. The DAP market is seeing what Mike described as regionalisation – US DAP exports no longer travel as far afield, and aside from India are directed mainly into the Americas. Europe is dominated by Russian and Moroccan exports, and OCP meanwhile is moving in on African markets in a big way, via several joint ventures or subsidiaries in Rwanda, Ethiopia, Nigeria etc. Africa remains the region with the largest growth potential for phosphate demand.

As far as the implications for the global sulphur market, Mike noted that China and Morocco have become the main sulphur import hubs, accounting for just over half of the merchant market for sulphur, and in North Africa at least, sulphur prices move in lockstep with DAP prices. Chinese sulphur prices also show high correlation with DAP prices. Morocco's MAP/DAP expansion plans have global significance, he said, as it is ideally positioned to serve Africa and the Americas, and has 80% of the world's phosphate reserves, while Chinese DAP production is set to continue to plateau, with further industry consolidation likely. Saudi Arabia is also becoming a global player.

Sulphur and sulphuric acid outlook

The final paper of the conference, looking at both sulphur and sulphuric acid markets, was jointly presented by **Fiona Boyd** and **Freda Gordon** of Acuity Commodities. Acuity's views on the global sulphur market can be found elsewhere in this issue, from pages 17 to 19. On the sulphuric acid side, there are more phosphate projects likely in South America, especially Brazil, and of course Morocco and Saudi Arabia, while the nickel market continues to be important in Oceania. There has been no noticeable impact yet from the copper price firming from November 2016. The development timescale for projects in Peru are key for acid availability from that region. While smelter acid shortages in North America may lead to increased imports, there is extra availability elsewhere in the Americas, and potential new capacity in Mexico. Japanese and Korean acid exports have moved away from Chile and now focus on India and southeast Asia. ■

Controlling refinery SO_2 emissions



A DynaWave scrubber *in a US-refinery, by now in operation for almost 15 years.*

PHOTO: DUPONT/MECS

DuPont Clean Technologies describes two wet scrubbing options to help refiners meet increasingly more stringent sulphur dioxide emissions legislation even during start-up, shut-down and maintenance conditions.

Refiners around the world are facing stricter emission limit requirements from national or regional bodies. The recent sulphur emission target changes in China are only one of the many examples. EU countries, as well as India are looking into the same matter. On the other side of the Atlantic, the United States Environmental Protection Agency (US EPA) is proposing a new Clean Air Act targeting the emissions of hazardous air pollutants from petroleum refineries. The suggested new rule – RIN 2060-AQ75 – would revise emission control requirements for flares, storage tanks and coking units at oil refineries, as well as eliminate emission limit exemptions during start-up, shutdown and malfunction (SSM) periods.

In the drive to continue satisfying market demand, the refining industry has also had to increase production from unconventional oil fields with heavy oil fractions. That has resulted in products with higher sulphur content, increasing the need for desulphurisation technologies. Refiners, therefore, now have to address a triple challenge: process increasingly sour crude while simultaneously reducing emissions and increasing output. That is not an easy task, particularly in the current market.

Abatement technologies

Many refiners struggle to control emissions effectively and efficiently. Common sources of airborne pollutants in a refinery are:

- Fluid catalytic cracking unit regenerators (SO_x, NO_x, particulates)
- Claus plants, with or without tail gas treatment units (H_2S, SO_x)
- Sulphuric acid regeneration units (SO_x)
- Fluid cokers (SO_x, NO_x, particulate)
- Fired heaters (SO_x, NO_x, particulate)
- H_2S flares (H_2S)
- Power plants and boilers burning HFO, coal, petroleum coke (SO_x, NOx, particulates)

In order to tackle this challenge, DuPont Clean Technologies offers two complementary, proven scrubbing systems as a solution for refiners who need to cut SOx emissions and/or need to control particulate emissions efficiently. By reducing atmospheric emissions of H_2S, SO_x, NO_x and particulates from major refinery sources, the *BELCO® EDV®* and the *MECS® DynaWave®* wet scrubbing systems together provide a holistic solution that makes air pollution control easy and reliable. Refiners that have installed such scrubbing systems have been able to handle the liquid and solid by-products of scrubbing with their existing on-site facilities and practices.

The *BELCO* wet scrubbing technology is well suited and widely used for treating flue gas from fluid catalytic cracking unit regenerators, fluid cokers, fired heaters and boilers. Its unique open-tower design and special non-plugging features control all emissions in a single upflow tower, eliminating the need for separate devices to individually control particulate, SO_x and NO_x emissions. The *DynaWave* wet scrubbing technology is a Claus tail gas treatment unit (TGTU) supplement or, in the case of small SRU's (lower than 50 t/d capacity), even an alternative to the Claus TGTU itself. By injecting the caustic liquid counter-current to the gas flow, this scrubber type will work under much higher liquid to gas ratios than conventional caustic scrubbers. This unique feature allows the scrubber to handle much higher acid levels and therefore operate even when the upstream TGTU is in start-up, shut down or malfunctioning ('SSM') mode. In addition, *DynaWave* technology is widely used in sulphuric acid regeneration units and is perfectly suited to treat H_2S flares. With the combination of these complementary refinery scrubbing technologies, DuPont Clean Technologies believes that it offers an integrated solution to refiners' environmental needs.

Continuous emissions control

An unscheduled shutdown of a major refinery process unit is not an option for the majority of refiners. Process units are expected to operate 24 hours a day, 365 days a year for multi-year operating campaigns. Whatever the scenario, emissions must be minimised while product is generated and sold to the market. *BELCO* technology is a proven and robust technology that can reliably control FCCU regenerator flue gas emissions in a single upflow scrubber tower for years of uninterrupted operation. With over 140 units licensed on FCCUs worldwide and additional systems on other major refinery processes (fluid cokers, fired heaters and boilers), this low energy wet scrubbing system has been recognised by oil refineries around the world as the leading scrubbing technology in its field. The *BELCO®* Technology supports FCCU operating campaigns typically running 3-5 years or more of uninterrupted operation, providing continuous emission controls with no maintenance shutdowns. This allows refiners to keep the FCCU running at all times, while controlling flue gas emissions and keeping emission control costs as low as possible, so they can focus on production.

> **An unscheduled shutdown of a major refinery process unit is not an option for the majority of refiners.**

Flexibility in use

As a result of the new regulations, oil refiners will not only have to meet air emission requirements for sulphur plants during normal operations, but now also during SSM periods. They must operate under these constraints while meeting production goals. In many regions that includes operating the facility continuously and reliably for a minimum cycle of four to five-years, and generating products that meet the market's quality expectations in an economically viable way. This had led a large number of refiners to consider parallel trains to assure continuous reliability, but is this cost really a necessity?

DynaWave technology is the only wet gas scrubber technology that makes it possible to fully bypass the Claus unit or the Claus tail gas treatment unit directly to the incinerator and still meet emission limits at the stack. *DynaWave* is >99% efficient in removing SO_2, which can bring emissions down to ultra-low levels under any given circumstances at the upstream sulphur plant. It offers a very reliable and easy to operate, low capital investment solution with a minimal footprint. The high on-stream reliability is proven in more than 400 installations in various industries worldwide. The technology combines gas quench, SO_2 removal, particulate elimination and sulphite oxidation all in one vessel, making it ideal for some of the most demanding applications. Around two dozen installations were specifically designed for sulphur removal tail gas treatment applications within refineries. Recently, *DynaWave* was integrated in an existing Claus unit design for a facility in the Middle East. Here, acid gas flaring in all possible operating scenarios, including start-up to shut-down and maintenance, will not lead to an increase of SO_2 emissions. Other operating examples like this exist in other regions like East Asia and North America and more new designs are being engineered as we speak in those regions, as well as in North-Africa

New refineries in Africa and Asia are currently also being designed to include both wet scrubbing technologies from DuPont Clean Technologies to meet environmental requirements under any given circumstance and to achieve continuous and reliable operation.

Conclusion

Emission control technologies must support refining production goals. Refineries must be able to operate continuously and reliably in order to meet market demand for quality and cost without generating emissions that violate regulations. By treating the main sources of SO_x emissions in the refinery segment with *BELCO EDV* and *MECS DynaWave* wet scrubbing technologies, DuPont Clean Technologies offers an integrated technical solution to SO_x emissions control for both new and existing refineries all around the world. ■

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 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56

Catalytic reduction of SO_2 to sulphur using natural gas

In recent years the urgency to solve the problem of sulphur utilisation from waste metallurgical gases has increased dramatically. **O.G. Eremin** and **A.V. Tarasov** discuss pilot investigations conducted by the State Research Institute of Non-Ferrous Metals (Gintsvetmet) in Moscow, Russia, to study the process of catalytic reduction of SO_2 using natural gas.

The Gintsvetmet Institute, in conjunction with the Norilsk mining and metallurgical plant, has formerly developed a high-temperature method of sulphur recovery from metallurgical waste gases, which was implemented on an industrial scale. However, this method of obtaining sulphur has a significant drawback, that is, the increased consumption of expensive natural gas (1,000 m^3 NG per tonne of S obtained). A reduction in the specific consumption of natural gas and an increase in the economic efficiency of the technology for sulphur recovery can, however, be achieved by using an active catalyst. The use of catalysts allows the reduction temperature to be decreased from 1,300°C to 750-950°C and the natural gas consumption to be reduced by 25-30%. This article reports on the results of pilot studies for the catalytic reduction of SO_2 using natural gas and an active alumina catalyst.

Laboratory studies have been previously conducted for the recovery of sulphur from sulphurous gas with a content of 25-35% SO_2 for application to metallurgical gases from autogenous smelting processes. These studies enabled Gintsvetmet to determine the optimal physicochemical process conditions for sulphur recovery. It was found that the catalytic reduction of SO_2 proceeds at a temperature of 750-950°C and a space velocity of 500-1,000 h^{-1}. The SO_2 conversion to sulphur was 60-65%, which corresponds with the equilibrium data. In order to develop the technology further, a pilot installation was built at the Ryazan experimental plant with a capacity for 1,000 m^3/hour. The pilot tests enabled Gintsvetmet to determine the effect of the oxygen concentration in the process gas on the catalyst temperature, the optimum space velocity with an industrial catalyst and to work out a process scheme to manage and recover a gas that is suitable for further processing to sulphur via the Claus process.

Test results with a catalytic reactor

The process for the catalytic reduction of SO_2 to sulphur using natural gas has been studied both in Russia and outside Russia. Noteworthy are the works of Russian scientists N.F. Yushkevich, V.A. Karzhavin and A.V. Avdeeva[1-3]. Recent studies conducted at Gintsvetmet have confirmed the potential of this technology for the recovery of sulphur from metallurgical waste gases[4-7]. New technical solutions to solve the problem of disposing of sulphur from flue gases from nonferrous metallurgical processes have been developed based on studies conducted under semi-industrial conditions.

Currently, due to increased environmental requirements, the relevance of these works has increased substantially and there was a need to continue research to develop technology to recover sulphur from waste gases from autogenous processes. Laboratory and pilot plant testing was therefore carried out using methane in a catalytic process to recover sulphur from the exhaust gases of Vanyukov furnaces.

In catalytic reduction studies, the objective was to determine the degree of conversion of sulphur dioxide to sulphur at various temperatures, the optimal temperature of the catalyst, the optimum space velocity, as well as achieving stable operation with fluctuating gas composition and other parameters. The space velocity of the process is defined as the amount of process gas passing through the catalyst bed volume of 1 m^3 for one hour. It should be noted that the source gas was prepared by mixing calculated quantities of concentrated sulphur dioxide, nitrogen and air. Gaseous sulphur dioxide was obtained by evaporation of liquid SO_2. It is possible to produce a source gas with a composition that corresponds to that of flue gas from autogenous smelting processes.

The reactor was a brick-lined vertical cylindrical vessel with a diameter of 2 m and a height of 5.5 m. The inner diameter of the reactor was 0.9 m. The catalyst was loaded on a heat resistant ceramic grate. The height of the catalyst bed was 1.4 m.

The reactor was heated with an ignition burner by burning natural gas with air. The reactor had five sample points for gas analysis by a chromatographic method.

The first gas sample was taken directly above the catalyst, the second, third and fourth samples were taken at different heights within the catalyst bed and the fifth sample was taken after the gas had passed through the catalyst. The experiments were conducted using five thermocouples which carried out continuous measurements of the temperature at different heights in the catalyst bed. A granular alumina catalyst with a granule size of

Table 1: **Sulphur dioxide conversion to elemental sulphur (η %) in a catalytic reactor (space velocity: 700 h^{-1})**

Temperature in catalyst bed, °C		Initial gas composition, %			Chemical analysis of gas after the reactor, %							η %
Middle layer	Bottom layer	SO_2	O_2	N_2	O_2	N_2	CO	CO_2	H_2S	COS	SO_2	
920	930	12.09	11.60	72.71	1.00	79.95	-	13.44	1.65	0.30	3.66	57.81
930	950	13.05	11.00	72.16	0.77	77.03	0.09	15.70	2.54	0.59	3.26	54.14
910	950	14.20	10.22	71.56	0.68	78.08	0.12	13.07	5.53	1.11	1.32	48.64
900	900	13.56	10.49	71.97	0.80	78.40	0.30	12.60	4.80	1.00	2.10	46.53
900	910	15.35	10.05	70.56	0.80	75.20	0.20	16.60	4.40	0.90	1.90	56.00
910	930	16.12	10.04	69.89	2.60	76.70	-	13.30	2.70	0.60	4.10	58.13
900	910	15.46	9.94	70.53	1.40	77.70	0.20	13.30	5.20	0.90	1.20	57.15
920	840	15.32	10.22	70.43	0.89	74.81	0.40	13.59	5.22	1.07	2.30	54.58
925	860	15.41	10.30	70.41	0.89	74.16	0.15	15.83	4.91	1.07	2.97	51.03
955	910	16.35	10.41	69.14	0.89	74.70	0.16	16.18	3.59	0.82	4.01	52.35
910	920	15.67	9.70	70.33	0.64	78.36	0.08	14.39	4.20	1.07	1.26	62.01
920		14.23	10.32	71.35	0.80	77.80	cπ.	14.70	3.32	0.80	2.55	57.02
910		16.69	9.79	69.63	0.76	74.80	-	17.10	4.76	1.03	1.52	59.24
900		19.27	7.71	69.38	0.58	78.54	cπ.	14.30	3.50	0.73	2.30	70.08
890		18.90	7.74	69.70	5.15	76.46	-	12.00	5.58	0.30	1.52	69.14
average		15.44	9.91	70.65		76.68			4.04	0.81	2.37	56.98

Conversion of sulphur dioxide to sulphur (η%) is calculated in a known manner[5].

4.7 x 6 mm was used in the experiments. This catalyst had a long life in laboratory testing and provided a high conversion of SO_2 to sulphur even at low temperatures of up to 700-750°C. The experiments were conducted as follows: The first stage was carried out by heating the catalyst to a temperature of 850-900°C by burning 15-20 m³/hour of natural gas in a flow of air over the catalyst bed.

Air was supplied to the reactor at a rate of 150-200 m³/hour. After heating the catalyst in the reactor, the process gas containing the calculated quantity of SO_2 was introduced. The composition of the process gas corresponds to the flue gases from Vanukova furnaces. The amount of process gas used in the experiments was up to 250-500 m³/hour. Tests were carried out with initial process gas at different SO_2 concentrations in the range of 12-20%. A separate series of experiments was conducted with an initial SO_2 concentration of 35-45%. The results of the experiments conducted at an average catalyst temperature of 900-950°C and a space velocity of 700 h^{-1} are presented in Table 1. The data obtained indicate that under these experimental conditions the average sulphur dioxide conversion to sulphur is 55%. By increasing the SO_2 content to 18-19%, the conversion increases and reaches 70%. It should be noted that in the high-temperature process, this SO_2 conversion does not exceed 55%.

Fig 1: **Changes in SO_2, H_2S, & CH_4 concentration in catalyst bed**

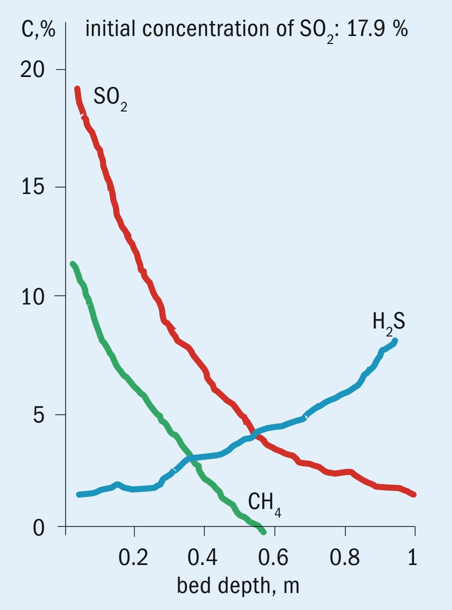


Fig. 1 shows the change in the concentration of SO_2, CH_4 and H_2S at different heights in the catalyst layer in the recovery of sulphur with an initial SO_2 concentration of 17.9%. Similar patterns were obtained when using higher SO_2 concentrations of 20.7% and 30.3 %.

Analysing the experimental data for the change in gas composition along the height of the catalyst bed as shown in the figure, it can be concluded that the top layer of catalyst works most effectively. In the top layer there is a sharp reduction in the concentration of sulphur dioxide and natural gas and the conversion process stops in the middle of the catalyst bed. From this it can be concluded that the catalyst volume can be almost halved, i.e., the space velocity can be increased to 1,500 h^{-1}. As shown in the figure, along with a sharp reduction in the concentration of sulphur dioxide there is a gradual increase in the concentration of hydrogen sulphide.

It is known that during the autogenous smelting of metallurgical raw materials using technical oxygen, the content of SO_2 in the waste gases can be 25-35% and higher. Therefore, experiments were conducted with a high SO_2 content of up to 35%. Figs 2 and 3 present data on the change in the composition of the recovered gas at different catalyst bed depths when the concentration of SO_2 in the source gas is 35.9%.

In this series of tests the experiments were conducted on a gas mixture obtained by mixing 100% SO_2 and air without nitrogen at a temperature in the catalyst 950-1,000°C. The space velocity during this experiment was 750-800 h^{-1}. As shown in Fig. 2, there is a sharp decrease in the concentration of sulphur dioxide and natural gas in the catalyst bed. At a catalyst bed depth of 400 mm, the concentration of SO_2 is reduced by more than 3-3.5 times. At a depth of 800 mm, full interaction of the natural gas was detected. Analysing the data obtained, it is concluded that the reduction of sulphur dioxide by natural gas finishes at a catalyst bed depth of 800 mm. This is confirmed by the change in the concentration of carbon dioxide according to the height of the catalyst bed. In the upper layers of the catalyst (at depths of lets than 800 mm), there is a sharp increase in the content of CO_2 in the gas, and in the lower layers the formation rate of CO_2 is reduced, i.e. the reduction of sulphur dioxide continues over the whole volume of the catalyst.

One can only assume that up to a depth of 800 mm sulphur dioxide is reduced by natural gas, and in subsequent layers the reduction is carried out by by-products of natural gas conversion. This assumption is partly confirmed by the changes in the concentrations of H_2S, COS, and CO at different catalyst bed depths (Fig. 3). At the top of the catalyst bed there is a sharp increase in the concentrations of H_2S, COS and CO, then the rate of formation of H_2S is reduced and the concentrations of COS and CO are reduced. Analysing the data, it can be concluded that the catalytic conversion of sulphur dioxide with natural gas proceeds in two stages. In the first stage at the top of the catalyst bed, sulphur dioxide reacts with natural gas to form S_2, H_2S, COS, CO_2 and CO. In some experiments, the presence of hydrogen at a concentration of 0.3 to 1.0% was detected in the gas. The bulk of the sulphur dioxide is converted in this first stage, since the rate of decrease of SO_2 concentration is much higher than the rate of formation of H_2S and COS. In the second stage, in the lower part of the catalyst, sulphur dioxide is converted to sulphur by carbon monoxide and hydrogen (by-products of natural gas conversion). At the same time, the following hydrolysis reaction may also take place:

$$COS + H_2O = H_2S + CO_2$$

The process for catalytic reduction of sulphur dioxide with natural gas at a space velocity of 700-1,000 h^{-1}, given the height of the catalyst layer enables a relatively high conversion of SO_2 into sulphur (70-72%). Due to the fact that the schemes will have an additional sulphur recovery stage Claus, as indicated above, the process for the catalytic reduction of SO_2 can be carried out at a higher space velocity of 1,200-1,400 h^{-1}.

Fig 2: **Changes in SO_2 ,CH_4 & CO_2 concentration in catalyst bed**

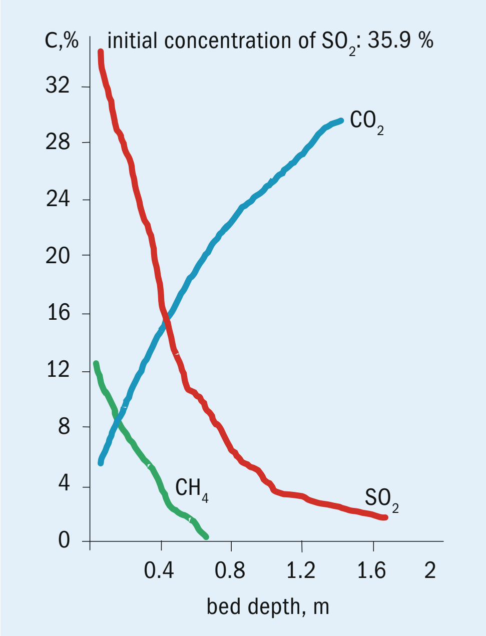
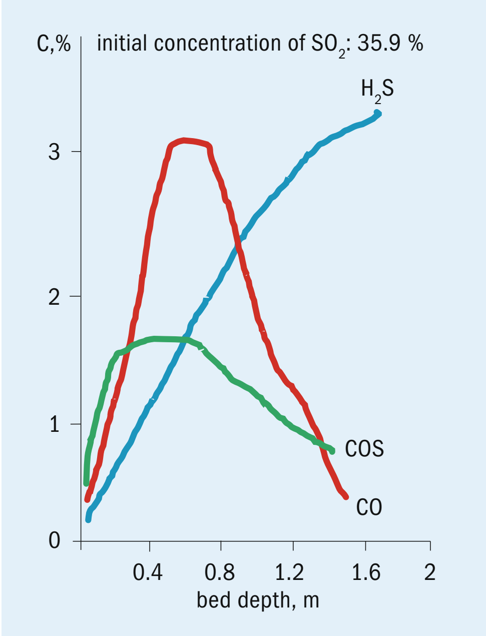


Fig 3: **Changes in H_2S, COS & CO concentration in catalyst bed**



It should be noted that when conducting research the reactor operated in a stable manner even with fluctuating gas composition and gas load in the range of 10-15%. Under these fluctuating conditions the performance of the catalytic reactor remained almost unchanged, which is important in the processing of real metallurgical gases, where the composition is not stable. Pilot plant testing, mainly confirmed previous findings of laboratory studies on catalytic recovery SO_2 natural gas when using as a catalyst of active alumina (Al_2O_3).

Studies have shown that it is possible to enhance the methane method for producing sulphur when using catalysts, enabling the process to take place at lower temperatures (750-950°C) compared to the high temperature process of up to 1,300°C. In addition, it is also possible to significantly increase the space velocity of the process at the temperature of 1,000°C.

Conclusion

It was found that during the catalytic reduction of sulphur dioxide (10-40 % SO_2) over active aluminium oxide at a temperature of 800-950°C, the conversion of sulphur dioxide to sulphur is close to the equilibrium value of 65-67%. It was also found that using the catalyst ensures smooth operation of the process even with significant fluctuations in the composition of the initial gas and gas load, while maintaining a high conversion of sulphur dioxide to sulphur. Apparently, this is due to the fact that the catalyst has thermal inertia, which ensures the stability of the temperature in the reactor even when the SO_2 and O_2 content of the source gas varies by 10-15%. The results of this work will significantly improve the economics of producing sulphur from metallurgical waste gases using the methane method.

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Improve performance with simulation

With the latest advances in simulation and modelling of the acid gas removal unit and sulphur recovery facilities, simulators have become a virtual process plant, providing operators with a useful tool to optimise operations while meeting product specifications and stringent environmental regulations.

Sulphur recovery facilities play an important role in industrial complexes, even if they are not classified as production units. The dangerous nature of H_2S, as well as the severe operating conditions of the sulphur plant make it mandatory to apply the highest levels of process design, operation, personnel and environmental safety for the entire plant life. Plant reliability and availability are also important, since unplanned SRU shutdowns can result in loss of production that cannot be tolerated in current market conditions.

Gas processors and refineries are looking for opportunities to reduce the cost of operations while minimising the risk of unit shutdowns or bottlenecks and meeting regulations that are becoming increasingly stringent. The acid gas removal unit and the sulphur recovery unit (SRU) are expensive, interdependent units necessary for meeting product specification and air emission regulations.

Meeting product and environmental specifications with changing feed conditions can be challenging. To ensure reliable operation, units are typically operated well within specifications. Accurate predictions of the sulphur and carbon dioxide content of the sales gas can allow producers to be confident that specifications will be met, while adjusting the process to minimise energy costs.

Where safety and environmental issues and production rates are concerned, it is important to fully understand how these process units are performing and to adopt the most effective strategy to achieve operational excellence, to minimise operational expenditure (opex) and to guarantee the long term performance of the units while reducing the environmental impact.

Process simulation serves as a means to address challenges in meeting specifications and can aid users to find opportunities for improvements while considering the interconnection of the units, and their performance degradation over time.

Process and simulation models are more reliable, predictive and extrapolative the more they are based on fundamental chemistry, physics and engineering. When calculations were done by hand, slide-rule or calculator, unit operations models relied heavily on empiricism, rules of thumb, and idealisations, without which calculations couldn't be done at all. But today, a cell phone has more computer power than all of NASA had back in 1969, when it placed two astronauts on the moon. Models rooted in fundamental engineering science are not just the way of the future – they are here now, today, and modern computing lets us solve even the most complex process flowsheeting and simulation problems in just minutes.

No simulator can be better than its ability to reproduce the thermodynamic and physical properties of the components and mixtures it purports to simulate. Elemental sulphur is a particularly challenging species because of its many allotropic forms of S_2, S_6 and S_8. And the fact that the average number of sulphur atoms in liquid sulphur is a function of temperature. This is a short chain polymer of variable temperature-dependent length – and H_2S can be in the simple form H_2S or the complex form H_2S_x with quite different solubilities in liquid sulphur.

ProTreat® simulator for gas treatment and sulphur recovery

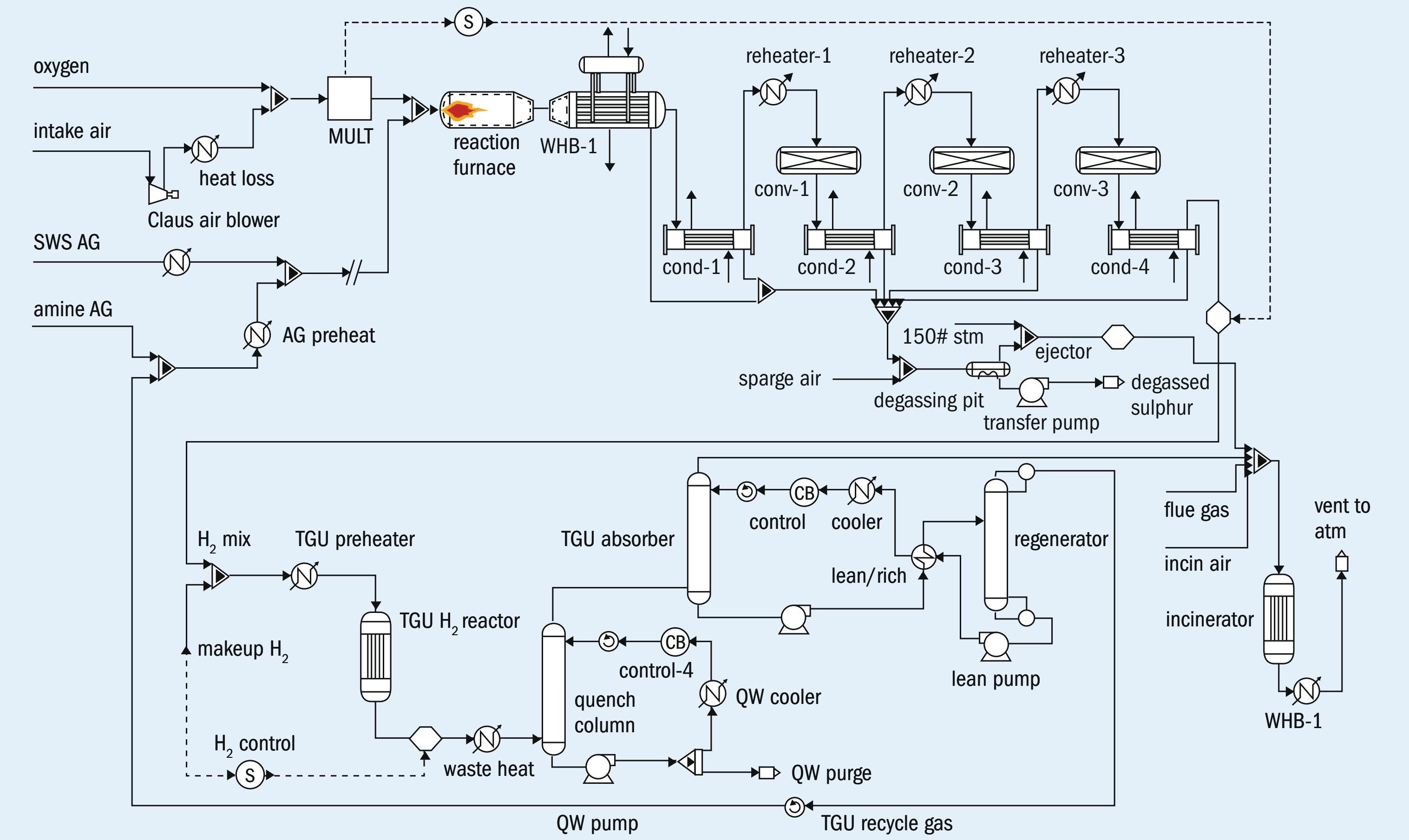
Since it was first introduced into the market in 2002, the ProTreat® simulator has always been completely mass transfer rate based. The advantages are a) you are never asked for information beyond what can be measured or read from a drawing, and b) there is no need to adjust parameters to match data from a properly operating plant, unless something is wrong with the instrumentation. ProTreat is 100% predictive – you do not fit to data and you do not adjust parameters – if calculated and measured values disagree, you find out what's wrong with the plant!

Fig. 1 shows a three-stage SRU integrated with a downstream TGTU. Endless configurations of upstream AGRs, AGEs, and SWSs, with a complex SRU, and TGUs can now be studied simultaneously in a single simulator using the full power of mass transfer rate-based simulation of the separation units and the full power of reaction kinetics based SRU simulation.

Gas treatment

In addition to conventional amines and amine mixtures, ProTreat includes the full suite of INEOS GAS/SPEC solvents, Tamin-co's AdapT solvents, and several Dow UCARSOL solvents. ProTreat is state-of-the-art for simulating piperazine-promoted MDEA treating systems, commonly found in ammonia and syngas operations and in LNG production, and it has been thoroughly benchmarked against a very wide range of plant performance data in both syngas and LNG applications areas.

Fig 1: **Integrated ProTreat® SRU/TGU model configuration**



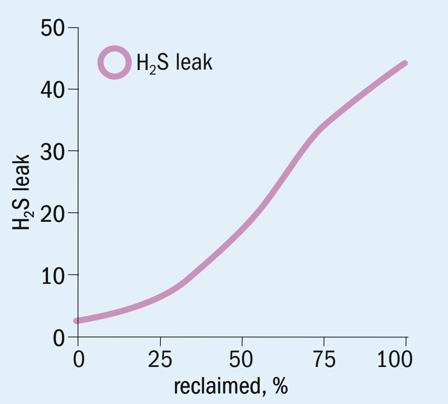
Source: Optimized Gas Treating

Removal of mercaptans, sulphur dioxide, hydrogen cyanide, phenol, ammonia, and methanol are all simulated as mass transfer rate governed processes. In many cases, these contaminants play an important role in process selection. The mass transfer rate approach overcomes the shortcomings of other simulators that take short cuts and miss the impact of these contaminants on the process and on each other.

For post-combustion carbon capture, in addition to most of the conventional amines, ProTreat contains a number of non-amine reactive solvents. These include the amino acid salts sodium glycinate and potassium dimethyl glycinate, which are completely non-volatile, as well as concentrated aqueous ammonia and potassium carbonate promoted both with amines and with enzyme catalysts. Certain solvents from ION Engineering can also be simulated. In the field of carbon capture, ProTreat is second to none. All the solvents of interest, even including high strength piperazine are available, and new ones are being added all the time.

ProTreat includes a physical solvents package having the mono, di, and triethyleneglycol group of solvents for dehydration, as well as the dimethyl ethers of polyethylene glycol familiar from the SELEXOL™ process, Coastal AGR® solution, and Genosorb. Sour water stripping and caustic treating packages are also seamlessly integrated into ProTreat.

Fig 2: **Effect of reclaiming from 0.81 wt-% HSS on H_2S to incineration**



Source: Optimized Gas Treating

At best, solvents in the real world are clean only when they are first unloaded into the treating system from the tank truck or rail car. After that, they are almost invariably contaminated. This is especially true in refinery amine systems where the presence of heat stable salts (HSSs) is the norm, often in significant concentrations. ProTreat accounts for the possible effect of up to 13 distinct, named HSSs on treating. Interestingly, small HSS concentrations can actually improve H_2S removal under certain circumstances so that sometimes reclaiming a solvent to an extremely clean condition can cause the treating unit not to achieve specifications on H_2S. It's far better to determine the optimal level of HSSs by simulation than to remove them all and find your tail gas treater far from meeting product specifications when the unit comes back up. ProTreat accounts for the unique effect of each HSS and provides solid guidance on how much HSSs to take out and how much to leave in. Fig. 2 shows an example of the effect HSS reclaiming level has on treating a tail gas with initial HSS concentration of 0.81 wt-%.

On the subject of HSSs, phosphoric acid is also a heat stable salt but it is purposely added to MDEA-based solvents to promote solvent stripping. This is particularly effective in tail gas treating where this additive can easily take the treated gas from 100-250 ppmv H_2S to less than 10

Fig. 3: Waste heat boiler.

parts per million. ProTreat is very effective at simulating such systems.

ProTreat efficiently simulates absorbers, regenerators, Stahl columns, dehydration units, sour water strippers, and quench towers containing an enormous array of random and structured packings. Mass transfer coefficient information needed by the rate model is built right into the software. The information used is known to be the correct information because it's been benchmarked against a large amount of commercial tower performance metrics. Random and structured packing data is included for both hydraulics and mass transfer – hydraulic calculations compare favourably with vendor-provided hydraulic performance guarantees. The same is true for trays, but trays provide an additional opportunity for significantly improving selectivity in gas treatment.

ProTreat accounts for the effect of turndown on separation performance, not just through hydraulics, but by using the effect of hydraulics on the flow regime of each tray's operation. Trays operating in the spray regime can provide greatly enhanced selectivity for H_2S in MDEA systems. This effect has been proven in the field, and quantitatively predicting it is a unique capability exclusive to ProTreat®.

ProTreat also simulates sour water stripping, including two-stage stripping, on a mass transfer rate basis. The rate basis allows the simulation accurately to predict the interactions between ammonia and hydrogen sulphide in the stripper, and correctly account for the presence of phenol and the injection of caustic soda to spring ammonia from sour water containing HSSs.

Corrosion is always of concern in amine units. ProTreat possesses a fundamental chemistry, diffusion, and hydraulics-based model for corrosion in CO_2-only, H_2S-only and H_2S passivated carbon steel and higher metallurgy piping and fittings. The model has been regressed to a great deal of data collected in a joint industry sponsored research program as well as to public domain information on corrosion rates measured in carbonated solutions.

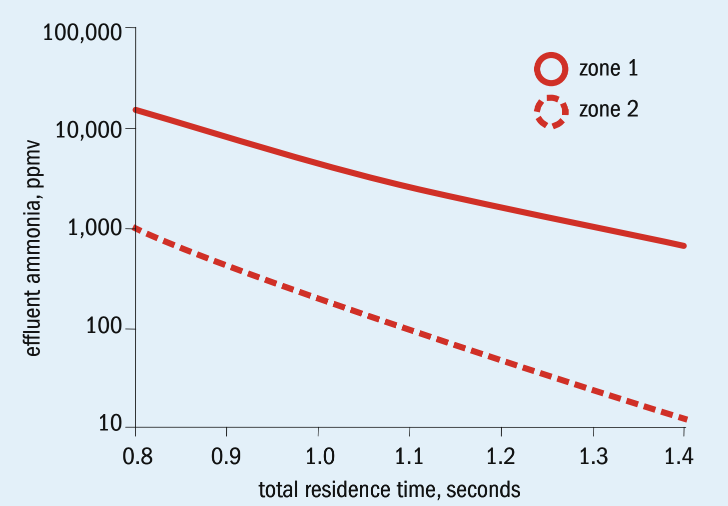
Sulphur recovery

The introduction of ProTreat Version 6.0 saw the already proven gas treating packages in ProTreat complimented by a state-of-the-art predictive sulphur plant simulator. For the first time, detailed reaction kinetics have been included as an integral and central part of the models for all major equipment items. ProTreat includes ammonia and BTEX destruction kinetics in the reaction furnace (RF) as well as H_2 and COS recombination reactions in the waste heat boiler (WHB) like the one shown in Fig. 3. The latter reactions have serious heat flux considerations at the critical tube-to-tubesheet joint in the WHB which is a common failure area in sulphur plants. Fig. 4 shows a ProTreat model of a two-zone reaction furnace with ammonia destruction as a function of residence time in the front and back zones at 30% bypass.

Fig. 5 is an example of a hard-to-model thermodynamic property that ProTreat reproduces extremely well, and that allows ProTreat to simulate sulphur degassing.

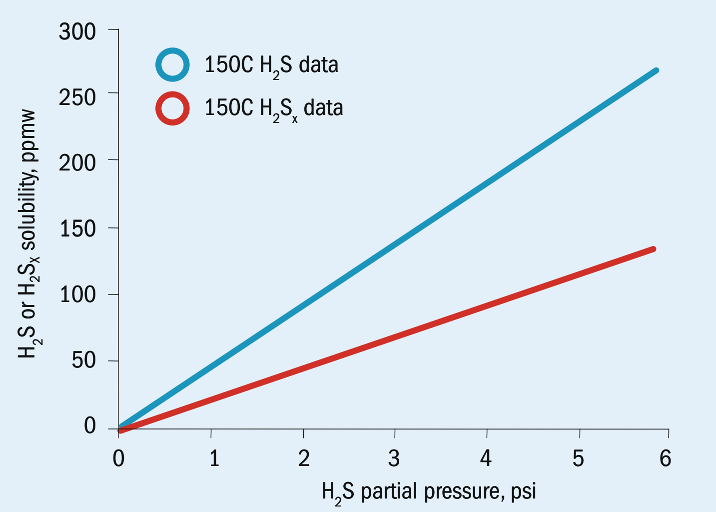
The ProTreat® simulator performs rigorous equipment rating or sizing as the

Fig 4: **Two-zone furnace NH_3 vs. total residence time**



Source: Optimized Gas Treating

Fig 5: **Solubility of H_2S and H_2S_x in liquid sulphur**



Source: Optimized Gas Treating

1 47 2 48 3 49 4 50 5 51 6 52 7 53 8 54 9 55 10 56 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46

PHOTO: BRONSWERK HEAT TRANSFER

Fig. 6: Sulphur condenser.

simulation is run, including composition-dependent radiation calculations, liquid sulphur condensation in the RF effluent and within Claus catalyst beds, and heat transfer design and rating calculations in sulphur condensers (Fig. 6). The model has been benchmarked against a collection of accurately measured operating plant performance data, comprised of:

- Claus bed temperature profiles;
- WHB and sulphur condenser steam generation with reheater steam consumption;
- combustion air demand;
- hydrogen production;
- sulphur recovery efficiency.

Because of the simulator's fundamentals basis, the response of SRU plant performance to varying inputs and operating decisions is predicted reliably and accurately from basic air-only operations to high-level oxygen enrichment. Fig. 7 compares the predicted results of fresh vs aged alumina kinetics options in ProTreat vs measured Claus converter bed temperature profiles.

A recent area of reliability focus in the industry has been to reduce the failures that commonly occur at the tube-to-tubesheet joint in the Claus WHB. Tube wall temperature predictions along with corrosion rates can aid plants in monitoring and predicting boiler life. An example of ProTreat's predictions of WHB tube wall temperature vs mass velocity of a moderately oxygen-enriched SRU can be seen in Fig. 8. This plot confirms the industry's observations that failure rates are reduced by operating the WHB at lower mass velocities.

With ProTreat, a study of the impact of sulphur charge rate on final condenser outlet temperature, pressure drop, and % sulphur recovery is highlighted in Table 1.

With its highly realistic models that are so detailed, and so science based, and with its solution algorithms that are so fast and so reliable, the ProTreat simulator is a virtual process plant.

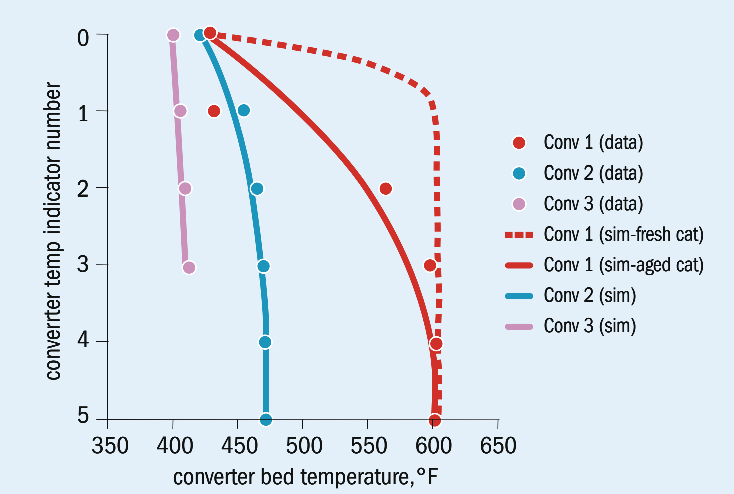
Sulphur condenser design and rating

In sulphur recovery units, condensing sulphur from the gas stream allows the Claus reaction to be continued downstream at lower temperatures with correspondingly more favourable equilibrium. This improves sulphur recovery. Additionally, sulphur condensers produce steam as a byproduct, thereby improving plant economics. The problem until now has been that designing and rating an SRU sulphur condenser has had to be done either manually or using software other than the SRU simulator itself. ProTreat® eliminates this problem. Now any sulphur condenser can be simulated in either design or rating mode as an integral part of the simulation, a unique and extremely useful capability of the software.

Sulphur condenser calculations are time consuming. ProTreat's sulphur condenser module, when run in design mode, automatically calculates the required sulphur condenser area, hence, the number and length of tubes. The resulting design can then be subjected to testing in rating mode for sensitivity of conversion and pressure drop to different turndown scenarios. The automated nature of the design calculations lowers the cost of the bidding process, while the rating feature allows more robust designs and more competitive bids.

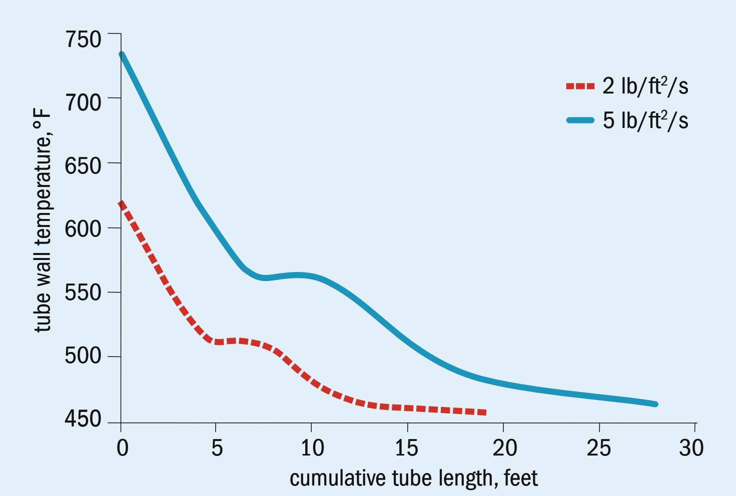
There are several advantages to performing sizing and rating during the actual simulation. Engineers can compare actual and predicted steam generation rates and pressure drop, providing an invaluable troubleshooting tool. For example, by

Fig 7: **Predicted vs measured converter bed temp profiles**



Source: Optimized Gas Treating

Fig 8: **Simulated tube wall temperature in a WHB**



Source: Optimized Gas Treating

Table 1: **Claus unit final sulphur condenser and unit performance vs charge rate**

Long t/d sulphur	100	75	50	25
Outlet temperature, °F	280.2	276.5	271.9	265.8
Pressure drop, psi	0.43	0.24	0.11	0.03
Sulphur recovery, %	96.58	96.64	96.71	96.83

Source: Optimized Gas Treating

being able to assess fouling effects on heat transfer and pressure drop, ProTreat® allows easier detection of steam leaks and quantification of overall condenser performance and physical condition.

Sulsim now part of Aspen HYSYS

With the acquisition and inclusion of Sulphur Expert's Sulsim in Aspen HYSYS, engineers can now optimise an entire plant from the hydrotreaters through acid gas recovery, sulphur recovery, and tail gas treating units in one environment, leveraging conceptual tools for economic evaluation, or energy recovery available within the Aspen HYSYS environment. This adds to new functionality in Aspen HYSYS for modelling the acid gas removal unit using rate-based distillation modelling technology. Having a single solution that is both trusted in its accuracy and powerful in its ability to streamline workflows, allows engineers to overcome challenges in less time and without risk of transcription errors.

With simulation of the SRU, problems can be identified early and reliably to meet regulations on sulphur emissions and to minimise costs by preventing equipment failure. Users can plan for catalyst degradation and optimise as well as predict the entire facility's sulphur removal needs in a single design.

The gas plant involves many different processes and has many interconnections, downstream dependencies, recycle streams, heat exchanger networks, and flare systems. Feed flow rates and compositions to the gas plant can change over time, and adjustments must be made in operations to continue to meet product and environmental specifications. Significant changes to feed or plant operational objectives may also require revamp work or new construction during turnaround. A full plant model, utilising the most accurate modelling technology for each section, will allow for an evaluation of where a constraint is violated and how to accommodate the change.

Sulsim has been used in the industry for decades, and has been proven to be one of the most accurate simulators of the modified-Claus process. When faced with sour feedstocks, Sulsim Sulfur Recovery allows engineering consultancies to make specification guarantees with confidence or engineers at plants to operate reliably while meeting regulations.

The SRU is sometimes a bottleneck in refineries and gas processing facilities by limiting the amount of sulphur that can be accommodated in crude oil, natural gas, and unconventional feedstocks, while still meeting flare specifications. By maximising sulphur recovery using Sulsim Sulfur Recovery, refiners and gas processors could accommodate more sour crudes or natural gas feeds in the slate for increased margins. Changing feed conditions can cause variability in operations. Engineers can use Sulsim Sulfur Recovery to pre-emptively predict sulphur recovery unit performance, adjust operating conditions to optimise the unit, and to ensure reliable operation and reduce number of upsets.

The sulphur recovery process involves many energy-intensive steps. Engineers can minimise opex in existing plants by identifying optimal temperatures for operation with Sulsim Sulfur Recovery. Designers with Sulsim Sulfur Recovery can build the right plant configuration to meet sulphur recovery targets for a given operating window at a minimum capex, while also ensuring that the design is flexible enough for the needs of the plant. The integration of Sulsim Sulfur Recovery into Aspen HYSYS is critical for global optimisation in design and for evaluating alternative configurations in strategic studies

Implementation of Sulsim Sulphur Recovery in Aspen HYSYS

The functionality available for decades as part of standalone Sulsim has been completely incorporated into Aspen HYSYS V9 and above. AspenTech and Sulphur Experts have independently validated and verified that all pre-existing functionality works as designed in the Aspen HYSYS environment.

In Aspen HYSYS, the Sulsim property package, sub-flowsheet environment, and unit operations can be used to accurately simulate all commercial process configurations for the Claus process with over 30 unit operations.

Standalone Sulsim has been fully integrated into Aspen HYSYS by implementation of:

- a specialised sulphur recovery sub-flowsheet environment;
- a dedicated Sulsim (Sulfur Recovery) property package;
- a specialised unit operations palette, including all previously available Sulsim unit operations as well as some new operations introduced in this release;
- a Sulsim-to-HYSYS case converter for easy customer migration.

Validation results: Sulphur Experts' Sulsim vs Aspen HYSYS

Aspen Technology and Sulphur Experts worked extensively and independently to ensure that the results were sufficiently equivalent. Aspen Technology and Sulphur Experts independently tested hundreds of cases, and no unexpected differences in the results have been observed between the two simulators. Sulsim Sulphur Recovery in Aspen HYSYS includes improvements to the underlying models available in Sulphur Experts' Sulsim that results in known differences, as noted in the in product help.

For example, as part of the validation work between the two simulators, the breakthrough of select sulphur species following unit operations such as the reaction furnace, waste heat exchangers, catalytic converters, etc. has been compared. Figs 9 and 10 are subsets of that data for the furnace (Fig. 9) and catalytic converter (Fig. 10). Sulphur Experts' Sulsim results are plotted on the x-axis and the results from Aspen HYSYS are plotted on the y-axis. Results in almost all tested cases were nearly identical.

Aspen Technology and Sulphur Experts have also compared the outlet temperature of key unit operations such as the reaction furnace, catalytic converters, HBED, etc. (see Fig. 11). The results were nearly identical in the majority of cases. In some cases, particularly when recycling sulphur from the tail gas section to the reaction furnace, Aspen HYSYS results were slightly different due to improvements in the HBED model and tighter solver tolerances.

Sulphur conversion efficiency is an important metric to optimise the SRU and

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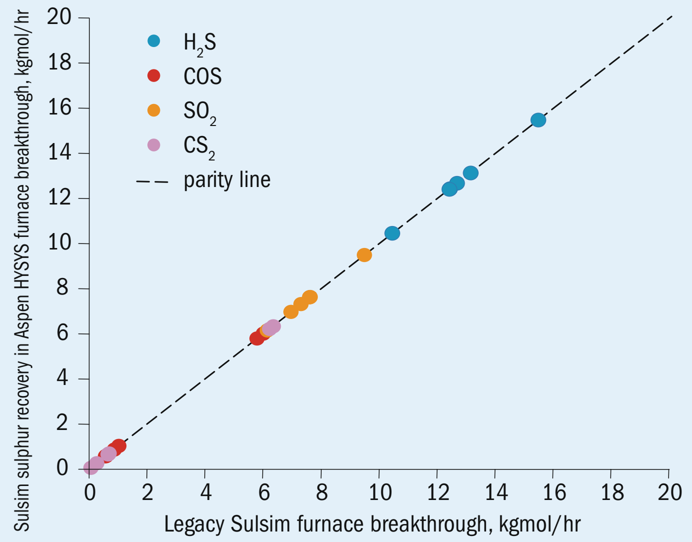
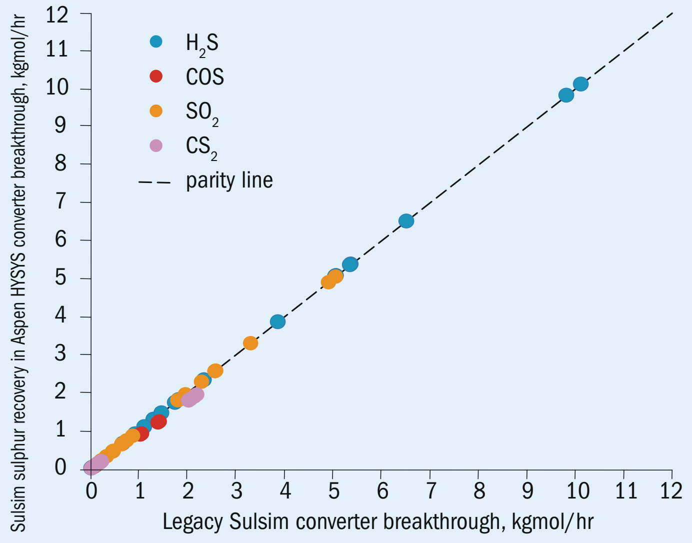
Fig 9: **Results from Sulphur Experts' Sulsim compared to Aspen HYSYS for reaction furnace breakthrough**



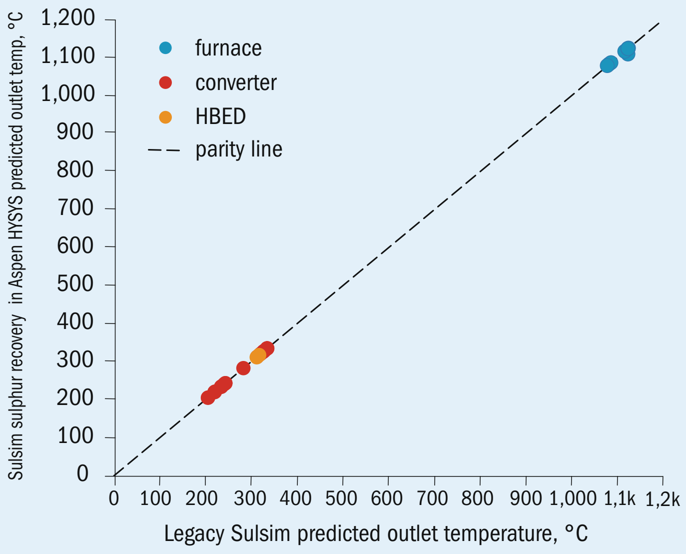
Source: Aspen Technology

Fig 10: **Results from Sulphur Experts' Sulsim compared to Aspen HYSYS for catalytic converter breakthrough**



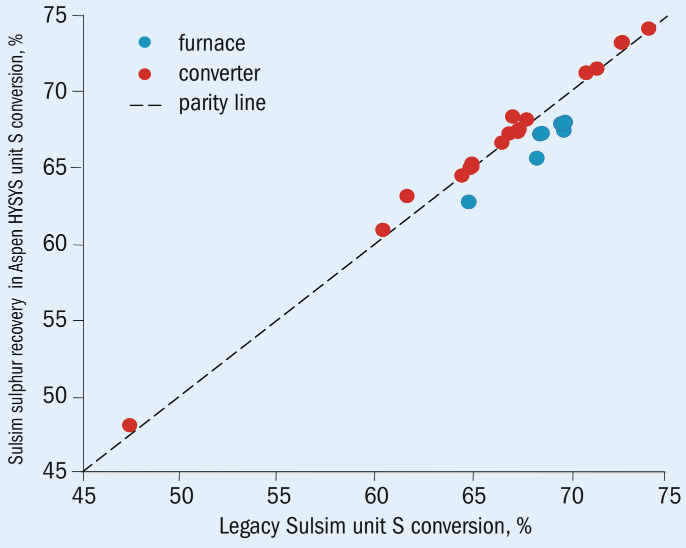
Source: Aspen Technology

Fig 11: **Results from Sulphur Experts' Sulsim compared to Aspen HYSYS for outlet temp prediction of key unit operations**



Source: Aspen Technology

Fig 12: **Results from Sulphur Experts' Sulsim compared to Aspen HYSYS for sulphur conversion efficiency**



Source: Aspen Technology

to understand the effect of operational changes. Aspen Technology and Sulphur Experts also compared the sulphur conversion efficiency in each stage of the SRU. Some differences were observed between Sulphur Experts' Sulsim and Sulsim Sulfur Recovery in Aspen HYSYS (see Fig. 12). However, these differences were expected as part of the model improvements made with Aspen HYSYS V9. In cases where significant differences were observed, results were compared against the original plant data and Aspen HYSYS results were generally found to be more accurate.

Extensive validation work was performed across many more properties and cases.

New SRU modelling

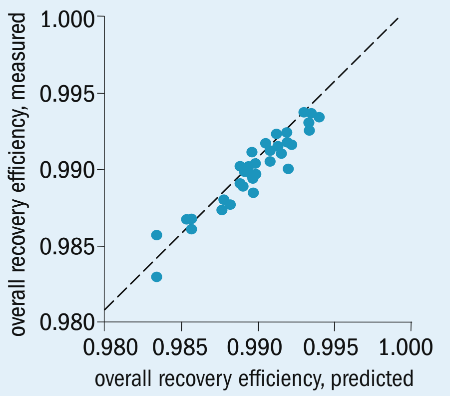
All previously available functionality in Sulphur Experts' Sulsim is made available in Sulsim Sulfur Recovery in Aspen HYSYS V9 and above. In addition to pre-existing functionality, Aspen Technology and Sulphur Experts have worked together to include a new suite of models and capabilities that cover a wider range of operating conditions and equipment configurations.

The Sulsim property package contains extended components S_1 through S_8, with full detail of these sulphur species reported to the user in the simulation environment.

Five new empirical reaction furnace models have been included in V9, extending the total number to nine models. These models were developed from 769 unique plant data sets and have been validated to be more accurate predictors of furnace operation compared to the legacy models.

A new incinerator model with kinetic correlations is now available, which predicts breakthrough of key sulphur species to the flare. The catalytic converter unit operations now include a model for simulating titania catalyst (including mixed bed), as well as alumina catalyst. A new model has been developed for the selective oxidation

Fig 13: **Measured recovery efficiency compared to Aspen HYSYS**



Source: Aspen Technology

converter, which now predicts conversion. A new simplified SO_2 absorber unit operation is also included.

New furnace models

With Aspen HYSYS V9, five new furnace models have been developed from 769 unique plant data sets. Aspen Technology and Sulphur Experts regressed the data to create predictive models for conversion, CO, COS, CS_2, H_2, etc. The new empirical models include support for the following feeds and configurations:

- straight through amine acid gas;
- sour water stripper (SWS) acid gas;
- split flow with lean acid gas;
- oxygen enrichment all acid gas;
- cofiring amine acid gas.

Extensive validation was done by Aspen Technology and Sulphur Experts. Between Sulsim 5 and Aspen HYSYS V9, twice as many data points were regressed and the new curve was shifted slightly.

Claus catalytic converter model

In V9, validation work was completed for support for titania catalyst for the Claus catalytic converter model, in addition to alumina. Models were developed for the titania catalysts for systems that reached and did not reach conversion equilibrium.

Selective oxidation converter

With Aspen HYSYS V9, the overall recovery efficiency can be predicted using the new model for the selective oxidation converter, such as the Jacobs SUPERCLAUS process. Work was done to compare the prediction to measured plant data. A comparison for a number of sample cases is shown in Fig. 13.

Degasser model in V10

With the addition of the degasser model, Aspen HYSIS V10 can now model the solubility properties of H_2S in liquid sulphur. The predicted concentration of the H_2S content leaving the condenser is now available as part of the stream. The degasser model can report on liquid sulphur outlet density, thermal conductivity, viscosity, heat capacity and surface tension.

The benefit of modelling the entire gas plant

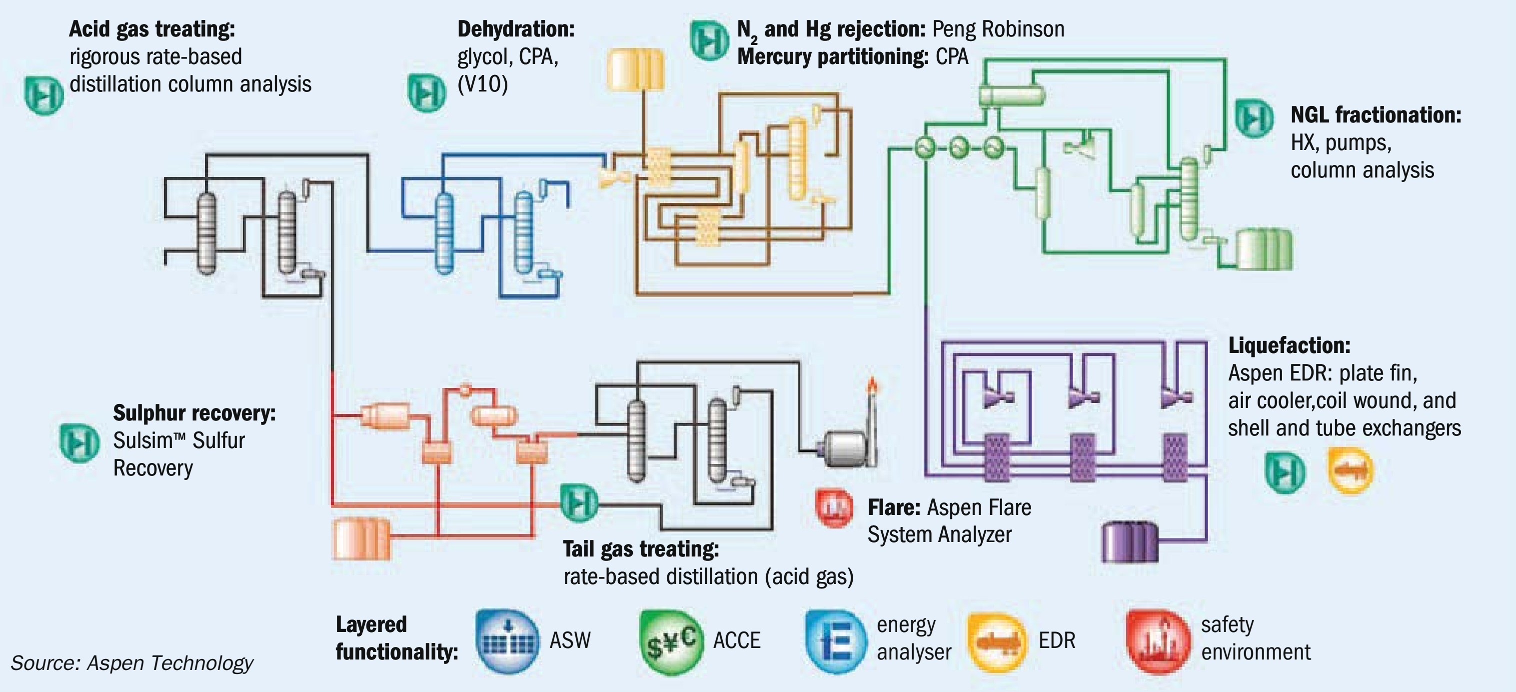
The gas plant in midstream and refining industries contains several units, with each having specific operational objectives. For a plant to be designed and operate at maximum efficiency, while meeting specifications and yield targets, a simulator is often required for global process optimisation.

Sulsim™ Sulfur Recovery in Aspen HYSYS can be used to optimise the sulphur recovery process within the gas plant, and can help with meeting sulphur recovery targets at minimal cost and maximum flexibility. However, the same Aspen HYSYS environment can be used to simulate other areas of the gas plant as well.

For the first time in Aspen HYSYS V9 and above, users can optimise all major gas plant processes in Aspen HYSYS (see Fig. 14).

Acid gas cleaning property packages can be used to simulate the acid gas treating and tail gas treating sections of the plant, with rigorous rate-based technology. This functionality has been expanded further in Aspen HYSYS V9, with new liquid-liquid treating capabilities as well as additional supported components and solvents. The Aspen HYSYS CPA property package can be used to model the dehydration process with MEG, DEG and TEG. The Peng Robinson property packages can be used in Aspen HYSYS to simulate removal of inerts such as N_2 and He. The mercury partitioning utility can be used to predict the formation of mercury in equipment to aid in the placement

Fig 14: **The full aspenONE engineering gas plant solution**



Source: Aspen Technology

of mercury removal units. The CPA property package is recommneded for mercury partitioning. Aspen HYSYS and Aspen Exchanger Design and Rating, or Aspen EDR, can also be used to simulate NGL fractionation, LNG liquefaction, and LNG regasification process. Finally, Aspen flare system analyser can simulate flaring with the goal of meeting environmental regulations.

Layered functionality from other AspenTech products are also available for use in areas of the Aspen HYSYS gas plant flowsheet, such as Aspen Simulation Workbook, Aspen Capital Cost Estimator, Aspen Energy Analyzer, and other safety environment functionality, such as BLOWDOWN® technology and relief valve sizing.

Case study: Modelling the SRU with the rest of the gas plant

In this case study the process comprises an acid gas removal step with sulfolane-DIPA, a two stage Claus process, and a tail gas treating unit. The first task of this case study is to see how the regenerator overhead from the tail gas treating unit affects the rest of the unit if it recycled back to the reaction furnace. The tail gas treating unit is simple in this case, but the rate-based distillation modelling technology for acid gas removal could have been used for greater accuracy. We want to see if this will affect the concentration of sulphur (COS + CS_2 + H_2S (mol)) and what can be done to improve the performance of the unit. In this example, let's assume the limit is 6.0 ppm.

The second task is to look at the acid gas removal unit and how a new feed will change the sales gas sulphur concentration. In this example, let's assume the sales gas specification is 3.0 ppm (H_2S (mol)).

Task 1: meet flare specification in the SRU

The sulphur concentration reported in the incinerator is 5.9 ppm, which is below the assumed 6.0 ppm flare spec. With the addition of the recycle block which circulates the overhead stream from the regenerator to the reaction furnace, the sulphur concentration in the flare increases to 6.1 ppm. The rest of the flowsheet adjusts to accommodate this change and convergence is reached in seconds.

Different opportunities can be explored for improving the performance of the unit.

Adjusting the air flow into the reaction furnace is one way of improving the process. With the addition of a case study with the air demand analyser tool, a user can adjust the ratio of H_2S to SO_2 by changing the air flow rate and observe the resulting sulphur concentration in the flare. By increasing the ratio from 2 to 3, the sulphur concentration decreases to 6.0 ppm.

Another way to improve the process would be to add an adjust block on the second catalytic converter. This adjusts the temperature of the inlet stream so that it is 10°C above the sulphur dew point. The resulting flare concentration is 5.9 ppm, below the assumed specification of 6.0 ppm.

Task 2: meet sales gas specification

Currently, the flow rate of sulphur going to the SRU through the acid gas stream is 760kgmol/h and the sales gas H_2S composition in 1.6 ppm.

The new feed has a flow rate increase of 5% and the composition is different with more sulphur. As a result, there is more H_2S going to the SRU, the H_2S in the sales gas is too high at 13.3 ppm for the assumed specification of 3.0 ppm. The amine loading is relatively low at 20.8 ppm.

An option to improve the process would be to increase the amine makeup rate. This significantly reduces the H_2S composition to 2.5 ppm and increases the amount of H_2S going to the SRU from 760 to 814 kgmol/h.

If you then go into the SRU, you'll find that with the adjust block the H_2S concentration in the flare gas is still within spec at 5.9 ppm. This is likely due to the adjust block on the second catalytic converter.

The case study showed that it was possible to see how changing the operation in the sulphur recovery unit can result in a reduction of H_2S in the flare gas. By modelling the acid gas cleaning unit and the SRU in one simulation, it is possible to quickly see how the two units can handle changes to the feed or the process.

KT's supervisory analytics: SA-SRU™

KT – Kinetics technology has developed supervisory analytics for the sulphur recovery unit, SA-SRU™, designed to simulate and model the SRU and to be provide an operational excellence management system, able to assess plant performance, minimise opex and avoid accidents.

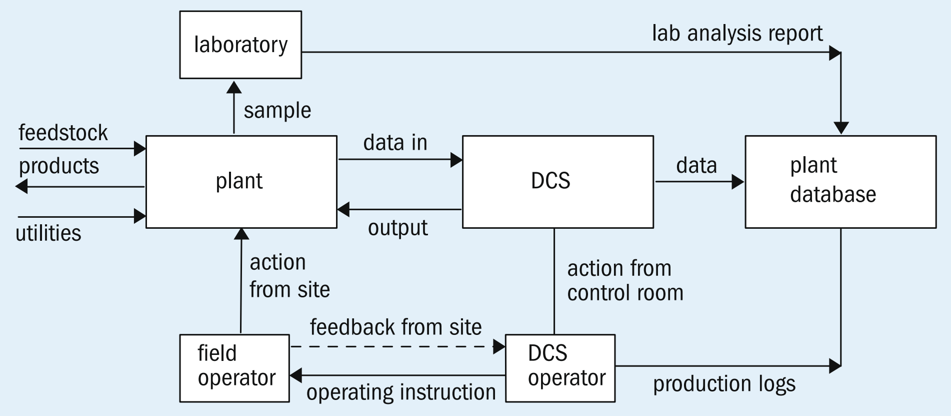
The idea to create a proprietary digital platform for the SRU came from customer's requests to be supported in their quest to optimise techniques for better leverage of the operational data already being generated by the distributed system (DCS) and other systems as part of operations.

Nowadays, huge amounts of plant data and laboratory data are produced, collected and stored to ensure the correct, safe and smooth operation of the unit and to monitor plant performance. Nevertheless, too often data is not used effectively and data management is not optimised, directly affecting plant operation and productivity.

Fig. 15 shows schematically the typical interconnection between process unit(s), the DCS and operations. The plant database represents the collection of DCS data, laboratory analysis and feedback from operations.

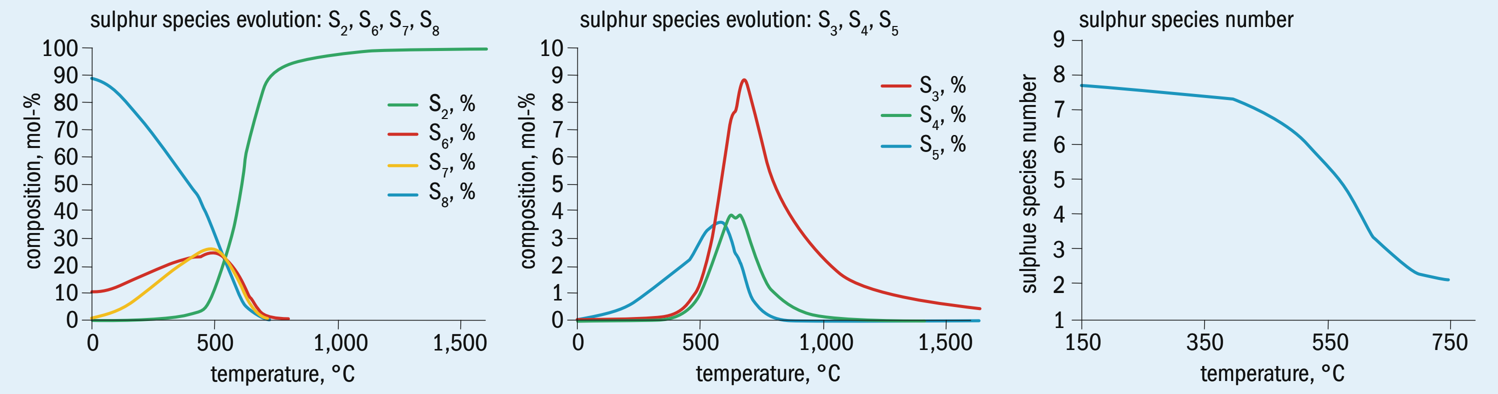
Plant data can be of poor quality due to noise corruption and may have poor statistical qualities. Sometimes data are not available on a continuous basis (like feedstock composition, fuel gas composition, flue gas composition, etc.) and DCS readings can be inconsistent, misleading or unavailable due to maintenance of the instrument, wrong installation, incorrect tuning and/or

Fig 15: **Interconnection between unit(s), DCS and operation**



Source: KT – Kinetics Tehnology and VMG – Virtual Materials Group

Fig 16: **Sulphur allotropes as a function of temperature (prediction by VMGSim™)**



Source: KT – Kinetics Tehnology and VMG – Virtual Materials Group

wrong selection of the instrument.

A typical example is when the plant is close to the end-of-run condition and it is suspected that the catalyst is deactivating faster than expected when compared with historical plant data. In this specific case, it is very difficult to know if the catalyst will last until the next scheduled shutdown and which operating parameters need to be changed to mitigate the on-going process. Predicting whether the catalyst will last and what action should be taken requires not only real time and historical operational data but also knowledge of the feedstock composition, process gas composition, thermal reactor efficiency and mode of operation.

In some cases plant performance data are misleading or inconsistent due to experimental error in the collection and analysis of the sample. A typical example of poor estimation of the sulphur recovery efficiency occurs when a gas sample from the reaction furnace is not rapidly quenched allowing hydrogen recombination to take place. It is also very common for the sulphur recovery efficiency (SRE) to be overestimated when the water contained in the sample is not quickly removed to prevent further reaction, as well as when samples are taken without suitable probes in quartz or Teflon tubes, sheathed in a stainless steel support.

Good knowledge of the process combined with operational experience and a deep understanding of the instrumentation output and analysis of results are all important when assessing the actual status of the unit from the viewpoint of optimal and safe operation. Even then, the task may not be easy to solve and the use of a robust engineering tool for simulating and modelling the sulphur plant is required to predict in real-time the expected operational parameters and relevant plant performance.

Engineering tool for simulating and modelling the SRU

KT has chosen to use VMG technology to provide simulation and modelling solutions for different aspects of sulphur recovery facilities.

Over the last 15 years, VMG has worked extensively in the area of SRU modelling with its proprietary process simulator VMGSim™. VMG has dedicated time throughout this period to investigate the best thermodynamic models for components involved in SRU processing, benchmarking with a critical approach using several sources: NIST database, published papers, ASRL data, GPSA Data Book.

Various sulphur allotropes manifest their presence in sulphur processing. VMGSim™ predicts the correct sulphur speciation through the reactive flash algorithm of the Claus property package (Fig. 16). The presence of one or another allotrope is clearly a function of temperature, with the properties of sulphur changing significantly depending on the molecular nature of the sulphur present.

One example of how properties can be strongly affected by the chemistry of sulphur allotropes is the viscosity of liquid sulphur. At low temperatures sulphur mainly exists in the form of S_6 and S_8 (as shown in Fig. 17). As the temperature increases the viscosity reduces, but at temperatures close to 160°C the sulphur ring structures start to open and sulphur starts to polymerise forming long linear chain molecules; this is the reason why there is an almost asymptotic jump in the viscosity. Polymerisation continues and viscosity increases by four orders of magnitude over a temperature interval of 30°C, reaching a maximum at about 190°C. Above 190°C viscosity starts to reduce again as a function of temperature.

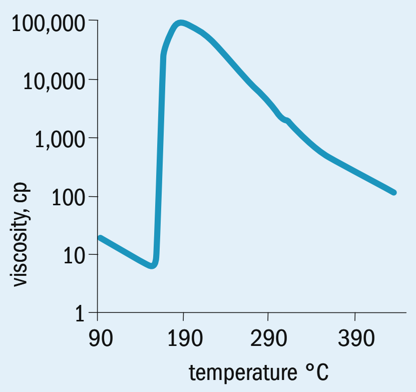
This behaviour is well known in the sulphur industry and it is the reason why any equipment handling liquid sulphur must be kept at an adequate temperature, above the melting point (120°C) but without entering the temperature range where polymerisation can occur.

Heat capacity has the same transition point as for viscosity, i.e. 160°C (Fig. 18). In VMGSim™ both the enthalpy and heat capacity for each elemental form of sulphur has been estimated based on regressed values. These provide accurate results for sulphur heat capacity, including estimating the heat capacity peak as well as accurately modelling the heat capacity for both sides of the heat capacity curve.

Equipment modelling

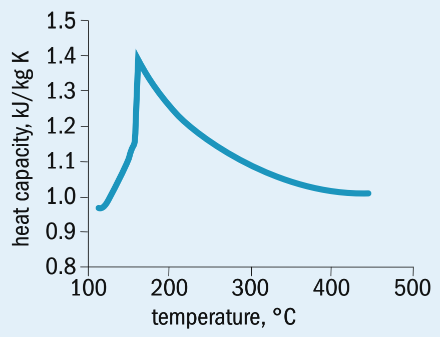
VMGSim™ can be used for the static and dynamic (for transient analysis) modelling of all unit operations in the SRU as well as the tail gas treatment unit (TGTU), with the possibility to extend the scope of the simulation to upstream acid gas removal

Fig 17: **Viscosity of liquid sulphur (prediction by VMGSim™)**



Source: KT and VMG

Fig 18: **Heat capacity of liquid sulphur (prediction by VMGSim™)**



Source: KT and VMG

and to further upstream units, in a refinery complex as well as in a natural gas plant.

The Claus furnace model has been developed to accommodate different feed types (gas plant or refinery), oxygen enrichment, high-efficiency or old-style burners, natural gas cofiring configuration and rigorous heat loss calculation. COS, CS_2, CO and other species are not considered at equilibrium and the effect of a different front side-split (if applicable) can be studied.

The waste heat boiler model can be implemented in reactive mode. In this mode the recombination of H_2S and other sulphur species has been taken in account and the correct duty and temperature behaviour is available for the design.

The Claus converters model simulates the catalytic conversion of H_2S and SO_2 to form sulphur and calculates the hydrolysis of COS and CS_2 to form H_2S, for regular alumina, promoted titania and full titania catalysts.

Processes or modes of operation besides the typical Claus plant with two, three, or four stage reactors can also be represented, including direct oxidation and sub dew point processes and SCOT TGTU.

The VMGSim™ model for the Claus thermal incinerator models the oxidation of commonly reduced sulphur compounds (H_2S, COS, CS_2 and sulphur vapour) to SO_2 prior to release to the atmosphere, as well as the combustion of non-sulphur compounds such as H_2 and CO. The kinetics are generic and completely configurable. The Claus incinerator model also takes into account the SO_2 and SO_3 equilibrium reactions and their dew point, heat recovery possibility, and hydraulic calculations.

KT customised VMGSim™ process simulator

KT has customised the VMGSim™ process simulator embedding KT's know-how in the unit design and operations. Over the years KT has developed proprietary mechanism models for all chemical reactions occurring in the sulphur plant including models for the destruction of ammonia, BTEX, hydrocarbons and other impurities. Rigorous equipment sizing and KT proprietary rating are integrated in the simulator. For example, the rating approach for a sulphur condenser defines the geometry of the equipment and can be used for accurate equipment modelling.

KT customised models in VMGSim™ make it possible to easily check the performance of equipment in all operating conditions, from turndown to design conditions, and in accordance with the real status of the equipment installed in the plant, thereby offering a unique approach for simulation and modelling of sulphur plants for KT clients.

KT has validated the modelling with historical data and the data from several real unit test runs. Fig. 19 shows a recent comparison performed to predict the temperatures of the two zones in an operating Claus furnace with a front-side split configuration vs DCS data, over an interval of time. The simulation model is in reasonably close agreement with the measured data, therefore the simulation prediction is shown as a solid line.

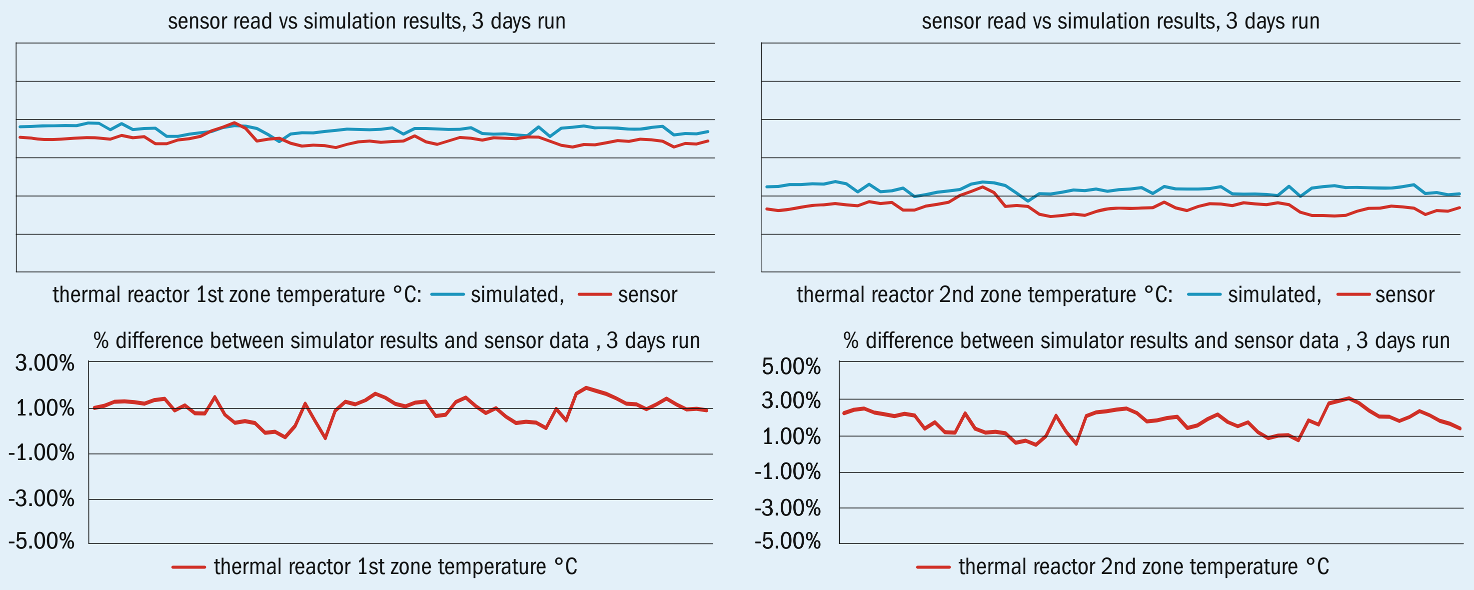
KT R&D work developed at a SRU laboratory plant capable of simulating any type of feedstock, located at the University of Salerno (UNISA), enables the testing and validation of more detailed reaction mechanisms and possible innovations in the field of acid and sour gas processing. All of the knowhow developed by KT is incorporated in VMGSim™ for continuous improvement of the predictive model.

Engineering tool for operators

SA-SRU™ is the KT engineering tool conceived to embed KT's knowhow for design and operation of sulphur recovery facilities together with VMG's expertise in thermodynamics and process simulation. The digital platform, developed by KT, fulfils in one unique application the four main pillars of the SRU operational excellence management system:

- monitor operation by providing key performance indicators;

Fig 19: **Model results vs DCS data (temperatures of 2-zone Claus furnace)**



Source: KT – Kinetics Tehnology and VMG – Virtual Materials Group

- optimise opex;
- operate in safety;
- provide instructions to plan maintenance.

SA-SRU™ can be tailored to each plant configuration utilising KT's rigorous sizing and proprietary rating of equipment which predicts all process variables required.

By using software connectivity, SA-SRU™ collects real plant data in real time, performs data validation and reconciliation, processes reconciled data through engineering models and finally provides the operator with the following information:

- historical information and guidelines on plant operation mode and process equipment status;
- key performance indicators;
- how to operate sulphur recovery facilities according to best practices;
- suggestions for asset optimisation;
- assessments on whether the plant is running safely;
- help to plan maintenance.

The main idea behind this tool is to provide operators with easily accessible key information and historical knowledge to provide the background needed to minimise risks and maximise operational effectiveness by having a complete understanding of "what is happing behind the steel of SRU".

Another example of deliverables useful to operators generated with the help of SA-SRU™ is operator training systems (OTS) for sulphur recovery facilities.

Thanks to the transient solver part of the VMGSim™ dynamics process simulator, SA-SRU™ allows a high fidelity operator training system (OTS) to be developed which provides a suitable platform for operators to practice on.

The OTS also provides an environment to perform unfamiliar process and control tasks in a safe environment, as any mistakes are made on a virtual plant without any real-life consequences, but will provide lessons to learn from. The connectivity to emulators of the control system is guaranteed through the VMGSim™ OPC functionality.

In operator training applications, SA-SRU™ can be used to:

- evaluate relief loads from causes such as reflux pump failure, fire, power failure;
- simulate process operability during upsets;
- develop start-up, shutdown and operating procedures;
- perform regulatory control system studies;
- evaluate process, equipment and control strategies;
- perform step testing off-line.

Value delivered to operators is focused on gaining a better understanding of operability of sulphur recovery facilities as well as gaining confidence in how to operate during infrequent abnormal situations. ■

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3. Colozzi M, Cortese S and Molinari L (KT – Kinetics Technology) and Manzulli M (Virtual Materials Group): "KT brings process expertise closer to operation for optimal and safe performance of sulphur recovery plant", written for Sulphur magazine (Jun 2017).

Acid catalyst upgrades

Sulphuric acid catalyst upgrades provide a solution to balancing operational and emissions requirements. In this article, Topsoe reports on the benefits of upgrading the catalyst loading in sulphuric acid plants, MECS discusses how a new DSC tool has been used to develop new improved sulphuric acid catalysts and BASF introduces its new caesium based catalyst.

Sulphuric acid producers are facing more challenging emissions legislation all over the world. Plants that were originally designed for 99.7% conversion of SO_2 are now being asked to meet conversion levels of 99.9% or more. At the same time, competition within the bulk chemical market in general, and the sulphuric acid business in particular, is fierce and plants need to run as efficiently as possible to stay profitable. Balancing the two requirements is not so straight forward, as reducing the cost per tonne acid produced, or gas volume treated, means trying to maximise productivity of the plant, while emissions reductions can require production capacity cuts, expensive revamps or operating scrubbers which will add to operational costs and potentially add waste. A cheaper option is to upgrade the catalyst loading in the plant.

Topsoe catalyst loading upgrades

The basic solution to improving the catalyst loading is to simply increase it. If there is room in the converter, and if there are no temperature limitations that force the use of more advanced catalyst, it will be a both effective and relatively cheap way to boost converter performance. As more and more catalyst is added, getting higher in conversion gets exponentially harder, see Fig. 1 for an example of a sulphur burning plant.

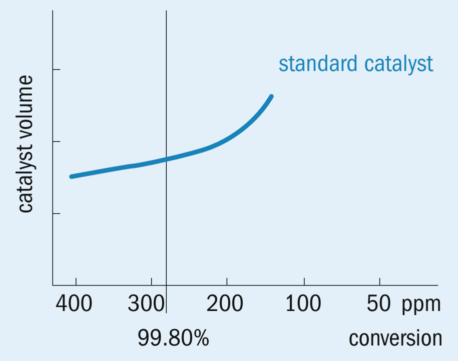
The main issue is that in most older plants, the plant capacity has already been increased, often multiple times. The effect of this is that in many cases, the available room in the converter has become a bottleneck, both for lower emissions and for further capacity increases.

Changing to more advanced catalyst

If the converter is full, or if the temperature required to reach a high enough equilibrium conversion is too low for standard catalyst, the next solution is to replace some, or all, of the final bed with more advanced caesium promoted catalyst. Due to its activity throughout the temperature range used in the last pass of a double absorption plant, the caesium promoted VK69 offers a step change in performance for the plant. Fig. 2 illustrates the conversion and emission achievable at different catalyst loadings for the same plant as in Fig. 1.

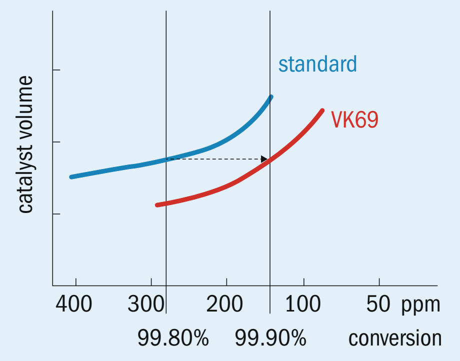
As shown in Fig. 2, a plant achieving 99.8% conversion of a 11.5% SO_2 feed gas with standard catalyst can boost its conversion to 99.9% by solely replacing the standard catalyst in the fourth bed with VK69.

Fig 1: Effect of increasing catalyst volume on converter performance



Source: Topsoe

Fig 2: Effect of advanced catalyst on converter performance



Source: Topsoe

From the curve it is also apparent that if there is enough room available in the converter and there are no temperature limitations in the plant, very high conversion is possible with this solution. The amount of VK69 in the last bed can of course also be tailored to meet the emission legislation, to take into account the specific limitations of the plant in question, as well as the performance of the other beds.

Although the example presented in Fig. 2 is for a plant with a 3+1 configuration, the trends will also be similar for 2+1, 3+2 or 2+2 configurations.

Case 1: replacing Bed 4 with VK69

The following industrial example illustrates how VK69 can be employed to reduce emissions, while not compromising on productivity. The plant in question is a 1,750 t/d sulphur burning plant located in Europe which had been operating for decades with a standard catalyst loading which achieved around 99.7% conversion. The plant had the following specification:

SO_2 source:	sulphur burning
Configuration:	2+2 DA
Design capacity:	1,750 t/d
Loading size:	200 L/t

The emission limit in the area where the plant is situated was to be reduced from 1,200 mg/Nm³ to 680 mg/Nm³. To tackle tightening emission legislation, the client decided to replace the standard catalyst in the final bed with VK69 (the VK69 volume was actually 5% lower than the volume of standard catalyst it replaced). The predicted and actual performance of the new loading can be seen in Table 1.

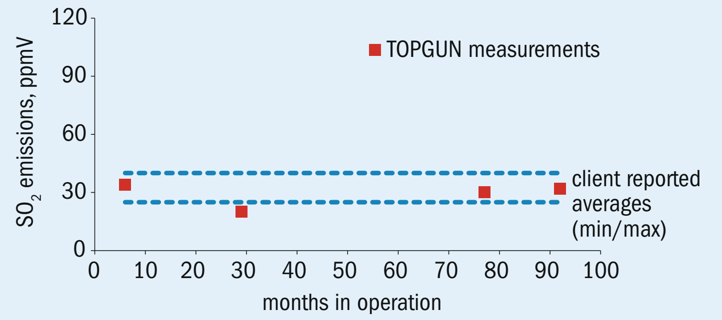
The performance even exceeded predictions, and with a comparatively small investment, the SO_2 emission was greatly reduced, while maintaining the design capacity. As an added bonus, the emission peak during start-up was reduced even

Table 1: Predicted and actual performance before and after installation of VK69

	Prior to loading (plant data)	SOR prediction	SOR (plant data)	9 months later (TOPGUN)	17 months later (plant data)
Production, t/d	1,750	1,750	1,500	1,700	1,400
Feed SO_2, %	10.1	9.8	10.1	10.9	10.4
Conversion, %	99.72	99.83	99.91	99.87	99.90
SO_2 emission, ppm	342	195	112	165	120

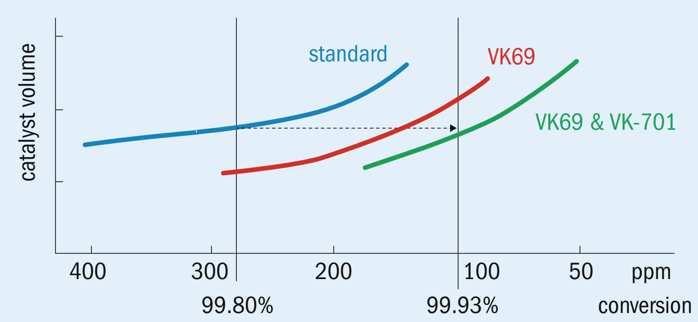
Source: Topsoe

Fig 3: Emission levels for 3+2 DA plant based on Cu smelting



Source: Topsoe

Fig 4: Emissions at different catalyst loadings for a sulphur burning plant (11.5% SO_2)



Source: Topsoe

more than the steady state emission. The client reports that the start-up emission peak after installing VK69 was reduced to 1/8th of the previous size.

Case 2: VK69 for long life and low emissions

The following industrial example illustrates that if a plant is designed to take full advantage of VK69, and if conditions are right, very low emissions can be achieved. Furthermore, the low emission is maintained for years without the need to replace significant volumes of catalyst.

In this case, the plant is a 2,350 t/d Chinese plant based on copper smelting. Due to the very strong gases that were to be treated, the plant was designed using VK69 in order to maintain acceptable stack emission. Some of the design parameters are listed below:

SO_2 source:	copper smelting
Configuration:	3+2 with Lurec
Design capacity:	2,350 t/d
SO_2 strength:	16.3%
Minimum conversion:	99.86%
Loading size:	195 L/t

After start-up in 2007, plant performance had been excellent. TOPGUN measurements have been carried out on four different occasions, all of which have shown emission levels below 35 ppm, corresponding to conversion levels of at least 99.98%. In addition to this, the client has reported emission levels within a similar range (see Fig. 3). All data has been taken at 84-97% capacity and SO_2 levels of 14+%.

Not only does the plant achieve an excellent conversion level, it has done so over a very long time and with very little replacement catalyst needed. Over the first eight years of operation, the total volume of make-up or replacement catalyst corresponds to less than 10% of the total installed volume.

One step further

Although the VK69 and VK59 caesium catalyst will empower most operators to achieve their emission requirements, Haldor Topsoe also offer the unique LEAP5™ catalysts for plants which have especially demanding requirements for emissions or production capacity.

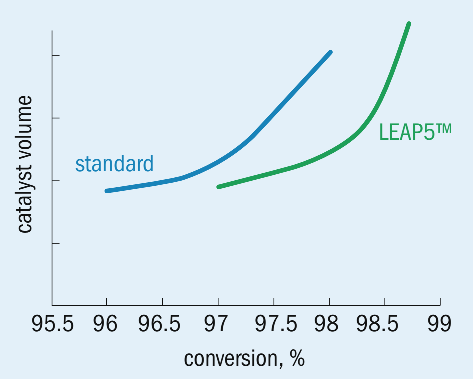
Having the option to use another level of catalyst can help the operator to avoid costly revamps of the plant or cutting production rates if new, more stringent, emission legislation are introduced. It can also be used as a quick solution to compensate for lacking performance in other catalyst beds or parts of the plant. LEAP5™ catalyst can be employed either in the third bed of 3+1 or 3+2 plants, or in the last beds of single absorption plants. Fig. 4 provides an example showing how LEAP5™ catalyst can be used in an existing double absorption plant to achieve higher conversion level.

The sulphur burning plant in Fig. 4 was able to reduce its emission by around 40% when installing LEAP5™ catalyst in addition to the VK69 already installed. This improvement is well in line with what has been seen in the industry for operators installing LEAP5™ catalyst which have seen an average emission reduction of around 50% when also replacing used catalyst.

Finally, LEAP5™ catalyst can be used in single absorption plants as a more advanced alternative to caesium catalyst to maximise the conversion. Depending on the local legislations and plant set-up, the increased conversion could either be used to reduce scrubber chemical consumption, or outright reduce the stack emission. Similar to the double absorption plant example shown in Fig. 4, significant improvement can be achieved in a single absorption plant without increasing the catalyst loading or reducing production rates (see Fig. 5).

As shown in Fig. 5, LEAP5™ catalyst could help a single absorption sulphur burning plant running with 11.5% SO_2 currently achieving around 97.5% conversion with standard catalyst to boost the conversion to close 98.5%. This is done with the

Fig 5: **Conversion for standard and LEAP5™ loadings**



Source: Topsoe

same catalyst loading size, and with no other demands on the plant than that the interbed cooling needs to remove some more heat.

MECS catalyst development using a new DSC tool

Sulphuric acid catalyst are designed to meet customer needs for strength, dust tolerance, and activity. The standard catalyst is made up of alkali metal and vanadium salts, diatomaceous earth support and binders.

Under reaction conditions, these salts form molten alkali metal vanadium pyro-sulphates that are supported within the pore structure of the diatomaceous earth. The accepted mechanism for sulphur dioxide oxidation is a catalytic redox cycle that involves V^{5+} and V^{4+} species in the supported liquid phase.

In the case of caesium catalyst, often used as a final pass catalyst, the caesium functions as an activity promoter, forming caesium and alkali metal vanadium pyro-sulphates that have a lower melting point and a higher activity.

MECS has developed a new in-situ differential scanning calorimetry (DSC) method to probe the thermal and catalytic behaviour of sulphuric acid oxidation catalysts. The method, for the first time, indicates the temperature range at which the alkali metal and vanadium pyro-sulphate salts melt in a working catalyst. The heat flow curves obtained from the DSC method reflect the reaction rate and allow the identification of a break-point temperature, T_B, defined as the temperature at which the activation energy of the catalyst changes by over a factor of 2. Catalyst activity, measured separately in a laboratory differential reactor, was found to increase with decreasing T_B, thus making this method a useful tool for screening candidate catalyst formulations.

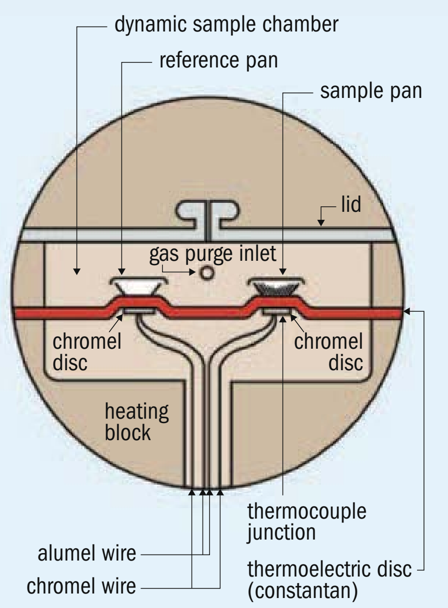
DSC, catalyst screening and selection

Differential Scanning Calorimetry (DSC) is an analytical technique for identifying and, in certain cases, quantifying phase transitions such as melting and crystallisation. A cross-section diagram of the TA Instrument's standard DSC cell is shown in Fig. 6.

The cell is based on a "heat flux" design which uses a constantan disk as the primary means of transferring heat to the sample and reference positions. The sample, contained in a metal pan, and the reference (an empty pan) sit on raised platforms formed in the constantan disk. As heat is transferred through the disk, the differential heat flow to the sample and reference is measured by area thermocouples formed by the junction of the constantan disk and chromel wafers which cover the underside of the platforms. Chromel and alumel wires attached to the chromel wafers form thermocouples which directly measure the sample temperature. This continuous direct measurement of sample temperature accounts for high transition temperature repeatability and accuracy. When the sample undergoes a phase transition, more (or less) heat will flow to the sample than to the reference to maintain both at the same temperature.

For example, more heat flows to the sample as the solid melts. The DSC instrument is designed so that the sample holder temperature increases linearly with time. For a pure compound (with no reaction), the instrument indicates a sharp negative spike in heat flow at the melting point temperature. Since the alkali metal and vanadium pyro-sulphate salts in the sulphuric acid catalyst melt in the presence of sulphur dioxide and are also oxidation catalysts, both endothermic melting and exothermic reaction may occur at the same time. At low temperatures we observe only the melting, as there is low reaction. At higher temperatures the DSC instrument only indicates heat from reaction, and the catalyst is at operating state. At temperatures in between, there may be both reaction and melting, and the technique cannot fully separate out exothermic reaction from endothermic melting.

Fig 6: **Cross section of TA instrument's standard DSC cell**



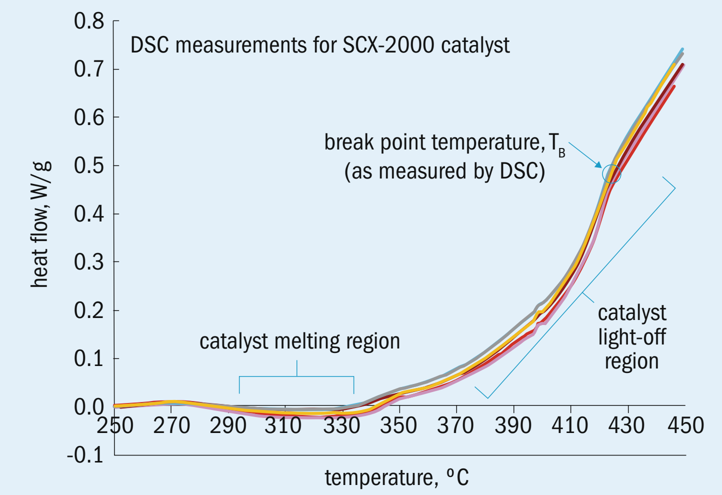
Source: MECS

A TA Instrument Model 2920 DSC with a gas switching module (GSM) was modified to pass air (or the reaction mixture) over the sample and to minimise corrosion within the instrument. The DSC cell/cup was made of silver and the surfaces were covered with several layers of aluminum foil (nominally < 1 μm thick).

The entire cell was covered with a disconnected liquid nitrogen cooling accessory adapter for improved thermal insulation. Custom aluminum lids with a stainless steel connecting pipe were used to close the cell. The stainless steel pipe acts like a "chimney" directing corrosive gases out of the cell into the exhaust system (while minimising contact with other surfaces). Each catalyst was ground using a mortar and pestle. Approximately 8 mg of the catalyst was loaded into a TA Instrument TZero® pan. A second TZero® pan of known weight was used as a reference pan for the measurements.

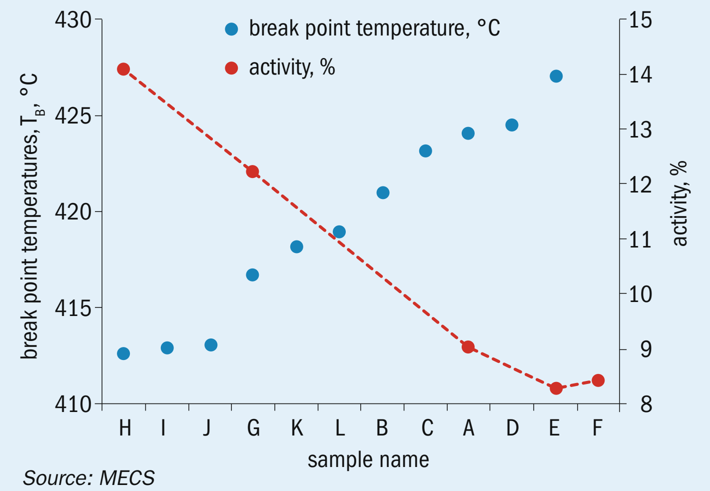
After calibration, the GSM was used to switch between air, the reaction gas mixture (of 4% SO_2 in air), and purge gas (house nitrogen). The flow rate of both room temperature air and the reaction mixture through the cell was 25 cm^3 per min. In a typical experiment, the reaction gas mixture flowed over the catalyst, which was heated with a fixed temperature increase of 5°C per minute to a maximum temperature of 450°C. The catalyst was then cooled with purge gas and heated up again at the same rate using air. The difference in the measured heat flow between the heat up curve for the catalyst using the reaction mixture and the heat up curve for the catalyst using air is shown in Fig. 7.

Fig 7: **Heat flow curve for SCX-2000 catalyst**



Source: MECS

Fig 8: **Comparison of break point temperature and catalyst activity**



Source: MECS

Fig. 7 shows that this DSC method is reproducible. A sample of the base case catalyst was examined several times to confirm reproducibility. Different samples having the same formulation were also examined. Fig. 7 shows a number of lines that characterise the heat flow behaviour from these experiments.

The measured heat flow as a function of catalyst temperature in Fig. 7 indicates both the catalyst melting and catalyst light-off behaviour. At the lower temperature, the phase change due to melting of the pyro-sulphate salts within the pores of the diatomaceous earth in the catalyst is indicated by negative heat flows. The relative magnitude of the heat flow is limited on account of the fact that the molten salt accounts for a small weight fraction of the catalyst and the catalyst exhibits highly exothermic behaviour at higher temperature. The fact that there is a broad temperature range with negative heat flow, instead of a sharp spike, suggests the possibility that more than one pyro-sulphate species may form and then melt. Some of these pyro-sulphate salt species, having vanadium oxidation states from +3 to +5, have been identified in the literature. Further, according to the Gibbs-Thompson relationship, the melting point for a species is higher if the pores in which melting occurs are smaller. Since commercial catalyst has a pore size distribution, a single species may melt at different temperatures.

As temperature increases, the heat flow on account of the exothermic sulphur dioxide oxidation reaction overshadows the endothermic heat of melting. Since the heat flow due to reaction is proportional to the reaction rate, information in Fig. 7 may be used to obtain kinetic information on the catalyst. The exponential increase in the reaction rate above 350°C in Fig. 7 may be represented on an Arrhenius plot and activation energy may be obtained. At around 420°C, there is a break point temperature, T_B, above which the activation energy changes.

In order to relate information obtained from the DSC instrument to catalyst activity, several laboratory formulations of commercial caesium-containing sulphuric acid catalysts containing K, Cs, Na, V, select additives, and diatomaceous earth (DE) were prepared. The various ingredients were mixed together and extruded into pellets. The pellets were dried and then calcined in an SO_3 environment. Catalyst formulations, referred to as Catalysts A through L, were each evaluated in the DSC and the T_B was obtained for each sample.

Separately, select formulations from the above group of catalysts were scaled up and the activity of 100 cm³ of each catalyst was obtained in a laboratory reactor. The inlet gas composition was 8% SO_2, 13% O_2, and the balance N_2. A gas hourly space velocity (GHSV) of 26,000 h^{-1} and an inlet temperature of 410°C was used. Catalyst activity was reported as percent conversion of SO_2.

In Fig. 8, the various catalysts formulations examined in the DSC were ordered by increasing T_B (shown on the primary y axis). The differential reactor activity of catalysts is also shown (on the secondary y axis).

The figure indicates that as the T_B increases, the activity of the catalyst decreases. Thus, the T_B measured by the DSC instrument provides an indication of the catalyst activity.

Based on the above results, the feasibility of scaling up catalyst formulations having low T_B (e.g., samples H, I, J in Fig. 8) was explored. An additional consideration was the ability to use existing equipment to produce catalysts that exceed physical specifications (e.g., hardness, attrition resistance, etc.). The catalysts were activated to the "gold-coloured" working state so that they would be able to oxidise sulphur dioxide without the need for further in situ activation.

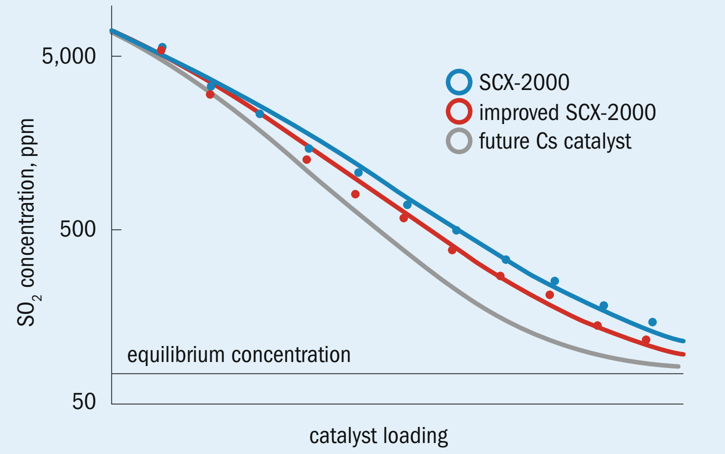
The selected formulation was tested, along with the base case formulation, in a pilot plant reactor under typical Pass 4 after interpass absorbing tower conditions (6,800 ppm SO_2 and 390°C). The concentration of sulphur dioxide as a function of catalyst loading is shown in Fig. 9. The data suggests that the new catalyst has higher activity than the base case catalyst. The screening work using the DSC instrument indicates a potential for further improvement (shown as the dotted line in Fig. 9).

The above discussion indicates that the DSC instrument is a competent tool for indicating the melting point of species in the working catalyst and the T_B. The T_B value correlates with the activity measured in a lab reactor with lower T_B values providing a higher activity. The formulation when scaled up provides an improved catalyst in pilot plant testing.

Benefits of improved formulation

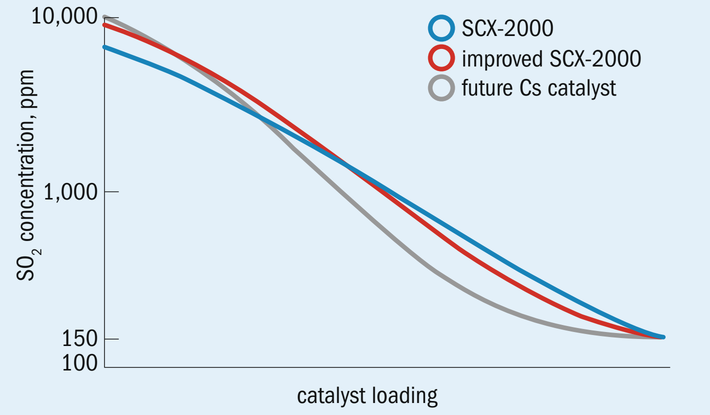
MECS has provided a caesium-containing SCX-2000 catalyst for many years. The improved SCX-2000 catalyst can provide the customer with several options for dealing with operational or emission issues. New plant installations can benefit from capital and operational savings.

Fig 9: **Comparison of SO_2 loading with catalyst loading**



Source: MECS

Fig 10: **SO_2 concentration profile at several inlet concentrations**



Source: MECS

As shown in Fig. 9, a replacement bed of the improved SCX-2000 catalyst can lower sulphur dioxide emissions. For a given catalyst loading, the improved catalyst indicates the potential for reducing emissions by as much as 100 ppm. Depending on the target emission level required, catalyst improvements indicate the potential for reducing catalyst loading up to 15 litres of catalyst per metric ton of acid produced. The actual reduction in catalyst loading to meet a target emission level or the reduction in emissions for an existing bed will depend on the activity of the catalyst that is being replaced and plant operating conditions (e.g., production rate, inlet concentration, average bed inlet temperature, base case catalyst loading, etc.)

When compared to XLP-110 standard (non-caesium) catalyst, the improved catalyst has the potential to reduce SO_2 emissions by up to 170 ppm for a specified catalyst loading. For a given emissions level, catalyst loading could potentially be reduced by up to 30 litres of catalyst per metric ton of acid produced by replacing a final bed of XLP-110 with the improved caesium catalyst. Note that the bed inlet temperature for the caesium catalyst is 20 to 30°C cooler than for standard catalyst such as XLP-110. Again, the actual reduction in loading or emissions depends on the specific application.

The improved catalyst also provides the customer with an option for dealing with more challenging operating issues. Increasing gas strength or acid production rate requires better catalyst performance in order to meet SO_2 emissions requirements. An aging plant can have various reasons, other than the catalyst itself, why initial design emissions cannot be met: heat exchanger leaks, converter leaks, converter gas-distribution issues, leaking valves and dampers, and temperature control issues due to fouled heat exchangers, heat losses (insulation), or deteriorating steaming equipment.

When the sulphur dioxide burden becomes too high, plants are forced to reduce sulphuric acid production to control the SO_2 emissions. As shown in Fig. 10, a more active catalyst, such as improved SCX-2000, can help a plant maintain the permit SO_2 level, even though the inlet SO_2 to the bed is considerably higher. The inlet SO_2 concentration to pass 4 in the base case is 6,800 ppm with SCX-2000 catalyst. With a pass 4 inlet SO_2 of 9100 ppm or higher, the bed outlet with Improved SCX-2000 is equivalent to the base case.

Typically, catalyst beds in sulphuric acid plants are screened and a portion of the bed is replaced with fresh catalyst during a plant turnaround. The customer now has the option of replacing a portion of the bed with the improved catalyst. Using improved formulation SCX-2000 as a replacement catalyst cap on top of existing caesium catalyst in pass 4 can provide improvement in SO_2 emissions as demonstrated in Table 2.

Table 2: **Potential reduction in SO_2 concentration based on Improved SCX-2000 cap**

Percent of bed as improved SCX-2000	Reduction in SO_2 concentration
0%	Base Case
30%	8-20%
50%	15-35%
100%	20-50%

Source: MECS

This step-by-step improvement is an economical approach to improving SO_2 emissions.

The reductions in sulphur dioxide concentration in Table 2 are based on a single set of process conditions.

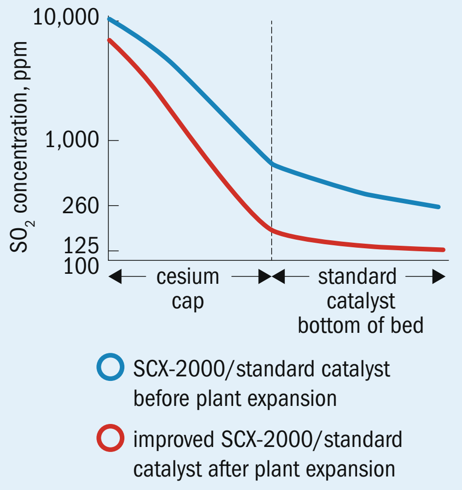
As mentioned before, the reductions may be higher or lower depending on the activity of the catalyst that is being replaced and plant operating conditions.

The implications of a catalyst performance enhancement are even greater for a grass-roots sulphuric acid plant. As shown in Fig. 9, a lower volume of improved SCX-2000 is needed compared to SCX-2000 for a given level of SO_2 emissions. For a new plant installation, the converter can be shorter in height due to the reduction in catalyst volume, reducing capital investment cost. Additionally, the fourth pass pressure drop will be lower, resulting in energy savings throughout the lifetime of the plant.

Commercial feedback

The Veolia – Borderland site, located in El Paso, Texas, USA, produces high quality sulphuric acid using two identical 3X1 sulphuric acid lines designed by MECS. The plant, a collaboration with Western Refining, features an integrated, on-site spent acid regeneration – sulphur gas recovery (SAR-SGR) facility that provides acid regeneration services and processes all of the high strength sulphur bearing gases from the refinery. The two identical lines provide a level of redundancy and robustness required to operate the refinery continuously. The facility replaced the existing Claus-tail gas units, making Borderland among the world's lowest emitting sulphuric acid plants.

Fig 11: PeGASyS data at client site



Source: MECS

Table 3: Data from Lines 1 and 2 at Veolia – Borderland

	Line 1	Line 2 (compensated for HEX leak)
Pass 4 catalyst	SCX-2000	improved SCX-2000
Plant rate, t/d	227	232
SO_2 into pass 4, ppm	5,600	5911 (compensated)
SO_2 at stack, ppm	80	55 (compensated)
Efficiency improvement, %	base case	31

Source: MECS

Table 4: Comparison of performance after installation of improved SCX-2000

	Before plant expansion	After plant expansion
Pass 4 catalyst cap (50% cap)	SCX-2000	improved SCX-2000
Plant rate, t/d	365	425
SO_2 into pass 4, ppm	10,300	6,760
SO_2 out of pass 4, ppm	260	125
Efficiency improvement, %	base case	36

Source: MECS

The two sulphuric acid lines were loaded with MECS catalysts, including SCX-2000 in the final pass. In October 2014, Line 2 replaced its fourth pass with the improved SCX-2000, while Line 1 stayed with SCX-2000. In June 2016, nearly two years after the fresh catalyst was installed, the converter and heat exchanger performance at the site was evaluated using PeGASyS (MECS proprietary Portable Gas Analysis System).

During the testing period, the plant rate, inlet SO_2 and O_2 concentrations, and bed inlet temperatures of the two lines were within 3% of each other. A comparison of information from the two lines is provided in Table 3. Efficiency improvement is defined as the comparison of the percent reduction in unconverted SO_2.

The PeGASyS measurements indicated a significant leak (5 mol-%) in the hot interpass heat exchanger in Line 2, causing a higher SO_2 concentration at the Line 2 pass 4 inlet compared to Line 1. Despite a large heat exchanger leak, the higher activity of Improved SCX-2000 allowed SO_2 emissions from Line 2 to remain 80 ppm without reducing acid production. Without the heat exchanger leak in Line 2, the estimated SO_2 emissions with improved SCX-2000 is 55 ppm; this is a 31% efficiency improvement over the base case.

Commercial success has also been demonstrated at a recent plant expansion where the client increased acid production by more than 15%. A total catalyst replacement included utilising improved SCX-2000 in the fourth pass as a cap on top of a traditional vanadium-based catalyst. PeGASyS testing was used to evaluate the plant's performance before and after the plant expansion with new catalyst. During the plant expansion, the pass 4 catalyst loading was increased by a modest 1 L/t. The inlet SO_2 concentrations and pass 4 bed inlet temperatures were within 2% of each other. The inlet O_2 content in this plant shows some variability, but was approximately 10% more favourable in the before plant expansion case.

Comparison of the SO_2 concentrations in and out of pass 4 are shown in Table 4.

The information in Table 3 is in line with expectations as shown in Fig. 11. Despite the higher rate after expansion, the higher activity of the Improved SCX-2000 cap catalyst significantly increases the conversion of SO_2 providing lower plant emissions.

Data obtained from plants using the Improved SCX-2000 catalyst confirm the higher activity of the catalyst. Improved performance was demonstrated with both a full bed installation and partial bed of the improved formulation catalyst.

BASF's new sulphuric acid catalyst

BASF has been continuously developing new sulphuric acid catalysts with superior performance since the start-up of the first sulphuric acid plant back in 1866. A decisive advantage in the development of new sulphuric acid catalysts is BASF's own sulphuric acid plants, where important findings on the performance of the catalysts can be obtained.

In 2016, BASF introduced its new sulphuric acid catalyst 04-115 Quattro to the market. Due to its unique geometric

PHOTO: BASF

New shape of BASF sulphuric acid catalyst.

shape of four tubes, this caesium based catalyst has a 30 % higher catalytic surface per litre of catalyst in comparison to conventional star-ring shaped catalysts. By utilising this new catalyst, sulphuric acid plants can increase the reactions in the catalyst bed by 30%, leading to a higher production output and simultaneously lowering SO_2 emissions. The new catalyst is therefore especially attractive for sulphuric acid plants with limited catalyst volume as the performance can be improved despite the restriction. In addition, BASF Quattro shows improved physical and mechanic properties: due to the increased catalyst hardness, for example, sieving loss can be considerably reduced.

When the new sulphuric acid catalyst 04-115 Quattro was first used in a reference plant for sulphuric acid production at Domo Caproleuna in the autumn of 2016, the plant manager was very satisfied with the performance: it immediately showed an increase in SO_2 conversion and simultaneously higher capacities.

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Subscription rates:
GBP 440; USD 880; EUR 680

Subscription claims:
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Previous articles from *Sulphur* from 1995 to the present are available digitally in PDF format. To make a purchase, or for a list of available articles, please see: www.bcinsight.com

ISSN: 0039-4890

Design and production:
JOHN CREEK, DANI HART

Printed in England by:
Buxton Press Ltd
Palace Road, Buxton, Derbyshire, SK17 6AE

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Published by: BCInsight Ltd
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