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# SULPHUR

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**Copper and acid demand**  
**India's sulphur balance**  
**Carbon beds in amine systems**  
**Copper smelter provides district heating**



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Cover: Copper smelting.  
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### Using waste heat

Heating a district using waste heat from an acid plant.



### Co-production of acid and SO<sub>2</sub>

Design options for integrating both processes.

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# SULPHUR

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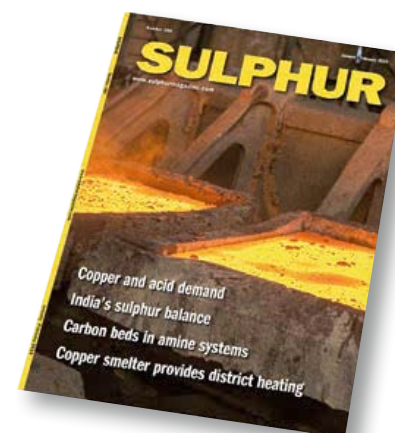
20	<b>India's sulphur balance</b>	India continues to see demand increase for sulphur from increased phosphoric acid production and use, which will not be offset in the short term by additional sulphur production from new refining projects.
24	<b>Copper market to boost acid production</b>	Following a period of overcapacity, the copper market has moved back into deficit, and increased demand and production is likely to generate additional volumes of sulphuric acid.
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30	<b>Sulphur &amp; Sulphuric Acid 2018</b>	A review of papers presented at the CRU Sulphur & Sulphuric Acid Conference, held in Gothenburg, Sweden, in November 2018.
35	<b>Carbon beds in amine systems</b>	M. Thundyil and D. Seeger of Transcend Solutions LLC analyse the utility of carbon beds in removing hydrocarbons in the context of a typical amine treating process and the typical contaminants that exist in the process. Other technologies that can be applied to leverage the efficacy of carbon bed treatment of amine streams are also evaluated.
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50	<b>Operation and performance of the Euroclaus® process</b>	B. Walton and G. Molenaar of Sulphur Experts Inc., O. Garcia of Parkland Refining BC Ltd, A. van Warners and T. Roelofs of Jacobs Nederland B.V. provide a comprehensive overview of the Euroclaus® basics. In addition, based on 15+ years of Euroclaus® performance testing, gathered plant data from the test work is presented and Euroclaus® performance reviewed.

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# Heavy metal



95% of the world's phosphate reserves will no longer meet the requirement.

The sulphur industry is used to having its future determined by environmental regulation. Indeed, arguably its existence in its present form is due to increasing attempts to control emissions of sulphur dioxide to air by removing sulphur compounds from oil and gas. The sulphuric acid industry too must contend with increasing crack-downs on emissions of sulphur dioxide, especially from metal smelting. But emissions of SO<sub>2</sub> and, in the case of sulphur recovery, H<sub>2</sub>S, are not the only concerns that regulators and environmentalists have, and heavy metals are also increasingly being targeted as a problem. Perhaps this began with the phase-out of lead from paints, gasoline, pipes and many of the other uses that lead had found for itself, but as concerns have mounted, it now finds a focus in, for example, airborne levels of arsenic from power plants, incinerators, and of course smelters. Nor is it just arsenic. As lower grades of copper ores are mined and processed, increasing heavy metal content of ores is also leading to an increase in emissions of other heavy metals such as mercury, lead and bismuth to air, water and in tailings. According to the International Copper Study Group, the average arsenic content of copper concentrates has increased by 92% this decade.

But it is a different heavy metal, cadmium, which may deliver one of the greatest upsets – not to the copper industry, but to the phosphate fertilizer industry, the major destination for sulphuric acid, after the European Commission agreed in November last year to reduce permissible levels of cadmium in phosphates in the EU. The agreement must still be ratified by the European parliament and member states, but is likely to do so. It aims to set a limit for the maximum permissible cadmium content in phosphate fertilisers to 60 mg of cadmium per kilogram of phosphate (expressed in P<sub>2</sub>O<sub>5</sub> terms), and establishes a “low cadmium” label for products falling below 20 mg/kg. The aim is to eventually progressively reduce the limit on cadmium content of phosphate to 40 mg/kg after six years, and finally 20 mg/kg after 16 years.

Cadmium in phosphates and what is a safe level has been a heated debate for some years, often conducted at one remove as an argument between Russian and North African (for which read Morocco) phosphate producers – Russia has predominantly igneous phosphate deposits, with very low levels of cadmium (less than 2 mg/kg), while Morocco's phosphates are sedimentary and cadmium levels range from 30 mg/kg to 70 mg/kg on average, although EU internal documents have suggested

that upper levels could be as high as 200 mg/kg. EU countries have very little domestic phosphate rock capacity, and so rely for phosphate production on imports from overseas. Traditionally about one third of this rock has come from Morocco, and about 20% from Russia. Critics of the new regulation argue that the EU has effectively allowed the Russian phosphate industry to gain a commercial advantage using poorly understood health concerns, and point out that once the EU reaches the lower limit (20 mg/kg), 95% of the world's phosphate reserves will no longer meet the requirement. The counter argument is that higher Cd bearing rock can be decadmiated, but this of course adds cost, and probably sufficient that it would still price such rock out of the European market. Nevertheless, given the EU embrace of the Precautionary Principle, Russian producers have been pushing at an open door.

At issue is cadmium's level of toxicity in the food chain. This has sometimes been hard to untangle, as a primary vector for cadmium entering human bodies has been through smoking – tobacco leaves naturally accumulate high levels of Cd. Acute cadmium poisoning caused severe health effects among Japanese rice farmers in the 1950s (so-called ‘painful’ or ‘itai-itai’ disease; softening of bones and kidney failure). But this was from high levels of cadmium uptake. In spite of some concerns about carcinogenicity, the effect on human health of lower levels of cadmium remains uncertain, and the route from rock to fertilizer to plant to human remains open to many variables which can affect levels of cadmium uptake, such as soil pH. Risk-based studies have appeared to show no long term health risks at much higher levels than those being introduced by the EU – US limits are up to 40 times higher.

For Morocco, currently massively expanding its phosphate production, the move has caused consternation as it threatens to choke off one of its major export markets, but for Russia it promises a phosphate bonanza as the years pass and the limits tick downwards.

Richard Hands, Editor

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*The future should not be foreseen, but made possible.*  
Antoine de Saint-Exupéry (1900-1944)

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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

The new year began on a sluggish footing across major global sulphur markets. This followed the downward trend in pricing seen since November. First quarter contracts started settling in some regions in early January but many negotiations were still ongoing. Downward corrections were anticipated across the board for outstanding contracts owing to the bearish trend in the spot market. Expectations for the upcoming quarter are for the market to stabilise once Chinese buyers re-enter the market and prices are expected to rebound, potentially leading to another run up in pricing.

Monthly price postings in the Middle East at the end of 2018 represented a turning point in the market as sentiment shifted following the price run. While tight supply prevailed, buyers in China and India moved to the sidelines, stagnating the market and leading to significant price erosion. Muntajat announced its January Qatar Sulphur Price (QSP) at \$126/t f.o.b., a \$9/t drop on December. State owned ADNOC in the UAE set its price at \$127/t f.o.b. Ruwais for liftings to the Indian market – down by \$28/t on the previous month. Meanwhile in Saudi Arabia, Aramco Trading did not set a price for December or January, leading to speculation in the market the producer may be changing its pricing strategy. On the contract front, ADNOC started settling Q1 2019 contracts at \$124/t f.o.b., marking close to a \$40/t

drop on the previous quarter, a clear reflection of the weaker sentiment.

Supply has been an issue for the NW European region and demand remained robust through the latter part of 2018. Spot sulphur interest was seen in December – thought to be a result of the ongoing tightness. Some refineries operated with lighter crudes, leading to reduced sulphur recovery. The issues at the Grossenkneten gas field in Germany in 2018 led to a significantly tighter balance in West Europe.

Vancouver sulphur exports dropped in January-October 2018, on the back of tighter supply. Increased exports via rail into the US also led to reduced availability for Vancouver shipments. Chinese trade saw a significant downturn while Australia resumed its place as the leading market for offshore Canadian tonnage. Spot prices saw a downward correction in the fourth quarter of 2018, on the back of China stepping out of the market and prices easing across all export regions. Vancouver spot prices eroded to \$122/t f.o.b., due to the international downturn at the end of 2018. Expectations are for prices to stabilise and potentially recover in the upcoming quarter, with the typical seasonal tightness also having an impact over the winter period. Western Canadian sulphur supply is expected to drop in 2019 following a local government mandate to cut crude oil output by 325,000 bbl/day from 1 January. Industry sources have made initial estimates of production reduc-

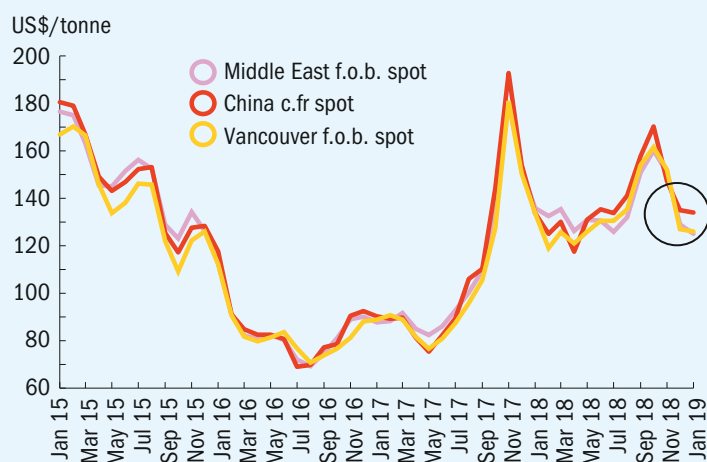
tions of around 400 tonnes per day but the full extent of the loss remains to be seen.

The domestic US market was balanced to tight in December, with some length noted in the US Gulf region. In the US, Tampa Q4 2018 prices were agreed at \$140/long tonne c.fr, compared with \$121/long tonne c.fr in the previous quarter. According to the USGS, US sulphur production totalled 7.44 million tonnes in the first ten months of 2018, a 60,000 tonne decrease on the same period a year earlier.

Meanwhile, US Gulf export sulphur prices also dropped on the back of fresh deals, down to \$112-117/tonne f.o.b., at the start of December. This came initially on the back of the need to reduce length in a deal to Morocco.

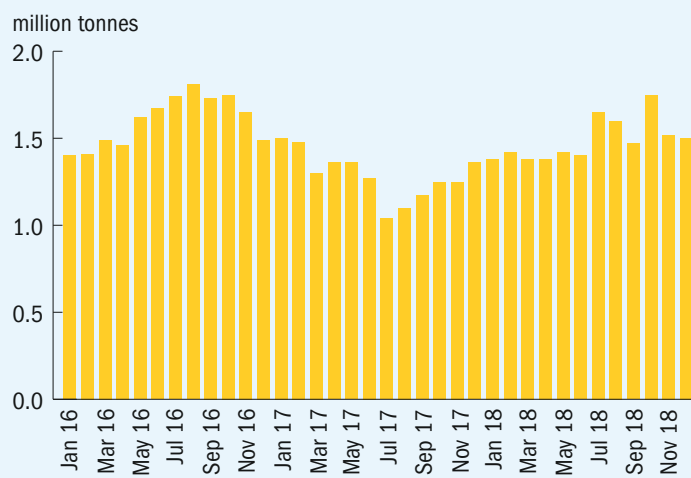
Spot prices in China dropped to \$120 – 140/t c.fr at the end of November, remaining in this range into the new year. This reflected the weak sentiment in the market and exerted downward pressure on global export prices as buyers took to the sidelines and paused purchasing activity. China's return to the market is expected towards the latter part of February when the Lunar New Year holidays come to an end. However, the continued absence of buyers in the market in the interim may lead to a significant price run once buying resumes. The downturn has partly been led by the uncertainty surrounding the downstream processed phosphates market, with export prices coming under pressure as well as flat domestic demand. Some buyers in the South region also reported healthy sulphur stocks, negating the need for fresh imports. The approaching holidays remained a deterrent to significant purchases and stockpiling in early January. Sulphur stocks at the major ports in China dropped to around

Fig. 1: Global sulphur prices, Jan 2015 to Jan 2019



Source: Integer, Argus

Fig. 2: China sulphur port inventory, Jan 2016 to Dec 2018



Source: Integer, Argus

1.2 million tonnes in January with declining stocks noted at river ports.

Indian market prices also fell in line with developments in China, ranging \$151-157/t c.fr in early January. Further tests to the market were expected from purchase tender awards due from buyers PPL and RCF. Initial offers were heard around \$150/t c.fr but sources were expecting prices in the \$140s/t c.fr. The potential reopening of the Sterlite Tuticorin smelter in 2019 may ease pressure on sulphur in the local and import market as the prolonged outage led to some buyers looking to cover the shortfall through increased sulphur burning. Indian sulphur imports totalled 989,000 tonnes in January – October 2018, up around 6% on a year earlier. Middle East supply accounted for 80% of all imports. Qatar shipments were up by 38% at 402,000 tonnes.

### SULPHURIC ACID

Supply was the main focus point in the global sulphuric acid market through 2018, with shortness sustaining high market prices into the new year. The first half of 2019 is expected to remain tight for acid but the latter part of the year remains in question, with the potential for a market correction should supply normalise. The news that the Sterlite Tuticorin smelter in India will be re-opening has shifted the tone for the Asian market and may tip the balance earlier than expected this year. The Supreme Court in India refused to stay an order for the Sterlite smelter closure. The company is now set to file an application

to the environmental regulator to operate the 1.1 million tonne per year acid smelter. There has yet to be a confirmation of a start up date but market sources estimate an April restart is a possibility. The outage through 2018 led to a direct impact on acid imports, sulphur and finished fertilizer product demand. Argus estimates Indian sulphuric acid imports totalled 1.4 million tonnes in 2018 – up by 59% in 2017. Once acid production resumes to normal levels at Sterlite, acid imports are expected to drop to more regular levels, potentially easing pressure on tightness in the market.

NW European spot acid export prices firmed to \$85-95/t f.o.b., in December, up \$15/t from November. Unplanned smelter outages as well as maintenance turnarounds and strong demand from import markets led to this run up in pricing.

The end of 2018 saw Chile annual contracts settling out following the protracted negotiations and shift away from traditional yearly pricing structures. This time around contracts included quarterly and half yearly prices – with buyers reluctant to agree high fixed prices for the full year period. Prices ranged \$125-135/t c.fr for the full year. Quarterly prices were heard in the range of \$110-150/t c.fr. Prices for the year reflect a seven year high – a reflection of tight supply and firm demand expectations for the coming months due to outages at smelters.

Moroccan acid imports remain a bright spot for the global acid market, owing to the size of imports in recent years. For 2018, acid imports totalled around 1.6 million tonnes –

representing a 5% rise on 2017 trade. OCP's expanding processed phosphates production accounted for this uptick in acid demand. For 2019, any potential growth will be a major focus due to the expected tight balance. North African acid prices were pegged firm at \$95-105/t c.fr in early January.

Sulphuric acid exports from China remain a key market talking point due to the significant rise through 2018 as well as the addition of smelter based acid trade to the export market – aside from the traditional shipments from sulphur based acid producer Two Lions. The upward trajectory in global prices spurred China export prices as the supply shortage propped up the market. January – October 2018 exports tallied 974,000 tonnes, with Morocco receiving the most significant portion, at 25% while Chile took 20%. Looking ahead to 2019 – there has been discussion surrounding new producer Chinalco – with production due to ramp up in July 2019 – however to date there is no export infrastructure believed to be in place. On the import front, trade appears to be softening as expected. Argus has collated data reflecting diverted volumes from Japan and South Korea. Overall, a 28% decline has been estimated for imports in January – September 2018, at 679,000 tonnes. South Korea remains the leading supplier at 624,000 tonnes while Japanese tonnes were at just 30,000 tonnes. Our view is that China will increasingly be well supplied by domestic production, due to the spate of copper smelters in development and this will ultimately reduce the country's import requirement for sulphuric acid.

## Price indications

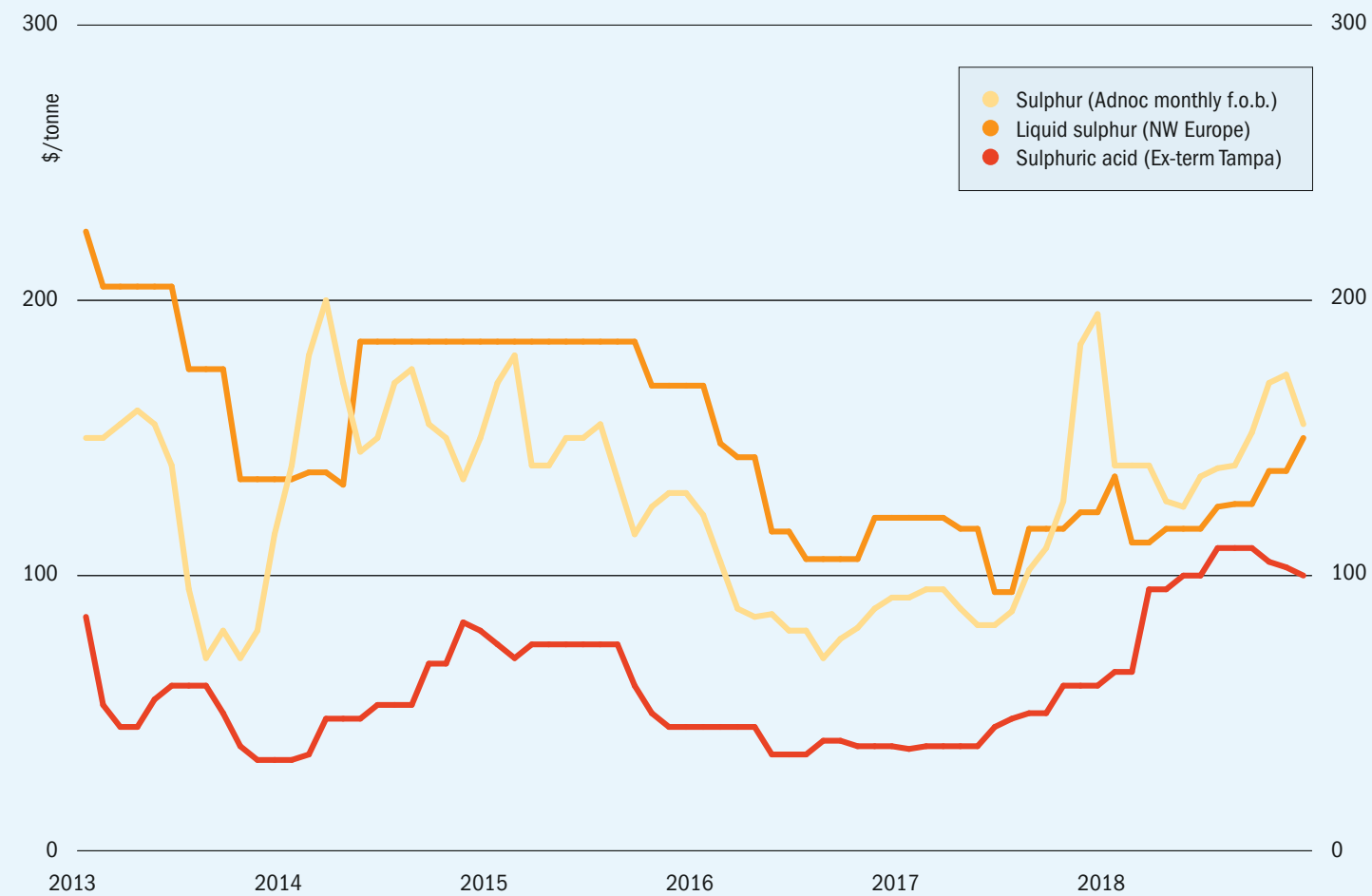
Table 1: Recent sulphur prices, major markets

Cash equivalent	August	September	October	November	December
<b>Sulphur, bulk (\$/t)</b>					
Adnoc monthly contract	140	152	170	173	155
China c.fr spot	175	190	190	176	153
<b>Liquid sulphur (\$/t)</b>					
Tampa f.o.b. contract	121	121	140	140	140
NW Europe c.fr	126	126	138	138	150
<b>Sulphuric acid (\$/t)</b>					
US Gulf spot	110	110	105	103	100
<i>Source: various</i>					



# Market outlook

Historical price trends \$/tonne



Source: BCInsight

## SULPHUR

- Increased sulphur production capacity is due to come online in the Middle East but any delays to projects in the pipeline could limit the downside to pricing in the outlook.
- The return of end users in China and India to regular purchasing activity will likely end the recent soft trend in pricing, with a rebound in pricing expected once restocking begins.
- OCP/Morocco is expected to remain a bright spot in the year ahead as its processed phosphates expansion continues to absorb increasing volumes of sulphur and acid.
- The changing tide of sulphur production capacity in China is expected to influence imports in the outlook and global trade. Chinese sulphur production totalled 5.6 million tonnes in January – November 2018, marking a 7% rise year on year. Growth continues to be driven by increased output from oil and gas projects. Production from new projects is set to be absorbed into the

domestic market, potentially leading to a drop in the need for imports.

- **Outlook:** Tight supply is expected to prevail in the sulphur market – with a rebound in pricing expected once Chinese buyers return to the market in earnest. Producer availability out of the Black Sea is squeezed over the winter period, supporting a floor to pricing. Extreme tightness in the sulphuric acid market also supports pricing in the short term outlook as some regions look to substitute merchant acid with increased sulphur burnt acid. Increased supply through the year from Kashagan in Kazakhstan and domestic output in China may support a softer sentiment in the second half of 2019.

## SULPHURIC ACID

- A timeline for the restart of Sterlite's Tuticorin smelter has yet to be confirmed but this will have a significant impact on trade to India as well as pricing.
- China's growing exports are expected to remain part of the trade picture in 2019. Increasing smelter capacity in the domestic market is likely to influence

both imports and exports to and from the country. Logistics could be an issue for some new copper smelters however, which may lead to erosion of imported tonnes as additional volumes stay within the country.

- Limited availability for spot tonnes from South Korea and Japan will keep the market balance tight for the short term in Northeast Asia.
- **Outlook:** Sulphuric acid prices are expected to remain firm in the coming weeks and early part of the year. Tight supply is set to prevail with the spate of planned turnarounds in Asia and Latin America reducing availability. While the Tuticorin smelter is to reopen, this is not expected to impact the market balance in the first quarter. These factors and healthy demand point to limited downside in the market for the first half of the year. The continued presence of OCP/Morocco in the market also adds to the firm expectations for European acid prices. There is uncertainty surrounding the second half of the year, with some regional pockets likely to see improved supply. ■



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## CHINA

### New sulphur limits on shipping boost low sulphur fuel demand

China has tightened its sulphur limit restrictions on shipping by imposing a 0.5% sulphur cap for bunker fuels not only in its initially designated Emission Control Areas but also along its entire coastline. The move is expected to support higher demand regionally for low sulphur marine gasoil and low sulphur fuel oil (LSFO). China's apparent demand for low sulphur MGO is expected to rise 32% year on year to 8.09 million t/a in 2019, while demand for LSFO and blended distillates will grow 44% year on year to 5.12 million t/a, according to S&P Global Platts Analytics.

China's Ministry of Transport announced the expansion of the Emission Control Areas from the initial designated region of

the Yangtze and Pearl River deltas and Bohai rim to encompass the whole of China's 12 mile coastal limit in early December. As part of the latest move, large vessels will be required to burn 0.5% sulphur bunker fuels while the smaller ones will have to use 10 ppm sulphur bunkers, in line with National Phase 5 & 6 emissions, when they are in inland waterways. The new policy also requires all seagoing vessels to use bunker fuel with 0.1% sulphur when they are entering inland waterways areas in China, starting from January 1st, 2020. The Ministry of Transport is also said to be considering plans for China to implement a 0.1% sulphur bunker fuel oil limit in all ECAs from January 1st, 2025.

### Huizhou Petrochemicals starts up diesel hydrogenation unit

DuPont Clean Technologies is pleased to announce the successful performance test of a 3.4 million t/a *IsoTherming*<sup>®</sup> diesel hydrogenation (DHT) unit by CNOOC Huizhou Petrochemicals Co., Ltd. at its Huizhou refinery in Guangdong. CNOOC completed calibration of the unit at 100% load in the third quarter of 2018, with the system meeting all design requirements and product quality targets. Earlier in 2018, the refinery also successfully started up a 2.6 million t/a vacuum gas oil (VGO) hydrogenation unit.

The *IsoTherming*<sup>®</sup> technology uses the reactor effluent as a liquid recycle stream rather than a recycle gas system to deliver the hydrogen required for chemical reactions. This eliminates the need for a costly recycle gas compressor, high pressure amine absorber and downstream high pressure separation equipment, significantly reducing the capital cost for the unit. With the application of the recycle pump and the efficient use of the available heat from the reactor effluent, the unit operates with a significant reduction in operating costs as compared to conventional hydroprocessing technology.

With a total installed capacity of 440,000 bbl/d in two phases, the CNOOC refinery has already previously invested in wet scrubbing catalytic cracking flue gas desulfurisation technology, licensed by DuPont Clean Technologies, for two sets of fluid catalytic cracking flue gas dedusting units (FCCUs). The CNOOC Huizhou refinery also contains a 160,000 t/a alkylation unit using *STRATCO*<sup>®</sup> alkylation technology to convert low value isobutane and olefins

into high value alkylate, a key ingredient for the production of clean gasoline.

## UNITED ARAB EMIRATES

### ADNOC to capture CO<sub>2</sub> emissions at Shah and/or Habshan

The Abu Dhabi National Oil Company says that it is moving ahead with plans to expand the capture, storage and utilisation of carbon dioxide (CO<sub>2</sub>), produced from either the Habshan-Bab gas processing facilities or the Shah sour gas plant. A decision on which plant to capture the CO<sub>2</sub> from first will be taken in 2019. The project will be engineered so as not to interrupt ongoing production from either facility, according to ADNOC.

The additional CO<sub>2</sub> capture will reduce the company's, as well as freeing up natural gas, which has previously been used for oil field injection, for other more valuable purposes, while simultaneously addressing growing global demand for oil by boosting recovery from its maturing reservoirs. The Shah plant, built and operated by a joint venture between ADNOC and Occidental Petroleum Corporation, is one of the world's largest facilities processing ultra-sour gas. It processes about 1.3 billion standard cubic feet per day (scf/d) of sour gas and associated condensates with a hydrogen sulphide content of over 20% and CO<sub>2</sub> content of 10%. By 2025, modifications to the facility would enable the gases to be captured as part of the sulphur recovery process and converted into pure CO<sub>2</sub> for enhanced oil recovery (EOR). Using advanced CCUS technology, more than 2.3 million t/a (120 million scfd) of CO<sub>2</sub> are planned to be captured and safely locked away underground.

Meanwhile, the Habshan and Bab complex could capture another 1.9 million t/a of CO<sub>2</sub> (100 million scf/d). The complex can process up to 6.2 billion scf/d of associated gas, making it the largest in the UAE and one of the biggest in the Gulf.

### Wintershall to be part of Ghasha development

German oil and gas producer Wintershall, a subsidiary of BASF, has taken a 10% stake in the Ghasha offshore sour gas mega-project, according to developer ADNOC. Ghasha concession consists of the Hail, Ghasha, Dalma and other offshore sour gas fields, including Nasr, SARB and Mubarratz. Wintershall will contribute 10 percent of the project capital and operational development expenses, marking the first time a German oil and gas company has been part of an ADNOC concession, and bringing the company's world-leading sour gas technology. Wintershall has more than 40 years of experience in the production of sour gas, developing 16 fields in Germany and producing 30 billion cubic meters of sour gas via four gas purification plants.

The Ghasha project is expected to produce more than 1.5 billion scf/d of natural gas. Wintershall joins Eni (which has a 25% stake) in the 40-year concession agreement. In addition to developing the Ghasha concession area, ADNOC plans to increase production from its Shah field to 1.5 billion scf/d and move forward to develop the sour gas fields at Bab and Bu Hasa. ADNOC will also tap other sources of gas including the giant Umm Shaif gas cap and the emirate's unconventional gas reserves, as well as new natural gas accumulations, which will continue to be



appraised and developed as the company pursues its exploration activities.

## INDONESIA

### Air Liquide to provide hydrogen unit for Pertamina

Air Liquide Engineering & Construction has been selected as a technology licensor by Indonesia's national oil and gas company Pertamina to provide a licence and basic engineering for a steam reforming based hydrogen plant with a capacity of 120,000 Nm<sup>3</sup>/h for Pertamina's refinery site in Balikpapan, Borneo. The contract is part of a Refinery Development Master Plan (RDMP) which will expand crude processing capacity as well as enable production of cleaner fuels conforming to Euro 5 standard.

## OMAN

### Duqm agrees \$4.6 billion loans

The new Duqm Refinery in Oman, a joint venture between the Oman Oil Company (OOC) and Kuwait Petroleum International, the downstream arm of Kuwait Petroleum Corporation, says that it has signed seven loan agreements worth \$ 4.6 billion with local, regional and international financiers. Under the deals, international financial institutions will supply \$1.43 billion into the project, located in the southeastern Al-Wusta province of the Sultanate of Oman.

Islamic banks will contribute a further \$890 million, local Kuwaiti and Omani commercial banks \$490 million, the UK Export Finance agency \$700 million, the Spanish export credit agency (CESCE) \$500 million, and the (South) Korea Trade Insurance Corporation (K-SURE) \$600 million.

Speaking at the signing ceremony, KPI CEO and chairman of Duqm Refinery Nabil Bourisli said that the deal reflects the trust of international financiers in the Kuwaiti and Omani economies. Deputy Chairman of Duqm Refinery Helal Al-Kharousi said international financial institutions realise the strategic importance of this project, which will drive economic growth in the region.

The 230,000 bbl/d refinery will occupy a 900 hectare site at the Duqm Special Economic Zone, which is being developed as an industrial centre for Oman, with an 80km pipeline and onshore export platform at Al-Duqm harbour, giving access to international shipping lanes in the Indian Ocean and the Arabian Sea. It aims to produce light/middle distillates, focusing on

naphtha, jet fuel, diesel and LPG as its primary products. The refinery will also include hydrocracking, hydro-treating and delayed coking units, along with sulphur recovery and hydrogen generation. Multi-national construction and engineering companies were awarded contracts to start developing the project last June.

## RUSSIA

### EuroChem starts up urea ammonium sulphate plant

Swiss-based EuroChem Group AG says that it has begun production at Russia's first urea ammonium sulphate (UAS) fertilizer plant. The new 600 t/d facility, built at EuroChem's existing Novomoskovskiy Azot site, 200 km south of Moscow, was developed in partnership with urea technology company Stamicarbon. EuroChem says that its total investment in the plant was \$84 million.

"Novomoskovskiy Azot has always been an innovation leader," Mr Nechaev, General Director of MCC EuroChem, commented. "This is where granulated urea, calcium ammonium nitrate, and low-density ammonium nitrate were all first produced in Russia and now, in another first, we have launched the country's only urea ammonium sulphate facility. This new fertilizer will meet the growing needs of Russian and European farmers."

UAS production will complement EuroChem's current portfolio of sulphur-enriched fertilizers, which includes ammonium sulphate (AS) and ammonium sulphate-nitrate (ASN).

## IRAN

### South Pars gas sweetening train comes on-stream

The third train at the gas sweetening plant for phases 22, 23 and 24 of Iran's South Pars gas field project has been commissioned according to Farhad Izadjou, the project director. The plant is currently producing 8 million m<sup>3</sup>/d of sweetened gas from sour gas supplied from South Pars phases 6, 7 and 8. At full production it will be processing 14 million m<sup>3</sup>/d (500 scf/d) of sour gas, as part of a complex capable of processing 1.5 billion scf/d \*42 million m<sup>3</sup>/d) of sour gas. South Pars phases 22-24 aim to produce at capacity 56 million m<sup>3</sup> of gas per day, 2,900 t/d of LNG, 2,750 t/d of ethane, 75,000 bbl/d of gas condensate and 400 t/d of sulphur (130,000 t/a).

## SOUTH AFRICA

### BP investing in refinery upgrade

BP Southern Africa (BPSA) says that it is investing \$250-290 million dollars in a refinery upgrade in South Africa as part of a \$1 billion programme of investment in the country. The refinery upgrade will be at the 180,000 bbl/d SAPREF refinery at Durban, South Africa's largest refinery, and will be aimed at producing lower sulphur diesel and meeting new MARPOL requirements for shipping fuels. SAPREF is a 50:50 joint venture between Shell and BPSA, a subsidiary of British oil major BP. Tie-ins for the upgrade will take place from



The SAPREF refinery, Durban.

May to June 2019, according to BPSA. The upgrade has been driven by new rules demanding lower fuel sulphur content and changing customer preferences for cleaner diesel, such as D50 and D10.

## CANADA

### Wapiti Gas Plant set for 2019 opening

SemCAMS says it has entered into a long-term take or pay agreement to process 70 million cfd of sour gas at its Wapiti Gas Plant for an unnamed company described as a "Canadian subsidiary of a large international oil and gas company.". The agreement will last for 10 years. The Wapiti Gas Plant is due to come on-stream in early 2019, producing 200 million scf/d of gas, 95% of which is now contracted for.

"We are pleased to secure this long-term processing agreement that effectively fills SemCAMS Wapiti Gas Plant and helps ensure the plant will operate in the most efficient and cost effective manner," said Dave Gosse, vice president and general manager of SemCAMS, in a statement.

SemCAMS has also received approval from the Alberta Energy Regulator to construct a new plant in the Pipestone area. The new plant will be able to process 280 million cubic feet of gas per day and connect to the Wapiti Gas Plant via the Pipestone pipeline. Construction on the pipeline itself is expected to be finished by late 2019.

### Shell sells Calgary technology centre to University

The University of Calgary has announced that it is purchasing Shell Technology Centre Calgary. The facility has operated in the University Research Park for three decades. The University is also purchasing the University Research Park from the province of Alberta in a deal valued at C\$97 million.

Shell's Technology Centre has made award-winning breakthroughs including improving yields in oil sands processing using paraffinic froth treatment, as well as innovations in sour gas, transportation fuels and chemicals. It will now be converted during 2019 into a Life Sciences Innovation Hub as a centre for research excellence and innovation according to the university.

Shell Canada chair Michael Crothers said; "We are delighted to enable the creation of the Life Sciences Innovation Hub for the University of Calgary through the sale and in-kind gift of our Shell Tech-

nology Centre Calgary. For more than 30 years, our teams at the site led energy sector innovation and it's fitting that the building's legacy of spurring innovation in Alberta will continue as part of UCalgary. Shell will continue pursuing research and development activities right here in Canada from our operating sites and with third parties."

### Ontario sets new sulphur dioxide rules

Ontario's Ministry of Environment, Conservation and Parks (MECP) has proposed new regulation to reduce sulphur dioxide emissions from Ontario petroleum facilities. Under the new sulphur dioxide regulations, petroleum facilities in Ontario are required to notify MECP of sulphur dioxide flaring incidents exceeding the established threshold and post the emissions on a website, as well as submitting a report as to the cause of the incident and corrective and preventative actions taken. They must also calculate SO<sub>2</sub> emissions from flaring incidents and install emissions monitoring equipment within 3 years; and assess the efficiency of sulphur recovery units. The threshold established by the regulation is 225 kg in a 24 hour period.

## KAZAKHSTAN

### TCO reaches almost 100% utilisation

TengizChevroil said in its 3Q 2018 results presentation that the gas utilisation rate at its Kazakhstan project is now over 98%. TCO said it has invested \$3 billion since 2000 on projects to minimise environmental impact, improving reliability to reduce the number of unplanned outages and consequent sour and acid gas flaring. The company said total air emissions generated per ton of oil produced have been reduced by 73% since 2000, at the same time that crude oil production has grown by 2.7 times as a result of investments in capital programs and equipment reliability.

## ROMANIA

### Lukoil to invest in new sulphur recovery plant

Russian energy group Lukoil says that it will invest \$100 million in its Romanian refinery Petrotel Lukoil near Ploiesti over the next three years. The company plans to modernise the coking plant, where a \$72 million project will be completed in 2021, and it will also construct a new sulphur

recovery complex, for which the company has earmarked a further \$29 million, also with a 2021 completion deadline.

## THAILAND

### Thai Oil to start clean fuel project

Thai Oil's refinery in Sri Racha, Chon Buri aims to switch from refining heavy oil to producing more high-margin products like diesel and jet fuel. The company, Thailand's biggest oil refiner by capacity, says it will proceed with investment in the Clean Fuel Project (CFP) after several years on the drawing board. The project is set for development spending during 2019-22 at a total cost of \$4.73 billion. Chatchai Siriwit, Thai Oil's investor relations manager, said the CFP is designed to improve productivity and lean operating costs because several new oil refineries across Asia-Pacific have developed operations over the last few years. The product slate will change towards production of low sulphur diesel and kerosene, which are expected to be in demand because of increased use in shipping due to new IMO regulations and increased demand for aircraft fuel as tourism increases worldwide.

## MEXICO

### Mexico to tender new refinery by March

President Andres Manuel Lopez Obrador lunched Mexico's national refinery plan on December 8th 2018. President Obrador took office a week earlier, pledging to reboot the country's refining sector following the failure of energy reforms a few years ago. As the first part of the plan, Mexico will tender for construction of a new 340,000 bbl/d refinery in Dos Bocas, Tabasco in 2019 as part of the country's plan to triple domestic gasoline production. State-owned Pemex's six refineries have a total crude processing capacity of 1.6 million bbl/d, but average refining capacity for 2018 ran at only 38%, requiring Mexico to import 80% of its fuel requirements.

The new \$8 billion Dos Bocas refinery will process Mexico's increasing domestic production of heavy sour Maya crude, which has a sulphur content of 3.3%. Construction is scheduled to be complete in just three years, although there are questions about the achievability of this target. The next phase of the refinery plan will add 600,000 bbl/d of capacity at the six existing refineries through upgrade works. ■



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## INDIA

### Tuticorin smelter gets reprieve

In early January the Indian Supreme Court rejected an appeal by the Tamil Nadu state government to keep the Vedanta-owned Sterlite copper smelter in Tuticorin closed. A ruling in December by the Indian environmental court, the National Green Tribunal (NGT), would have allowed the smelter to recommence operations, but the future of the plant was put in doubt again after Tamil Nadu's government appealed to the country's Supreme Court, claiming that the NGT did not have jurisdiction to hear the matter. The smelter was closed in May 2018 after the plant's operating license was not renewed by Tamil Nadu due to environ-

mental concerns that had driven a huge local protest movement, leading to riots in which police killed 13 demonstrators.

The closure has removed 1.2 million t/a of sulphuric acid from the market, leading to a price spike in India as phosphate fertilizer producers scramble to find acid from elsewhere. The price increase – Indian acid prices are around \$100/t – double their level last year – has led to increased demand for sulphur and phosphate imports as well as sulphuric acid. Vedanta says that potential remedial work caused by the long shutdown may possibly require additional time to resolve, and no production is now expected before April 2019. ■

## FINLAND

### Outotec to supply leaching technology for Terrafame

Finnish metal manufacturer Terrafame Ltd, has awarded Outotec a contract for the delivery of pressure leaching and solvent extraction technologies for a battery chemicals plant to be built in Sotkamo. The contract is worth €34 million according to Outotec. Outotec were also Terrafame's partner for the pre-feasibility study phase. The company's scope of delivery comprises technology and engineering of the leaching and solvent extraction plants, supply of proprietary equipment as well as advisory services for installation, training, commissioning and start-up. The battery chemicals plant, expected to be ready for commissioning in 2020, will have the capacity to produce 170,000 t/a of nickel sulphate and 7,400 t/a of cobalt sulphate to be used in electric vehicle batteries. The plant will also produce 115,000 t/a of ammonium sulphate as a by-product, for sale into the fertilizer and industrial markets. It will consume just over 100,000 t/a of sulphuric acid.

"We are pleased to be Terrafame's trusted technology partner in this project. The demand for battery chemicals is expected to grow significantly in the future, and we have the required expertise and proprietary equipment for their processing", said Kalle Härkki, head of Outotec's Metals, Energy & Water business unit.

## UNITED STATES

### Alon Refining to use DuPont alkylation technology

DuPont Clean Technologies has been awarded the contract to supply Alon Refining Krotz Springs, a part of Delek US, with

a license and engineering services for its *STRATCO*® sulphuric acid alkylation technology at the refinery in Krotz Springs, Louisiana. The 6,500 bbl/d alkylation unit will enable Alon to generate low-sulphur, high-octane alkylate with zero olefin content, improving the quality and quantity of the refinery's gasoline pool to meet increasingly strict clean fuel standards. The *STRATCO* process uses sulphuric acid to catalyse low value olefin conversion into high value alkylate.

"DuPont looks forward to working with Alon Refining on this project. Adding an alkylation unit to the refinery enables Alon to increase its production volume of gasoline while producing multiple grades of summer fuel," said Kevin Bockwinkel, global licensing business manager, *STRATCO*® Alkylation Technology.

### Mosaic to begin Ona operations in March

Mosaic said in December that it had acquired its final remaining permit for the Ona phosphate mine project in Hardee County, Florida – a US Army Corps of Engineers 404 permit. The company now says that it plans to move to mining operations by March 2019. The project adds 160 million tonnes of phosphate rock across 16,000 acres and adds reserves which will extend the life of Mosaic's Four Corners operation by 14 years, as well as providing mining for decades at the South Pasture mine once production resumes at that facility. South Pasture was idled in August 2018 because Mosaic had sufficient rock from other mines to meet current production requirements. Reopening it depends on a resumption of production at Mosaic's Plant City fertilizer plant, which closed in late 2017, and depends on an increase in global phosphate demand and pricing.

"This important project helps secure the continued operation of our Florida manufacturing facilities," said Mosaic President and CEO Joc O'Rourke. "It will deliver tremendous value to the local community, our employees and our investors well into the future."

## MEXICO

### Silver sulphate project award

Outotec has been awarded a contract for the delivery of a minerals processing plant for a precious metals project in Mexico. The company will also deliver process equipment for upgrades of two other silver sulphide ore processes for the same customer. The total value of the contracts is approximately €30 million, and covers the entire process flowsheet of grinding mills, flotation machines, concentrate and tailings thickeners, as well as concentrate filters, automation, and various spares and supervision services for the new precious metals concentrator. For the upgrade of existing silver processes, Outotec will deliver additional flotation machines and multiple fine grinding equipment for improved recovery. The deliveries will take place in the end of 2019.

"We are pleased that we were chosen to deliver our leading technologies and services that enable our customer to improve their profitability in a sustainable way", says Kimmo Kontola, head of Outotec's minerals processing business.

## SOUTH AFRICA

### Vedanta concerns over zinc expansion

Vedanta has said that its plans to increase zinc output in southern Africa sixfold over the next decade could be scuppered by concerns over power supply. South African power company Eskom has faced major





Skorpion Zinc, Namibia.

financial troubles and struggled to meet capacity needs, leading to power cuts. Vedanta operates the Gamsberg and Black Mountain zinc mines in North Cape, as well as the Skorpion zinc mine in Namibia, and had been looking to increase output from 157,000 t/a to 1.1 million t/a by 2030. The company has spent \$400 million on the first phase of a fully integrated zinc production site at Gamsberg, which is projected to produce 250,000 t/a of zinc as concentrate at a cost of less than \$1,000/t, putting it in the lower quartile of world zinc output in cost terms, against a market price of \$2,700/t. Gamsberg is projected to eventually produce 600,000 t/a, with output at Black Mountain and Skorpion to reach 200,000 t/a each. Phase Two of the Gamsberg expansion plan is expected to require an outlay of \$350-400 million on the mine itself, with an additional \$700-800 million for a nickel smelter and refinery, which will require 200 MW of power. The company is looking generating sulphuric acid from the smelting process which it hopes to sell on to fertilizer producers, and there are discussions involving the South African Industrial Development Corporation to attract an investor to set up a fertilizer plant. In the absence of that, generation of so much sulphuric acid could make the project non-viable.

## AUSTRALIA

### King River now looking to sulphuric acid leach

King River Resources Ltd, which is developing the Speewah Vanadium Project in the East Kimberley region of Western Australia, says that the company's board is now focusing on a more flexible, modular engineered project strategy that better takes into consideration the flat, surface lying nature of

the vanadium resource, and that it is now looking at on-site sulphuric acid vat leaching and the processing of  $V_2O_5$ ,  $TiO_2$ , iron oxide and other high purity products (vanadyl sulphate and high purity alumina), as well as on-site production of acid, to generate surplus heat, steam and electricity. The next phase of pre-feasibility (PFS) work will examine more detailed costings of beneficiation and review in more detail the capital and operating costs for a vat leach operation and sulphuric acid plant, with the planned publication of a PFS Study in 2019.

### Centrex to concentrate on Ardmore phosphate project

Centrex Metals is selling its Port Spencer landholding in South Australia to FREE Fyre, a local rural investment business, for A\$1.4 million. The company had been looking to develop the port for the export of bulk commodities, including the company's iron ore project. However, Centrex says it has now taken a strategic decision to switch out of iron ore and into the fertilizer market, using the proceeds from the sale of Port Spencer into its flagship Ardmore phosphate rock project in Northwest Queensland, which the company says is "fast approaching" production. In October, the company released a definitive feasibility study and maiden ore reserve for Ardmore. The reserve at Ardmore said to be 10 million tonnes at 30.2%  $P_2O_5$ , giving a 10-year mine life with an annual production of 800,000 t/a of wet phosphate concentrate. The company anticipates start-up operations at Ardmore will produce 30,000 tonnes of concentrate in mid-2019 to provide 5-6,000 tonne trial shipments to "priority customers." In December it received an environmental permit from the Queensland Department of Environment and Science for the project's start-up mining and processing operation.

## EUROPEAN UNION

### EU passes law on cadmium in phosphates

The European Parliament, European Council and European Commission have reached an agreement on new rules to promote biologically-based fertilizers. The new law, which will amend the EU's Fertilising Products Regulation, is aimed at facilitating the access of organic and waste-based fertilizers to the EU single market. However, the new rules will also introduce limits for cadmium and other contaminants in phosphate fertilizers. According to the EU lawmakers, this will help to reduce waste, energy consumption and environmental damage, as well as limit the risks to human health. However, the 60 mg/kg limit on cadmium will effectively block the use of phosphate fertilizer from Morocco, where there is a higher concentration of cadmium in the rock, and leave the EU dependant on higher purity phosphate from Russia.

## CHINA

### China removes export tax on phosphates

And the end of December 2018, the Chinese government announced revised rates for tariffs on a variety of goods for 2019. Over 700 different products see changes, aimed at promoting the Chinese economy and grow its import and export trade, according to the Ministry of Finance. Export duties on 94 items such as chemical fertilizers, apatite, iron ore, slag, coal tar, wood pulp and various other materials have been cancelled. Tax rates on eight commodities, including wheat, will be unchanged; import tariff rates for urea, compound fertilizers and ammonium phosphates will be subject to a 1% tax rate. In the phosphate arena, export tax on phosphate rock is now zero, down from 10% in 2018. All other phosphate fertilizer products have also been revised down to zero import tariff rates. The import tax for sulphur remains unchanged at 1%. VAT on the import of sulphur and ammonia has been reduced from 17% to 16%.

## CANADA

### Arianne secures second offtake deal

Arianne Phosphate says that it has entered into its second formal offtake agreement for the purchase and marketing of high-purity phosphate concentrate from its Lac à Paul project, currently under devel-



opment. Arianne said that the deal was with “an industry leading global trader of fertilizer products, including phosphate concentrate and phosphoric acid”. Under the terms of the agreement, the buyer commits to purchase a specific annual quantity of phosphate concentrate, with an option to purchase additional amounts under certain terms and conditions. Arianne announced a previous offtake deal in September 2018.

“This agreement is yet another validation of Arianne’s Lac à Paul project,” said Brian Ostroff, CEO of Arianne Phosphate. “By entering into this relationship, Arianne’s product will now have an even greater global reach by leveraging on the operations and relationships of a long-established, well respected international fertilizer traders. As well, by entering into this agreement, it allows us to expand our potential customer base beyond our focus on the larger multinational buyers by gaining access to many regional buyers through the trader’s current ongoing relationships.”

## ALGERIA

### China to invest in \$6 billion phosphate complex

China will partner Algeria in developing a \$6 billion phosphate joint venture in Tebessa province in eastern Algeria. At the signing ceremony, Algerian Prime Minister Ahmed Ouyahia called it “the biggest economic project that Algeria has seen in more than a decade.” The joint venture will be a 51%-49% partnership between Algerian state firms Sonatrach, Manal and Asmidal on the one hand and the Chinese state-owned CITIC Group on the other, China’s biggest conglomerate. The project



Copper smelting at Antofagasta.



The concentrator at Kokola Copper Mines.

plans to expand the output of the Bled El-Hadba phosphate mine in the eastern region of Tebessa from 1 million t/a to 10 million t/a, with production from the first phase commencing in 2022. It also aims to capture greater downstream value from the phosphate by conversion to ammonium phosphate and other products. The joint venture envisages 1.2 million t/a of new ammonia production and 4 million t/a of finished fertilizers.

Algeria has the third largest phosphate reserves in the world, after Morocco and China, but has not developed them to the same extent that neighbouring Morocco or even Tunisia have. Now however the country is looking to increase phosphate production from 2 million t/a to 30 million t/a by 2030, turning it into one of the world’s largest phosphate and fertilizer exporters and helping diversify the economy away from its reliance on oil and gas exports.

## CHILE

### Copper smelters shut for emissions upgrades

Chile’s Codelco shut down two of its four copper smelters in December as part of a move to bring them into line with new tighter laws on emissions which require metallurgical plants to capture 95% of their emissions of sulphur dioxide and arsenic. The Chuquicamata and Potrerillos smelters will be idle for several weeks while the work is carried out on the \$2 billion upgrades. Most of Chile’s seven copper smelters are already compliant with

the tighter requirements, including units owned by Anglo American and Glencore, and Codelco’s Ventanas complex. The Caltones smelter at its El Teniente mine also recently came into compliance, according to Codelco, with an upgrade to the flash furnace. However, more work has been required at Chuquicamata and Potrerillos, including two new 2,000 t/d acid plants at Chuquicamata, concentrate drying system and gas treatment plant, and an acid plant revamp at Portrerillos. The shutdown is expected to continue until the end of February, after which acid output from the smelters will increase by up to 150,000 tonnes per month (1.8 million t/a).

## ZAMBIA

### Konkola suspends operations at Nchanga

Konkola Copper Mines (KCM), owned by India’s Vendanta group, has announced that it will downsize its operations after the Zambian government introduced a new tax regime which took effect on January 1st 2019. Operations at the Nchanga smelter were suspended from January 4th due to lack of availability of concentrates – the company said that the government’s imposition of a 5% import tariff on copper concentrates made smelting of imported concentrates commercially unviable. This in turn led to lack of acid availability for operations at the Nchanga Underground Mine and a consequent suspension of operations there, as there was not enough acid to work the associated tailings leach plant. ■



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# People



*Dmitry Konyaev.*

**Dmitry Konyaev**, deputy chairman of the board of directors of Uralchem has been elected as one of the five members of the Executive Board of the International Fertilizers Association (IFA). The decision was taken at an IFA Board of Directors meeting during the IFA Strategic Forum held in Beijing, China on November 13th and 14th. The Board also renewed Dmitry Konyaev's term as chairman of IFA's Communications & Public Affairs Committee until the 2019 annual meeting.

Antofagasta plc has announced that **Francisca Castro**, an independent non-executive director since 2016, has been

appointed chair of the company's Remuneration and Talent Management Committee with effect from 1 May 2019. Ms. Castro succeeds Tim Baker, who will continue to serve as a member of the Remuneration and Talent Management Committee. Ms. Castro has been a member of the Remuneration and Talent Management Committee since 1st January 2017.

**Hashim Sayed Hashim** has been appointed CEO of Kuwaiti NOC Kuwait Petroleum Corporation, following the expiration of the three year term of his predecessor, Nizar Al Adsani. Hashim will also assume the position of vice-chairman of the board of the state-owned company.

Acron Group has announced several changes in its managing board. **Dmitry Balandin** has been appointed as the Group's Vice President for Finance. **Alexander Lebedev** has been appointed as Vice President for Domestic Business. They replace Oscar Valters, who is leaving Acron Group, and Ivan Antonov, who remains with the Group as an advisor to the CEO, but who will no longer be on the Managing Board.

Dmitry Balandin graduated from Kurgan State University with degrees in finance, credit and law, and received a PhD degree in economics upon defending his doctoral

thesis in the Higher School of Management at St. Petersburg State University. He has been with the Group since 2013 as Director for Corporate Finance. Previously, he held several management positions in Gazprom Neftekhim Salavat.

Mr Lebedev graduated from Vladimir State University with a degree in marketing. He has worked at Acron since 2011, serving as head of the organic and non-organic chemical product sales team, deputy head of the sales department and head of the sales department. In November 2018, Mr Lebedev was appointed Vice President for Domestic Business.

"The new Managing Board is aligned with the Group's new strategy, which includes investments in developing our production capacity and our sales network in Russia and abroad", commented Alexander Popov, chairman of Acron's Board of Directors. "On behalf of our Group, I would like to express our deep gratitude to Mr Valters, who has been with Acron for over 20 years and decided to retire from his position as Senior Vice President. Mr Valters has made an invaluable contribution to the Group's business development, built an effective system of finance management and ensured sustainability of our production facilities". ■

## Calendar 2019

### FEBRUARY

4-5

SulGas Gas Treating & Sulphur Recovery Conference, MUMBAI, India  
Contact: Conference Communications Office, c/o Three Ten Initiative Technologies LLP, 12-1-16 Waltair Main Road, Visakhapatnam, Andhra Pradesh, India.  
Web: [www.sulgasconference.com](http://www.sulgasconference.com)

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](mailto:tsutteer@ou.edu)

### MARCH

11-12

Sulphur and Sulphuric Acid Conference, SWAKPOMUND, Namibia  
Contact: Camielah Jardine, Head of Conference, South African Institute of Mining and Metallurgy  
Tel: +27 (011) 834-1273/7  
Fax: +27 (011) 833-8156  
Email: [camielah@saimm.co.za](mailto:camielah@saimm.co.za)

17-19

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

25-27

Phosphates 2019 Conference, ORLANDO, Florida, USA  
Contact: CRU Events  
Tel: +44 20 7903 2167  
Email: [conferences@crugroup.com](mailto:conferences@crugroup.com)

25-28

Sulfuric Acid Round Table, ORLANDO, Florida, USA  
Contact: Kathy Hayward, Sulfuric Acid Today  
Email: [kathy@h2so4today](mailto:kathy@h2so4today)  
Web: [www.acidroundtable.com](http://www.acidroundtable.com)

### APRIL

16-17

The Sulphur Institute (TSI) Sulphur World Symposium, PRAGUE, Czech Republic  
Contact: Sarah Amirie, Director of Operations  
Tel: +1 202 331 9586  
Email: [SAmirie@sulphurinstitute.org](mailto:SAmirie@sulphurinstitute.org)

28-2 MAY

Sour Oil and Gas Advanced Technologies (SOGAT) 2019, ABU DHABI, UAE  
Contact: Nick Coles, Dome Exhibitions  
Tel : +971 2 674 4040  
Fax: +971 2 672 1217  
Email: [nick@domeexhibitions.com](mailto:nick@domeexhibitions.com)

### JUNE

7-8

AIChE Clearwater Convention, CLEARWATER, Florida, USA  
Contact: Ashley Rubright, AIChE Central Florida Section  
Email: [vicechair@aiiche-cf.org](mailto:vicechair@aiiche-cf.org)  
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11-13

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# India's sulphur balance

Essar Oil's Nayara Energy Refinery at Vadinar, Gujarat.



PHOTO: ROSNEFT

India continues to see demand increase for sulphur from increased phosphoric acid production and use, which will not be offset in the short term by additional sulphur production from new refining projects.

India is the world's fastest growing major economy, with GDP rising at 6.6% in 2017 and 7.2% in 2018-19. While China's growth figures have been similar, the latter is on a declining trend as its economy and population matures, but while India's population growth is falling, it is still forecast to reach 1.5 billion people by 2030 and 1.7 billion by 2050. This continues to require more food and is leading to more vehicle use, which are driving greater sulphur production from refineries on the one hand, and greater sulphur/sulphuric acid consumption for the phosphate industry on the other.

## Refining

India is a major importer of crude oil – the third largest importer in the world after China and the United States, taking an average of 4.9 million barrels per day in 2018. This figure has nearly doubled over the past decade, and is projected to continue to grow rapidly as the country's middle class and associated car use expands.

Research and consultancy group Wood Mackenzie said in a recent report that India is set to overtake China as the biggest source of growth for oil demand by 2024. It is projected that India's oil demand will increase by 3.5 million barrels per day from 2017 to 2035, which will account for a third of global oil demand growth.

This in turn will need a lot of new refining capacity. India's refining capacity stood at 4.97 million bbl/d in 2017, allowing the country to in theory produce all of the refined products that it needs, although the product slate is heavily tilted towards diesel. About 60% of this is owned by state-owned companies Indian Oil Corp (IOC), Bharat Petroleum, Hindustan Petroleum and Mangalore Refinery and Petrochemicals. IOC has 11 of the 23 refineries, but only 35% of capacity, as its refineries are smaller than the larger private refineries such as Jamnagar, owned by Reliance Industries.

In India, demand for refined fuels has grown by 6% per year from 2010-2018, and is forecast to grow by a further 4% year

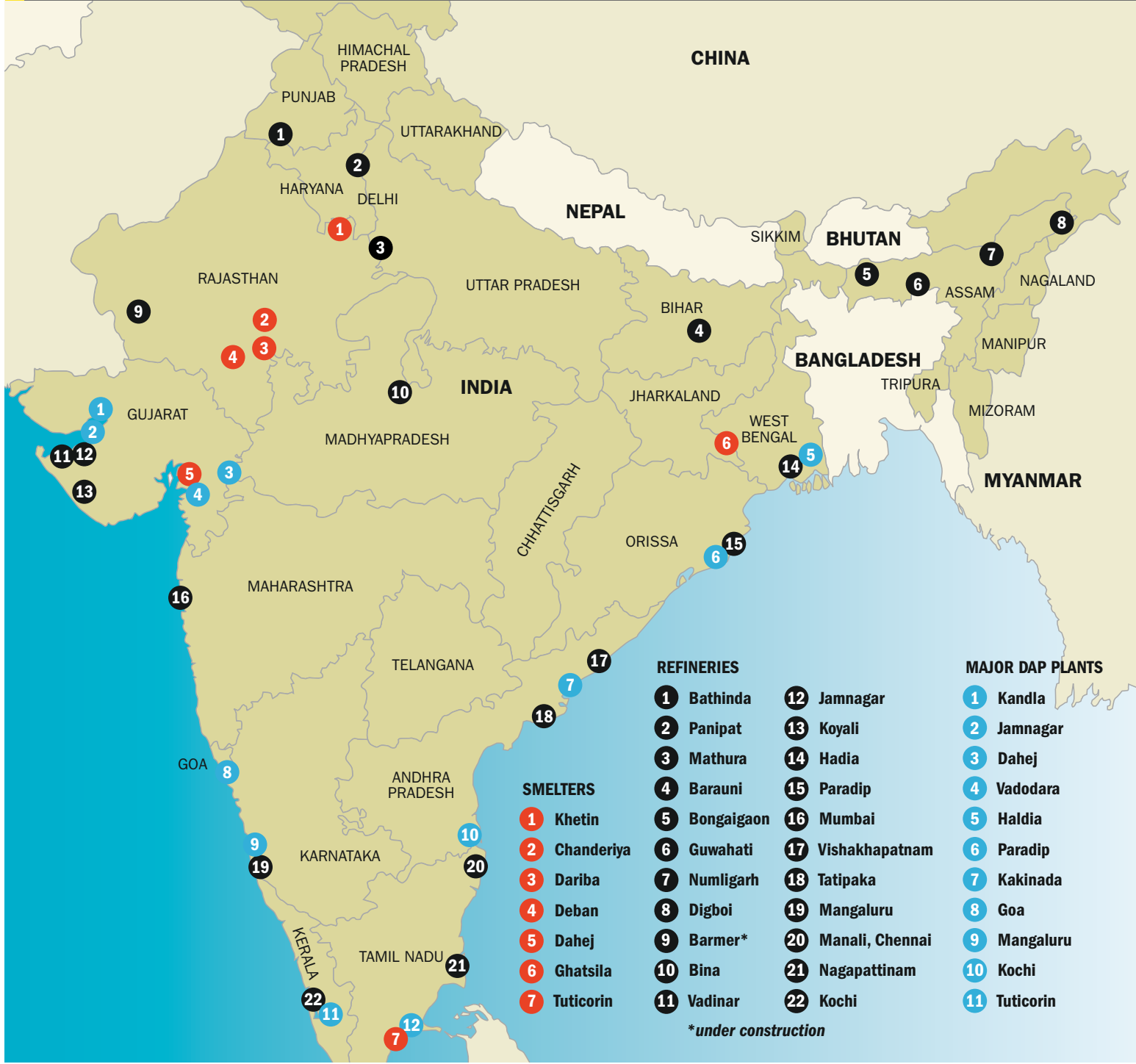
on year out to 2025. Apart from demand for gasoline in passenger cars and diesel for road haulage, India's appetite for jet fuel is also expected to grow as the country upgrades airport infrastructure and plans to build about 200 new airports in the next 10 years.

Wood Mackenzie argue that India needs between 3.2 and 4.7 million bbl/d of new refining capacity by 2035, and caution that the slate of new product developments could mean that the country slips into shortage from 2020. The country's government is aware of this, and Petroleum Minister Dharmendra Pradhan has said that India will need to invest \$300 billion over the next 10 years in order to double its oil refining capacity. As the initial part of the development, the government has authorised several brownfield projects which are expected to add 55 million t/a (1 million bbl/d) of additional capacity at existing refineries by 2025, but there are also two major new greenfield refineries under development to add a further 69 million t/a (1.2 million bbl/d) of capacity. Outside the scope of current projects, Reliance is also believed to be developing a second refinery to run alongside its current massive refinery at Jamnagar by 2030 – the company is looking to increase its refining capacity to 2 million t/a by that time. In January 2018, Reliance up-rated the capacity of the existing Jamnagar refinery to 1.24 million bbl/d.

The largest of these new refineries is under development by a consortium consisting of the Abu Dhabi National Oil Company (Adnoc) and Saudi Aramco, who collectively own 50% of the project following signing up to it in June 2018, while the remaining 50% will be split between Indian state-owned oil firms the Indian Oil Corporation (IOC), Hindustan Petroleum Corp. Ltd. (HPCL) and Bharat Petroleum Corp. Ltd. (BPCL). The \$44 billion development of what could become the world's largest refinery and petrochemical complex will be sited in the Ratnagiri district of Maharashtra state on India's west coast. The refinery is to be built in two phases, with the first, 40 million t/a (700,000 bbl/d) phase taking 5-6 years to build from acquisition of the land, and therefore not likely to be active before 2023.



Fig. 1: India's sulphur and sulphuric acid industries



The other new refinery will be a 180,000 bbl/d refinery for HPCL at Barmer in Rajasthan, which is also slated for completion by 2023. The cost of this is put at \$6.8 billion, partially borne by the state government of Rajasthan, via a \$2.6 billion loan to HPCL over 15 years. However, the remote landlocked desert location and associated transportation costs of bringing imported oil to the refinery have led to some scepticism about the refinery's profitability.

Finally, according to the government of southern Tamil Nadu state, a "Middle Eastern refiner" is in talks with it to set up a large refinery on the east coast, but further details remain sketchy at this stage.

Environmental regulation

At the same time, Indian fuel standards continue to tighten. In 2000, India permitted fuel sulphur standards of 500 ppm in diesel and gasoline, but has since progressively moved to a so-called Bharat State IV (equivalent to Euro-IV) standard of 50 ppm, which came into force in April 2017, and the country is now skipping the Euro-V level to move to a national Bharat/Euro-VI standard of 10ppm maximum sulphur content in April 2020 (some cities, such as heavily polluted Delhi, have already moved to a Euro-VI standard). At the same time, the new International Maritime Organi-

sation standards on sulphur content of marine fuels is also leading to a push to produce more low sulphur fuel oil and marine gasoil.

This in turn is necessitating extra investment in sulphur recovery in existing refineries, with a slate of refinery closures set for 2019 as new equipment items are tied in, including naphtha hydrotreaters, catalytic reforming units, isomerisation units, diesel desulphurisers and diesel hydrotreaters. In addition, some refiners have to revamp or set up new gasoline treaters, hydrogen production and sulphur recovery units. IOC, for example, plans a roughly month-long shutdown of gasoline- and gasoil-producing

units at all of its 11 refineries, while HPCL will shut its diesel and gasoline units while upgrading the crude units at its Vizag and Mumbai refineries for 30 to 45 days this year. BPCL has upgraded two of its refineries, and is revamping its fire-hit Mumbai refinery.

A related issue for India is petroleum coke (petcoke), which has often been used by refineries as a 'sulphur dump' – petcoke often contains 4-7% sulphur by weight. While coal has had a clean energy tax applied to it since 2010 in an effort to discourage its use (now standing at \$1.44/metric tonne), petcoke has hitherto escaped this, leading to it becoming favoured as a feedstock for power stations and cement plants. Petcoke demand expanded at 15% year on year to reach 24 million t/a in 2017. But concerns about the pollution caused by burning sulphur-rich petcoke has led to a ban in April 2017 on its use in New Delhi and neighbouring states, albeit later partially rescinded for cement companies. There is now talk of a national ban on its use as a fuel, and it is no longer clear what refiners will do with their surplus petcoke afterwards, although the Jamnagar Refinery complex has successfully set up a large-scale petcoke gasification facility to provide power and hydrogen for the refinery, and there have been suggestions of running a coke gasification-based ammonia/urea plant on surplus petcoke, as the sulphur would then be removed during the gasification process, and it would help India with its domestic shortage of nitrogenous fertilizer.

## Sulphur production

The upshot of the rise in refinery capacity and tightening sulphur regulations has been an increase in sulphur production. For example, according to the Ministry of Mines, India's sulphur output from state-owned refineries was 560,000 t/a in 2017, up from 470,000 t/a in 2016. Overall sulphur production stands at just over 2.5 million t/a. India's sulphur situation is slightly complicated by the fact that refineries on the east coast tend to export sulphur to Asia, whereas phosphate producers tend to import sulphur from the Middle East. This means that India is a significant exporter and importer of elemental sulphur.

Indian exports of sulphur were 616,000 tonnes in 2016-17, down slightly from

628,000 tonnes for the previous year. The exports were mostly (85%) to China, with Indonesia and South Africa also taking some cargoes. Imports were 1.34 million tonnes for the same period, for a net import of 725,000 tonnes, down from 1.43 million t/a (net import of 800,000 tonnes) for the previous year. India's imports of sulphur came mostly from the Middle East (85%), primarily Saudi Arabia (41%), Qatar (23%) and the UAE (18%).

Additional volumes of sulphur will come from the refinery expansions mentioned above, but the timescales of most of the major are such that they may not affect the sulphur balance much in the short to medium term.

## Sulphuric acid

India has a large number of sulphuric acid plants, although many of them are extremely small and associated with small scale chemical production. India's sulphuric acid production is split between sulphur burning acid plants which run on the domestically generated and imported sulphur, and several metallurgical acid plants associated with base metal smelting; copper, zinc and lead. On the metallurgical acid side, Hindustan Zinc Ltd (HZL) is the largest producer, with production from its lead smelter at Chanderiya, and zinc smelters at Debari and Dariba. In 2016-17, acid output from the three smelters was 545,000 t/a, 225,000 t/a and 500,000 t/a respectively, for a total production of 1.27 million tonnes. Close behind is the Tuticorin copper smelter, owned by Sterlite, a subsidiary of Vedanta. Sterlite's acid plant has a design capacity of 3,600 t/d (1.2 million t/a). In addition to these, Hindustan Copper operates two more acid plants at Khetri and Ghatsila, and Hindalco has three sulphuric acid plants with a total capacity of 1.67 million t/a at its Dahej copper smelter at Birla. Sterlite, Hindustan Copper and Hindalco all operate downstream phosphoric acid plants and in some cases phosphate fertilizer production. Metallurgical acid production generally runs at about 3.6 million t/a, but this has fallen recently with the closure of the Sterlite copper smelter (see below).

India's smelter acid production is set to increase over the coming years as the country begins to mine more copper to meet anticipated domestic demand from energy, automotive and other indus-

trial sectors. India's sole copper miner – state owned Hindustan Copper – produced 3.8 million tonnes of copper in 2017, but plans to increase this to 6.1 million t/a by 2021 by investing about \$700 million in six expansion projects including a near tripling of production at its largest mine, Malanjkhand in Madhya Pradesh from 2 million t/a to 5.2 million t/a from September 2019 by building an underground mine under the current open-cast operation.

While there are no plans for new smelter capacity, the country already has about 1 million t/a tonnes of smelting capacity, greatly in excess of its current requirements, and increasing local demand for copper could see higher utilisation rates for India's copper smelters, reducing the country's need for sulphur burned acid. As our article elsewhere on copper notes, credit agency Fitch is predicting that India's refined copper production will increase to 1.8 million t/a by 2027, averaging 7.3% annual growth.

On the sulphur-burning acid side, most of the plants are associated with downstream phosphate fertilizer production. The Indian Farmers Fertilizer Cooperative is the largest, with 7,000 t/d (2.3 million t/a) of acid capacity at Paradeep in Orissa. Paradeep Phosphates has 1.3 million t/a of capacity at Paradeep. Gujarat State Fertilizers & Chemicals Ltd has two sulphuric acid plants with a combined capacity of 1,750 t/d (580,000 t/a). Fertilizers and Chemicals Travancore has two acid plants, at Cochin and Udyogmandal, with a combined capacity of 710,000 t/a, although production only ran at 200,000 tonnes in 2016. Coromandel Fertilizers has 2,100 t/d (700,000 t/a) of sulphuric acid capacity in two plants at Ennore in Tamil Nadu. Mangalore Chemicals and Fertilizers has a 330,000 t/a acid plant, and Khaitan Chemicals and Fertilizers operates 270,000 t/a of sulphuric acid capacity to feed its single superphosphate production. Acid production was 106,000 tonnes for 2016-17. Some smaller plants are present at BEC, Bharat Fertilizers

Finally, outside of fertilizer production, there are some sulphuric acid plants associated with the chemical industry. Trident Chemicals and Bodal Chemicals add another 450,000 t/a of sulphur burning acid capacity, and there are numerous smaller units across the country. There is also some small production from pyrites roasting (<100,000 t/a).



Tuticorin

One of the great uncertainties for the Indian sulphur and sulphuric acid industries has been the fate of the Sterlite copper smelter in Tuticorin. The smelter was closed in May 2018 after the plant’s operating license was not renewed by Tamil Nadu due to environmental concerns that had driven a huge local protest movement, leading to riots in which police killed 13 demonstrators. But this ruling was overruled by a decision in December by the Indian environmental court, the National Green Tribunal (NGT), which would have allowed the smelter to recommence operation. As a result the Tamil Nadu regional government appealed against this decision, and the case went to the country’s Supreme Court, with the Tamil Nadu government claiming that the NGT did not have jurisdiction to hear the matter. The court threw out the appeal in January 2019, but Sterlite has said that potential remedial work necessitated by the long shutdown might require another few months to resolve. Sterlite claims that the original decision was flawed, as a study had provided that 90% of the sulphur dioxide emissions in the region were as a result of thermal power plants, and only 1% from the smelter, and that the company had in 2013 after a previous complaint installed a fence-line monitoring system with a threshold set at half the permissible SO<sub>2</sub> emission limit that should automatically shut down the plant. Sterlite has also attempted to rebuild its image with the local populace, pledging to build a school, hospital and desalination plant and contribute to youth development schemes and plant a million trees, at a total cost of \$14 million.

In the meantime, the closure has removed 1.2 million t/a of sulphuric acid from the market, leading to a price spike in India as phosphate fertilizer producers scramble to find acid from elsewhere. The price increase – Indian acid prices are around \$100/t – double their level last year – has led to increased demand for sulphur and phosphate imports as well as sulphuric acid. Over the second half of 2018, Indian prices of sulphuric acid have shot up from \$45/t to \$170/t.

Phosphates

As noted, most sulphuric acid in India (about 75%) is used in the phosphate fertilizer industry. The remainder goes into the chemical industry (about 10%), sugar production (about 10%), as well as iron and steel, paint, rubber and other industries.

Indian phosphate fertilizer demand stood at around 8 million t/a P<sub>2</sub>O<sub>5</sub> in 2010-11, but took a dive in the period to 2014 to 5.7 million t/a. This was at least

in part due to high phosphate prices internationally and a subsidy policy which advantaged urea at the expense of all other fertilizers. The consequence was a growing nutrient imbalance in Indian soils and falling soil fertilizer, which in turn led to lower agricultural yields. Since then there has been a recovery in phosphate demand to around 7.1-7.4 million t/a P<sub>2</sub>O<sub>5</sub> over the period 2015-

17, and this has reduced nutrient application imbalances to an extent, but this is still down on the situation a few years ago. India’s latest subsidy policy change is to allocate subsidy money not to fertilizer producers, to reimburse them for selling at controlled rates below market prices, but rather directly to farmers to allow them to purchase fertilizers at market rates and determine what works best for them. It remains to be seen how this scheme will work out in the medium to longer term.

What has happened over the past few years is that the share of phosphate fertilizer produced domestically has increased, rising from 56% in 2015 to 72% in 2017, due to increased production of diammonium phosphate (DAP) and single superphosphate (SSP). However, both still depend largely on imported phosphate rock. Currently, India has 12 DAP plants with a total capacity of 7.3 million t/a, but capacity runs at only around 65% or so. India produced 4.65 million tonnes of DAP in the 2017-18 fertilizer year, up from 4.33 million t/a for the previous year, but this still leaves a shortfall which is made up with imports, of 4.22 million t/a in 2017-18. In addition to this, there are a large number of single superphosphate plants, many of them quite small, with a total capacity of more than 7 million t/a. SSP

production for 2017-18 was 3.9 million t/a, down from 4.4 million t/a for the previous year.

Indian phosphate producers tend to have higher costs than imported DAP, however, and at last November’s Sulphur and Sulphuric Acid conference in Gothenburg, Juan van Gernet of PhosAgro predicted that India’s finished phosphate imports would rise again this year. Looking to the longer term, CRU forecasts a rise of just over 1 million t/a P<sub>2</sub>O<sub>5</sub> in Indian phosphate demand over the next five years, with demand being helped in the short term by lower phosphate prices compared to historical longer term trends.

Impact on sulphur demand

The Indian situation for sulphur demand is complicated by what proportion of phosphates will be processed domestically, requiring acid consumption, and what proportion imported. There is certainly capacity to produce more phosphate domestically, but this depends on phosphate pricing. However, an increase of 1 million t/a in phosphate demand, if supplied 50-60% from domestic production, would require an additional 500-600,000 t/a of sulphur or the equivalent volume in sulphuric acid out to 2023. Again, however, the question is how much sulphuric acid will be available domestically to fulfil this, and here the future of the Tuticorin smelter and new plans for copper production will be a decisive factor one way or the other. In its absence, India will need to either produce or import the sulphur to feed sulphur burning acid capacity, or, as has partially happened in 2018, idle domestic phosphate capacity and import finished phosphates instead. The ability of some major fertilizer producers to switch between sulphur burning acid and imported or domestically purchased sulphuric acid is another complicating factor, making Indian acid capacity quite sensitive to prevailing prices.

Finally, although refinery expansions could generate significant extra volumes of sulphur, the number of these that are scheduled to be completed before 2023 is actually relatively limited, with most of the major expansions happening beyond that period. The upshot, then, is that India is likely to be importing more sulphur and finished phosphates over the next few years, but exactly how much of which remains a difficult balancing act to predict.

Increasing local demand for copper could see higher utilisation rates for India’s copper smelters.



# Copper market to boost acid production

Following a period of overcapacity, the copper market has moved back into deficit, and increased demand and production is likely to generate additional volumes of sulphuric acid.

Above: Copper cathodes waiting for shipment at La Escondida, Chile.

After the phosphate fertilizer industry, the copper industry is one of the largest determinants of sulphuric acid production and consumption. Production of acid from the sulphur dioxide off-gases generated by smelting of copper sulphide ores is the most important source of acid apart from sulphur burning plants, while consumption of acid for the leaching of copper oxide ores is also a major factor for sulphuric acid demand, representing about 8% of acid demand overall.

### Copper markets

The uses of copper reflect its excellent electrical and thermal conductivity, while having good formability and strength as well as high corrosion resistance, making it ideally suited for use in electrical engineering, electronics and telecommunications. Its use is rising due to increasing demands on information and communication technology, and greater use of electricity as an energy source, especially in applications like vehicles. Every mid-range car contains about 25 kg of copper, and larger models can have more than twice this amount, while electric vehicles require up to 85 kg of copper per vehicle. It is also often used in plumbing and air conditioning, as well as roofing and building facades. Increasing

urbanisation is also expected to drive increased copper demand in future.

Asia has become the main driver of growth in copper demand, with Europe and North America largely stagnant in demand terms. Asia's share of copper demand has risen from 10% in 1960 to 70% in 2017, due to the rapid industrialisation of developing economies there, and China alone now accounts for around 45% of total world copper demand, with an annual copper demand of nearly 10 million tonnes, and most incremental demand since 2000 has come from the rapidly growing Chinese economy.

As a result, the copper price rose from a mid-2000s level of around \$2,000/tonne to over \$8,000/tonne in 2009 as demand took off in China. Although there was a sharp dip in 2009 due to the global financial crash, in fact copper prices rebounded quickly, and were soon back above \$7,000/t and even reached almost \$10,000/t as China continued to require copper for electrification projects, construction, manufacturing and other industrial uses. In turn, high copper prices led to a huge increase in copper mining, and also copper smelting and leaching operations to produce refined copper from concentrate.

However, the gradual slowdown in the Chinese economy took its toll from about 2012, and as copper production began



to run ahead of demand, prices began a long slide before bottoming out in 2016-17. This slump forced the closure of some of the more expensive copper production capacity and led to a fall in mined production in 2017. The indications are that this has succeeded in reining in some of the excess supply in copper markets, and prices have been rising again.

A recent copper supply and demand outlook published by Fitch Solutions has said that global refined copper consumption will see steady growth over the coming years, driven by demand from the power industry, rising electric vehicle (EV) production and a positive global economic growth outlook. Every electrically powered bus requires 300 kg of copper to produce, and every megawatt of wind farm power generation an average of 9 tonnes of copper. The company predicts that global copper demand will increase from 23.6 million t/a in 2018 to 29.8 million t/a by 2027, averaging an annual growth rate of 2.6%. But it also predicts that the copper market will see persistent undersupply over the next few years, as consumption continues to outpace supply growth. Fitch says that there was a net deficit between supply and demand of 247,000 tonnes in 2018, and this undersupply will continue until at least 2021.

Meanwhile, CRU has called the potential growth in electric vehicle-related copper consumption “jaw-dropping”, noting in a recent report that it may rise from approximately 100,000 t/a in 2017 to over 3 million t/a in 2030 and 6 million t/a in 2035, the latter being equivalent to 20% of 2017 total world copper demand. China

may be one of the largest beneficiaries of this, forecast to represent 50% of electric vehicle sales over the period.

Chile

Developments in Chile also affect the copper market – Chile is the world’s largest copper producer, representing 25% of world mined copper in 2017 with an output of 5.5 million tonnes Cu, and production increased still further in 2018, with copper production for the first three quarters of the year rising 7.3% year on year to 4.25 million tonnes, boosted by a sharp increase in production at BHP’s Escondida copper mine, where production was up by nearly 60% in 2017 to 950,000 tonnes – Escondida suffered a strike during 2017 which shut down production for several weeks. The country’s second-largest mine by output, Collahuasi, co-owned by Anglo American and Glencore, increased production by 5.8% to 400,000 tonnes over the same period, while production from state-owned miner Codelco was fairly stagnant at 1.29 million tonnes. There are expansion projects in the pipeline. Antofagasta, for example, is increasing production at Los Pelambres, raising copper production by 55,000 t/a from Phase 1, which is expected to go into production in 2021, and another 35,000 t/a in Phase II. However, in the longer term, the Chilean Copper Commission (Cochilco) continues to forecast that production from existing mines will fall by 19% to 4.46 million t/a in spite of expansion and optimisation projects because of falling ore grades at these mines – any growth will come from

new projects, and overall copper output may actually be fairly flat.

Chile is also the world’s second largest producer of refined copper, although only the third largest operator of copper smelters. This is because Chile was a world leader in hydrometallurgical copper production via solvent extraction/electrowinning (SX/EW), which has been a major consumer of sulphuric acid in the country. Chile came to dominate SX/EW production, and there are currently 31 such operations, but this is forecast to drop to 18 over the next decade due to depleting reserves of copper oxide ores, and Cochilco is projecting that hydrometallurgical copper output will fall from 1.6 million t/a in 2017 to just 0.55 million t/a in 2028, with concomitant effects on sulphuric acid demand within Chile.

Conversely, copper concentrate production will account for an increasing share of production, rising from 71.2% to 88.4% in 2029 growing from 3.92 million t/a in 2017 to 5.8 million t/a in 2028. This continuing growth in copper concentrate production has reignited debate in Chile about whether there should be new investment in smelting capacity in country. There are currently seven smelters in Chile; two privately owned (Altonorte and Chagres) and five state owned – Chuquicamata, Poterillos, Ventanas, Caletones and Hernan Videla Lira. Total sulphuric acid capacity is 4.7 million t/a, with Caletones (1.2 million t/a), Altonorte (1.0 million t/a) and Chuquicamata (0.97 million t/a) being the largest.

However, Chile is also tightening its environmental regulations, which could make investment in new capacity less attractive. New regulations on capture of arsenic and sulphur dioxide came into force in 2016 for smelters with a double contact acid plant (Chagres, Ventanas and Altonorte), and December 2018 for the remainder, lifting the capture rates for sulphur dioxide from 95% to 98% and arsenic to 99.97%. This led to several shutdowns while remedial work was done, reducing output at the end of 2018. State copper company Codelco has embarked on a \$1 billion upgrade to its Chuquicamata flash smelter, taking it offline for 60-80 days to make adjustments to bring it into compliance.

India

India is forecast to be one of the major growth areas for copper demand over the coming years, as copper consumption

Fig. 1: Copper prices, 1989-2019 (\$/tonne)



Source: InfoMine.com

per capita lags far behind other countries, especially China. India has only one copper mining company – state owned Hindustan Copper – which produced 3.8 million tonnes of copper in 2017. However, the company has ambitious plans to lift this to 6.1 million t/a by 2021. Hindustan Copper plans to invest about \$700 million in six expansion projects including a near tripling of production at its largest mine, Malanjkhand in Madhya Pradesh. The mine would increase production from the current 2 million t/a to 5.2 million t/a from September 2019 by building an underground mine under the current open-cast operation. Malanjkhand has almost 70% of India's copper reserves (200 million tonnes of copper ore) and represents around 60% percent of Hindustan Copper's current output. The company also plans to reopen its closed mine in Rakha (Jharkhand) and expand existing mines in the Khetri Copper Complex (KCC) in Rajasthan, as well as exploring options for new mine output.

However, the company is not looking at significantly expanding smelting capacity since India already has about 1 million t/a tonnes of smelting capacity, which is far in excess of its current requirements, and Hindustan Copper believes that the margins on mining are far better than smelting. The company has about 100,000 t/a of smelter capacity, at the Gujarat Copper Project, Ghatsila, and Khetri, although one of the smelters at the latter has been idled since 2008. Nevertheless, increasing local demand for copper could well see higher utilisation rates for India's copper smelters, reducing the country's need for sulphur burned acid.

India's copper smelting industry gained a boost very recently by the Supreme Court's decision not to allow an appeal against the National Green Tribunal (NGT), which was in favour of Sterlite Copper (part of the Vedanta Group) which will allow the reopening of the 400,000 t/a copper smelter in Tuticorin. India's output of refined copper is expected to be around 380,000 tonnes for the financial year 2018-19, down 55% on the previous year, against expected demand of 430-435,000 t/a. The drop in domestic output led to a sharp increase in imports and fall in exports, turning India into a net importer of refined copper, as well as a shortage of sulphuric acid for fertilizer production, especially in southern India.

Looking to the longer term, India is expecting greater copper demand from its 'Smart City' initiative, renewable energy and demand from automotive, railways and defence sectors. Fitch is predicting India's refined copper production will increase to 1.8 million t/a by 2027, averaging 7.3% annual growth.

## China

China has set the pace for copper markets over the past two decades, and while demand has slowed, it continues to rise at a healthy rate. On the other hand, there are fears that the ongoing trade spat with the US may damage growth in the short term – GDP growth forecasts for 2019 have already been cut from 6.6% to 6.2%. Even so, medium term forecasts average around the 6.0-6.5% per year level, so China's economy continues to grow healthily, even if not at the spectacular growth rates seen a few years ago. This is likely to mean continued good demand for copper, with electric vehicles set to be important in China

as elsewhere. CRU forecast Chinese copper demand to rise from 12.6 million t/a in 2017 to 13.8 million t/a in 2022.

Likewise Chinese refined copper production is forecast to see steady growth as producers take advantage of higher prices and strong domestic demand, with predictions of a growth in copper production from 8.8 million t/a in 2018 to 11.4 million t/a by 2027, averaging 3.1% annual growth. More to the point, most of this growth will come from smelting – China recently caused ripples in copper markets by putting tariffs of 25% on imports of scrap copper, widely remelted to be repurposed, which form 18% of global copper output. This has led to a drastic fall in imports of scrap copper. Instead, China continues to invest heavily in new smelter capacity, and now represents about 40% of copper smelter production worldwide. Chinese copper smelter capacity has risen from 3.8 million t/a in 2010 to about 7.2 million t/a in 2018, and another 2.7 million t/a of capacity is expected onstream over the period 2018-2022. China represents almost two thirds of copper smelter capacity growth over the period 2017-21. To help provide raw materials for these smelters China has become a major investor in overseas copper projects, especially in Africa, and this

also feeds into the so-called Belt and Road Initiative.

Major smelters starting up in 2018 included Chalco's Ningde smelter, Lingbao Jincheng Metallurgical, and Tongling's Ausmelt project. Chinese copper concentrate imports – a marker of how much smelting is going on, rose by 14% in 2018 to 19.7 million t/a. The addition of 700,000 t/a of new capacity in 2018 has taken utilisation rates down in the short term, and there is more new capacity in 2019, including the expansion of Yunnan Copper's Chifeng project in Inner Mongolia to 400,000 t/a from 130,000 t/a, and Guangxi Southern Copper is expanding capacity to 300,000 t/a. This is sure to lead to closures of some higher cost, less efficient capacity, but equally, some of the expansions have been at some of this smaller, less efficient capacity, aimed at preserving them as a going concern via modernisation to meet new emissions targets and greater economies of scale. Much depends on prevailing copper and sulphuric acid prices, and the current run of higher acid prices has been good news for smelters.

## Smelter output

Of course, this does not automatically equate to a global rise in smelter acid production. Indeed, much of the sulphuric acid price rise in 2018 was of course due to supply disruptions caused by smelter acid production downtime, including the shutdown of the Tuticorin smelter in India, shutdowns for environmental upgrades in Chile and production issues in Japan and the Philippines. In all, around 1.5 million tonnes of acid was lost to the market in 2018 from production problems, and 2019 continues to see disruption, with the Tuticorin smelter not due back on-stream until April at the earliest.

Nevertheless, the waning popularity of SX/EW production (with the exception of southern Africa, where some more projects are under development) and limitations on China's recycling of scrap copper mean that much of the new copper production over the next few years is going to have to come from smelter production, which means more acid from smelters, whether that is in China, India or elsewhere. Refined copper production is projected to rise at about 3% year on year over the next few years, from 23.2 million t/a in 2017 to 26.9 million t/a in 2022, with a concomitant increase in smelter acid production of around 10 million t/a, most of it in China. ■

**China continues to invest heavily in new smelter capacity.**





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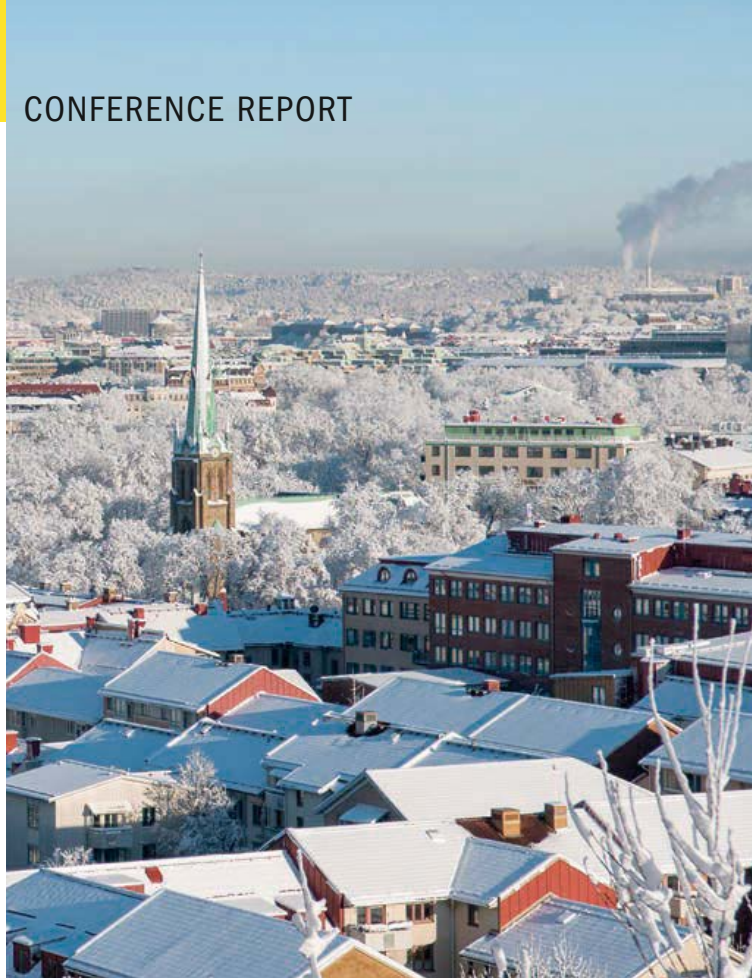
PHOTO: AL HOSNI GAS

Sulphur storage at the Shah project, Abu Dhabi (Middle East, centre of the sulphur world, Mar-Apr p18).



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	Zimphos revamp nearing completion	Jan/Feb	14



# Sulphur & Sulphuric Acid 2018

Gothenburg was the venue for the annual CRU Sulphur Conference at the end of 2018, now with a slight change of identity to emphasise the acid component of the meeting.

This time around the annual CRU Sulphur Conference changed its name to include sulphuric acid, although the programme of course, as in previous years, had always covered both topics. However, one innovation that did take place this year was the addition of an app which delegates could download allowing immediate straw polls to be taken and active responses to speakers' questions. One illuminating statistic on the subject which this generated was that 40% of delegates were concerned primarily with the sulphur industry, 20% with the sulphuric acid industry, and perhaps a surprising 40% with both, endorsing the change of name.

## Sulphur and sulphuric acid markets

The conference kicked off as usual with a look at the market situation for sulphur and sulphuric acid. "Another year, another price spike" said CRU's Peter Harrison, although he contrasted 2017's price spike, where prices had risen from \$85/t to \$220/t c.fr China due to delayed buying from the first half of the year and a consequent boom in Q3 with what had happened in 2018. While there was a similar pattern in terms of panic buying in China driving up prices, Chinese buying had actually been more stable compared to 2017, and it was supply and logistics issues which had led to the sudden shortage. The market was, he said, slowing now as demand had been satisfied, but supply remained tight. While it had been a week year for demand growth

(only 1 million t/a extra compared to 2 million t/a in 2016 and 2017), it had been similarly weak on the supply growth side with only an extra 1 million t/a of sulphur added. This masked a reorganisation in trade flows, however, with Morocco, Brazil and to a lesser extent Indonesia all growth markets and additional seaborne imports into the US, but falling demand in China due to industry rationalisation, and the closure of the Ravensthorpe nickel leaching operation in Australia ending demand there. On the exporter side, Canada had continued production issues, while Russia was seeing more sulphur go to the domestic market and less international availability. Kazakhstan had forming production issues and there had also been production issues in the Middle East, and finally a fall in exports from Japan and South Korea. Overall, production growth continues to shift to the Middle East, Central Asia and China out to 2019, and 2019 in particular should see more availability from more accessible coastal locations.

The outlook for demand from phosphates continues to see Morocco and Saudi Arabia as new demand for sulphur, with lower demand in the US and China, but overall a 2 million t/a increase in sulphur demand in 2019, and 6 million t/a out to 2023, dominated by Moroccan projects, but also including Egypt, Brazil, Russia and Indonesia. Outside of phosphates, Ravensthorpe may return to production in 2021, and industrial demand will occupy an extra 1.8 million t/a of sulphur over the medium term, but Katanga in the Democratic

Republic of Congo will be producing extra acid and hence requiring less sulphur.

Production growth continues to focus on the Middle East and East Asia. European production continues to fall, and there is little growth from Canadian oil sands and in Russia, Norilsk has been pushed back to 2023. Kashagan is still ramping up and may start drawing down from its stocks from 2019. But Saudi Arabia has an extra 3.2 million t/a of sulphur slated, mainly from sour gas, and Kuwait 1.3 million t/a from refining. In the UAE, the Shah expansion may provide extra sulphur from 2022. Iranian production has increased, but mainly for supply to the domestic market, especially with fresh sanctions concerns. In China, refining will add another 3 million t/a, and refinery expansions and upgrades in Korea and India, Vietnam and Malaysia will also add volumes as refiners struggle to meet the new IMO fuel requirements for ships.

The overall market balance sees a continuing surplus in 2019 and 2020, though not as large as might have been feared a few years ago, but thereafter a deficit. There may also be questions of accessibility of sulphur to markets, and logistics and remelt costs could see a price floor as high as \$120/t.

Turning to sulphuric acid, Nick Waters of CRU noted that acid prices had strengthened in 2018, led by the Chilean market. The previous year had seen smelter acid supply disruptions in Japan and Korea, and this year a stronger copper market, coupled with the Tuticorin closure in India and PASAR in the Philippines had led to



8 year highs for acid prices. The start of 2019 will see smelter upgrades in Chile for environmental reasons, reducing output by 300,000 tonnes per month in Q1, albeit with higher production from Q2 onwards. One facet of the high prices and smelter lack of availability has been a rise in exports from sulphur burning acid plants, such as Two Lions in China and El Boleo in Mexico, up to 2 million t/a extra in seaborne trade compared to 0.5 million t/a in 2015, bringing the seaborne acid market to 14 million t/a in 2018. However, higher acid prices will also crimp SSP production, lowering demand. China in particular has become a net acid exporter, 1.2 million t/a in 2018. This may be exacerbated by the start-up of the Chinalco smelter in 2H 2019. Moroccan acid demand will fall from 2019 as new sulphur burning capacity comes on stream at OCP, but demand will also increase from the new JPH and Laayoune phosphate hubs over the longer term. Overall Nick predicted a peak to prices in early 2019, with falling sulphur prices weakening acid prices support, and a correction downwards to \$40-60/t f.o.b. in 2H 2019.

## Phosphates

Juan van Gernet, formerly of CRU, now with PhosAgro, gave an industry player's view of the phosphate market. He pointed to several factors in the current market, including the idling of capacity North America leading to increased import demand, record demand in Brazil that had been disrupted by the truckers' strike (responsible for delivering 90% of product to market), slowing demand in Europe, and the ramp up in capacity in Saudi Arabia and Morocco. Chinese policy decisions and a maturing domestic market are also having a major impact, as are extreme weather events, such as the very hot and dry summer in Europe in 2018 – European demand was down 20% in 2018 compared to 2017, with low water levels on the Rhine contributing to logistical difficulties.

In India, 2015-17 had seen an increase in domestic production, but in 2018 this was reversed due to competition from lower priced imports, and this situation looks set to continue in 2019. It has been a similar story in North America, where phosphoric acid production has fallen from 12 million t/a in 2005 to 7 million t/a (P<sub>2</sub>O<sub>5</sub> basis) in 2019, and Juan noted the closures of Plant City, Geismar and Redwater. In the Middle East and North Africa, over the same period an extra 15 million t/a of phosphate

capacity (P<sub>2</sub>O<sub>5</sub>) has come on stream, much of it low cost, mainly in Morocco, but also Saudi Arabia, Jordan and Egypt. The cost curve continues to fall.

Longer term there are positive demand factors, including the encouragement by OCP of African demand, and the conversion of pasture land to farmland in Brazil's Mato Grosso region, requiring large inputs of nutrients of all kinds. But there is also more than 15 million t/a P<sub>2</sub>O<sub>5</sub> of potential new supply on the horizon over the next 5-6 years, running ahead of demand growth to at least 2023-24.

## Central Asia

Sergei Sushko of World Fertilizer Market looked at the sulphur and sulphuric acid situation in Central Asia. Russia is the dominant producer, with an output of 6.6 million t/a in 2017, of which 3.6 million t/a was exported, but Kazakhstan exported 2.3 million t/a from an output of 2.8 million t/a. Logistics are difficult because of frozen rivers in winter and low water levels during the hot season. Rail shipments from the north Caspian area can take 10-13 days to reach the Black sea, 15 days to reach the Ukraine, and 13 days to the Chinese border. Liquid sulphur tends to go to the domestic market, while exported sulphur is all formed. The region aims to move from crushed lump sulphur to completely granulated shipments over the next couple of years.

## Regulation

The onset of new limits on sulphur in bunker fuels in January 2020 continues to cause headaches for the industry. James McCullagh of Energy Aspects ran through the issues. There is already an oversupply in high sulphur fuel oil (HSFO) that is likely to worsen from mid-2019 as the deadline approaches. Around 4 million bbl/d is currently produced. There are only 1,400 ships currently equipped with scrubbing technology, too small to make much of a difference, and even taking into account cheating, waivers, and refinery upgrades to convert HSFO to other fractions, the fact that there is some spare delayed coker capacity (in the US, for example), and even a potential increase in supply into the power market, there will still be an excess of HSFO come 2020. Refinery closures are likely due to the collapse in the HSFO market, like Petrotrin in Trinidad and PetroJam in Jamaica. US Gulf refiners, however, who

have invested to handle higher sulphur feeds, look to be well placed to take advantage of the changed market, he said.

The impact of regulation of a different kind was the subject for Dr Moncef Hadhri of Cefic. Europe is responsible for 15% of world chemical sales and 25% of world chemical exports in value terms, with 2/3 of EU chemicals supplied to the industrial sector, but there is a competitiveness issue, he said, to do with raw materials and energy costs and over-regulation. The cost of regulation to producers has doubled over the past 10 years. The issue is convincing the European Commission that regulation costs are discouraging investment in the EU.

## Industry 4.0

Tuesday afternoon saw a panel discussion on the impact of digitisation and machine learning on the industry – the so-called 'Industry 4.0' transition, involving Oliver Lieske of PwC, Stefan Brauner and Collin Bartlett of Outotec, Mike Allenspach of nVent Thermal Management, Frank Scheel of Jacobs and Kent Kalar of Topside Solutions.

While the consensus from the audience was that 70% of their companies either had a digitisation strategy or expected one to be in place in the next 12 months, the question was what these developments could mean for plant operators, and what as operators they were looking to achieve. Mike Allenspach highlighted one application – generating a profile of a sulphur pipeline from a continuous fibreoptic line and coupling it with softer analytics to be predictive and proactive and deal with issues before they become problems, while Outotec mentioned an optimiser system which adjusts process values to allow for higher production, or lower emissions, or lower energy use, according to what parameters the customer sets – this is now installed in four locations.

The audience also highlighted the possibility of knowledge management – capturing lessons learned and presenting and transferring them to younger engineers, although there could be issues with liability or intellectual property agreements. Perhaps the greatest value might be found in predictive maintenance.

## Long term sulphur supply

The last paper on Tuesday's commercial section was a look by sulphur stalwarts Angie Slavens of UniverSUL Consulting and Peter Clark, now with his own consulting company,

Canadian Sulfur Consulting, at the longer term future of sulphur supply. One of the concerns is that increasing electricity production from renewables and increasing use of electric vehicles will mean a fall in use of oil and gas and consequent reduction in production for sulphur at the same time that demand for sulphur to process phosphates is increasing. Fossil fuels currently provide 75% of sulphur in all forms (metal smelting of sulphide ores generates most of the remainder). In 2018 this represents about 82 million t/a (in all forms of sulphur), but by 2050, assuming continued growth in the phosphate fertilizer and other markets, this could be 118 million t/a. Peter argued that electric vehicles may not have the impact that we expect (there are concerns about expense, and whether there is sufficient lithium available for their batteries), and hence sulphur production effectively depends on the uptake of non-fossil fuel energy sources. Peak oil production is expected somewhere between 2023-2040 by most commentators, capping oil derived sulphur production at around 35 million t/a. He noted that countries such as the UAE and Saudi Arabia have an ambition to produce 45% of their energy from such sources by 2050, so there will probably still be a large amount of sour gas being processed in the Middle East, but even so, it seems unlikely that more than 55 million t/a of sulphur will be coming from this source by 2050. This leaves a projected shortfall of 28 million t/a. Even if the world re-started Frasch mining, peak production of Frasch sulphur was no more than 12 million t/a. It seems likely, he concluded that we may end up processing highly sour gas for its sulphur content rather than its methane content. Angie concluded by showing that sulphur produced from a hypothetical such plant might only need a price of around \$350/t to justify the investment, and if a very high H<sub>2</sub>S content gas (60% or more) can be used capital expenditure and the required sulphur price come down considerably.

SRU operations

The technology section of the conference began on Wednesday, split as is traditional into separate sulphur and sulphuric acid streams. In the sulphur stream, the day began with papers on sulphur recovery units. Domenica Misale-Lyttle of Industrial Ceramics began with a paper on ceramic insulating paper as a boiler tube protection system. There are claims using computational fluid dynamics that the paper is gas

permeable and so does not protect tubes, but empirically it seems to work. The investigation showed that the paper is permeable, but not in the flow direction that obtains within a boiler tube, and hence gas bypass does not occur.

Simon Weiland of Optimised Gas Treating and consultant Elmo Nasato continued with the theme of waste heat boilers, discussing their design and operation, showing that there are many factors which impact heat transfer performance. Tube ligament spacing and the cleanliness of the water side is paramount to reliability, while mass flux is an important parameter but limiting it will result in less economic designs. Problems with service life are driven more by water side heat transfer performance vs process side mass flux choices.

The importance of water treatment in SRUs was also emphasised by Tobias Roelofs of Jacobs Comprimo and Mohammed Ajirjawi of Cool Separations BV, the latter showcasing their Eutectic Freeze Crystallisation technology, achieving zero liquid discharge at high capacities. The system comes as easily transportable modules to standard cargo container sizes.

Ben Walton of Sulphur Experts described the EuroClaus process, examining its operation with reference to two case studies, while Tobias Roelofs of Jacobs Comprimo presented StrataClaus – an improvement on the EuroClaus system with a new catalyst which maintains H<sub>2</sub>S selectivity at higher temperatures and which can give a higher sulphur recovery efficiency for similar investment cost in a grassroots system, and which can be easily revamped to create a margin in SO<sub>2</sub> emissions.

Rob Marriott of ASRL presented some work that had been carried out by the organisation on the effect of ammonia on corrosion rates in Claus plants. Wet sulphur contact corrosion is the most damaging in most Claus plants, and ammonium salts can reduce this – it is believed by forming a protective layer of ammonium ions next to the steel.

Tail gas treatment

Moving further downstream, Ciro di Carlo of Siirtec Nigi showcased a re-start of a TGTU at the Mellitah complex in Libya. The plant had operated for five years from 2004, but had had a long-term shutdown from 2009 until 2018 and was in a sorry state when examined. Most of the shells in the

lean amine cooler were out of service due to leaks, and MDEA concentrations were down to below 40%. The boiler feed water cooler was also out of service due to leaks, and there was liquid sulphur carryover. Once these issues had been corrected, the tail gas treatment catalyst was unloaded and a fresh batch loaded, but hydrogen had to be bought in for commissioning as there was none available locally.

As required sulphur emissions standards continue to tighten, but there is pressure to move to higher throughputs and use sourer feeds, so the stresses on an SRU can increase. Gerald Vorberg of BASF described ways of meeting these challenges, including acid gas enrichment integration into the tail loop, and oxygen enrichment of the gas feed, as well as advanced solvent technologies provided by co-author ExxonMobil with higher capacities and greater specificity.

In what he said was his industry swansong, Bob Van de Giessen of EuroSupport highlighted the advantages of titania cobalt-molybdenum catalysts over alumina in Claus units and TGTUs; higher activity, longer lifetime, easier to activate and to revive after poisoning. The disadvantage of course was cost, restricting it to niche applications until environmental regulations tighten sufficiently that it becomes required.

Finally, Steve Pollitt of WorleyParsons and Helge Rosenberg of Haldor Topsoe noted that – if you want to achieve sulphur recovery efficiencies of >99.9% while reducing life cycle cost by up to 50%, using a Topsoe wet gas sulphuric acid (WSA) plant instead of a tail gas treatment unit is a very real option – provided that there is a ready use or market for the sulphuric acid in the vicinity.

Gas enrichment

Three papers on the Thursday looked at gas enrichment of various types – first acid gas enrichment (AGE), with Angie Slavens of UniverSUL Consulting and Simon Weiland of Optimised Gas Treating presenting some “new wrinkles” on the process, such as a tie-in to the TGTU, as was mentioned above. The work compared AGE with natural gas co-firing, oxygen enrichment, and considered leaner acid gases, as well as climatic conditions (whether air refrigeration was required). As usual Angie took delegates through a comparison of various configuration cases, concluding that AGE improves acid gas quality and SRU operation, and routing lean acid gas to the



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TGTU absorber or quench column improves enrichment but has little effect on life cycle cost. However, at lower H<sub>2</sub>S concentrations the benefits of AGE become more apparent. Natural gas co-firing is less attractive, both technically and commercially, while oxygen enrichment alone cannot achieve an adequate reaction furnace temperature.

Uday Parekh, now with Blasch Precision Ceramics, was able to return to his favourite subject – that of oxygen enrichment of SRUs. There was a widespread misconception, he said, that an oxygen plant needed to be available to consider O<sub>2</sub> enrichment in a grassroots plant. However, one can be built at a fraction of the cost of an SRU, and brings all of the familiar advantages in terms of improved capacity etc. In small applications, liquid oxygen can even be delivered by truck at relatively low cost.

Bernhard Schreiver of Linde in his paper on oxygen enrichment pointed out that it can also help with furnace temperature optimisation, and can be more reliable, use lower utilities and bring enhanced flexibility compared to co-firing or other solutions.

## SUDIC specifications

The last part of the sulphur session was a look by Jerry d'Aquin of Con-Sul and Paul Davis of ASRL at the SUDIC sulphur specifications, a topic which Jerry covered in an article in our September/October 2018 issue (*Sulphur* 378, pp26-35). The duo took delegates through the history of sulphur forming, and the pressures that SUDIC was under to produce a specification geared to what was being produced in Canada at the time (and lest we forget, that time was the 1970s). Of course, as has been well demonstrated, specifications for sulphur 'as produced' can have little impact on what is finally delivered to a customer after weeks at sea and some rough handling at ports. Given the proven benefit that moisture content can have on dust suppression, were the SUDIC moisture levels still relevant? Paul Davis also rehearsed the argument for there being an H<sub>2</sub>S specification for formed sulphur, as well as discussing the possibility of a sulphur specification for 'as loaded', based on 80% of particles being within 1-20 mm and moisture content between of 1-5%.

## Sulphuric acid: operator experience

The sulphuric acid technical sessions began with a series of case studies of acid plant construction or revamping. Collin Bartlett of

Outotec focused on the stringent emissions standards that Boliden's new sulphuric acid plant at its Harjavälta smelter in Finland had had to meet. The 2,200 t/d plant takes off-gas from copper and nickel smelting operation, and had to take account of a complicated footprint at the existing site as well as tight Finnish emissions limits on SO<sub>2</sub> and NO<sub>x</sub> – the former less than 100 ppm at the stack, the latter requiring a gas cleaning section. The absorption section also required removal of significant amounts of waste energy.

Glencore and DuPont Clean Technologies presented work undertaken at Nikelwerk in Norway to replace an old drying tower at the acid plant there, designed by DuPont and using MECS ZeCor alloy construction and Brinks mist eliminators. Meanwhile Bodrick Mumba of Kansanshi Mining in Zambia described debottlenecking of the acid plant, which had been a limiting factor in operation of the smelter there. Since the debottleneck to 4,200 t/d, the smelter has achieved its design capacity of handling 1.2 million t/a of copper concentrate per year.

Atlantic Copper illustrated improvements made to operation and maintenance at the gas cleaning section of their acid plant at Huelva, Spain, including improvements in gas temperature control of radial control scrubbers, homogenisation of acid concentration and impurities in the waste gas plant, and increased impurity removal capacity in order to improve gypsum quality.

## Plant and process design

Rene Dijkstra of Chemetics presented a flowsheet for a single train sulphuric acid plant design with a capacity of 10,000 t/d or more – the so-called MEGA acid plant. Oxygen is used to reduce the plant footprint and investment cost, and the oxygen plant can run on power generated by the process.

Naneen Chenna of Valmet Technologies showcased his company's process for sulphuric acid production from pulp mill non-condensable gases. Most pulp and paper mills operate a sodium-sulphur cycle, but sodium losses in the cycle tend to lead to a sulphur excess, which leaves the plant in various gas streams. If this sulphur could be recovered and converted to acid then that acid can be used in other parts of the plant – plant operations becomes more efficient and pulp mill demand for sulphuric acid is almost eliminated.

At Mutoshi in DRC Outotec is building three 250 t/d acid plants using a modular

design to get the plant components the 3,000 miles from the delivery port in South Africa to the mine site itself. Anne Mohsler of Outotec explained the design considerations and challenges behind the development.

Maurizio Verri of Desmet Ballestra explained the design options available for integrated production of liquid sulphur dioxide and sulphuric acid via a low temperature cryogenic process. One such plant was completed in 2012 and a second is now under construction.

Nelson Clark of Clark solutions described his SAFEHR process, which cools hot acid with an inert indirect fluid, increasing safety by minimising damage due to leaks and reducing hydrogen generation due to corrosion. It also offers the possibility of increasing heat recovery.

Heat management was also the topic for Andres Maheca-Botero of NORAM Engineering, discussing the design, fabrication, commissioning and start-up of pre-heating systems.

Sven Anderson of Babcock & Wilcox described a patented sulphur recirculation technology for reducing high temperature boiler corrosion and dioxin formation in waste to energy plants. SO<sub>2</sub> is separated from a tail wet scrubber using hydrogen peroxide, and is then injected into the boiler, creating a sulphur loop, increasing the gas concentration in the boiler and producing a less corrosive environment.

## Improved plant operation

The final acid session showcased a number of technologies for improving acid plant operation. Ohio Lumex illustrated their innovative sorbent traps for sulphuric acid mist measurement, Spraying Systems presented an advanced injector technology for increased molten sulphur injection efficiency into an acid plant, Matthew Thayer of Koch Knight looked at ways of optimising tower design, and Sophie Boisvert of Norda Stelo stressed the importance of thermomechanical analysis in the age assessments of stainless steel converters. Finally, two catalyst papers rounded off the conference, Marten Granroth of Haldor Topsoe highlighted the importance of catalyst technical services and proactive maintenance of catalyst in achieving optimal plant performance, and Marco Kennema of BASF described the process of catalyst development as it applied to the company's current portfolio of acid catalyst offerings.



# Carbon beds in amine systems

Carbon beds are an integral part of most amine-based gas treating units. In some cases, the carbon bed is on the rich amine stream, although it is often on the lean stream. In most cases, there is a small slip stream 5-25% (of the main flow) that contacts the carbon. The ostensible reason to use a carbon bed is for hydrocarbon removal. **M. Thundiyil** and **D. Seeger** of Transcend Solutions LLC analyse the utility of carbon beds in removing hydrocarbons in the context of a typical amine treating process and the typical contaminants that exist in the process. Other technologies that can be applied to leverage the efficacy of carbon bed treatment of amine streams are also evaluated.

**G**as streams containing acid gases ( $H_2S$ ,  $CO_2$ ) are often treated with aqueous solutions of alkanolamines such as monoethanol amine (MEA), diethanol amine (DEA), methyl diethanolamine (MDEA), diisopropanol amine (DIPA), amino-ethoxy-ethanol (diglycolamine, DGA) etc. The alkanol amine absorbs the acid gases in the absorber. The “rich” amine is then sent to the stripper column, where the acid gases are released under heat and reduced pressure. The resulting “lean” amine is returned to the top of the absorber column for acid-gas absorption. A simplified schematic of the amine treating system is provided in Fig. 1.

The recirculating amine system can concentrate contaminants that are removed from the inlet sour gas; or contaminants that are formed in the system through corrosion, degradation or other mechanisms. The most common contaminants that accumulate within amine systems are solids (usually corrosion products, but also solids that enter from the inlet gas), heavy hydrocarbons, amine degradation products, heat stable salts, and surfactants.

The most common systems used to remove these contaminants from the amine stream and prevent their infinite accumulation are: (a) rich flash tank; (b) particle filters; (c) packed carbon bed; and (d) reclaimers. The rich flash tank is intended to remove heavy oils by settling. The particle filters are expected to remove solid contaminants by filtration.

The reclaimers are intended to remove amine degradation products and heat stable salts, although some (such as vacuum distillation and thin film evaporation) can also remove solids and hydrocarbons. Carbon is usually claimed or believed to be capable of removing amine degradation products and hydrocarbons.

This article investigates (a) whether carbon, in the quantities that are used, offers a significant means of hydrocarbon removal; and (b) if there are other better mechanisms that can be used to leverage the carbon bed.

## Carbon adsorption

Adsorption is a process whereby molecules passing through a packed bed of highly porous solids are attracted to and held to the solid surface by attraction forces that are weaker and less specific than covalent or ionic chemical bonds. Energy is typically released when the molecule adsorbs on to the surface of the solid. Adsorption capacity increases as temperature declines. Increasing available surface area generally increases the available capacity for molecular capture. As a result, good adsorbents tend to have very high specific surface areas (surface area per unit volume).

Adsorption is often confused with absorption. Adsorption is a surface phenomenon; whereas absorption is a process by which another substance is taken up within the bulk of absorbing medium expanding the

size or shape of that medium. Activated carbon is an adsorbent, which means that the availability of its microporous surface area is essential to its efficacy.

Activated carbon is a graphite form of carbon with an amorphous structure. It can be formed from a variety of carbonaceous materials (coal, asphalt, wood, coke, coconut shell, etc.), through a process that results in the formation of a highly porous structure. Since it can be produced from inexpensive materials, activated carbon is a very cost-effective adsorbent for a variety of contaminant removal requirements. The activated carbon structure will depend on the raw material from which it was derived, with differing physical and chemical properties (Fig. 2). Activated carbon typically has very high surface area (800-3,000  $m^2/g$ ). Once the owner/operator decides that the carbon is spent, the carbon is either removed from the vessel and replaced with fresh carbon or regenerated in-situ. The spent or used carbon may be regenerated during which the adsorbed molecules are generally released by reducing the pressure or increasing the temperature of the carbon. Activated carbon is generally best regenerated and reactivated in a furnace.

Micropores are typically defined as pore radii less than 1 nm, mesopores are pore sizes with radii between 1-25 nm, and macropores are pore sizes with a radius greater than 25 nm. The macropores and mesopores are essential to allowing transport into the carbon, whereas the micropores

Fig. 1: Amine system loop

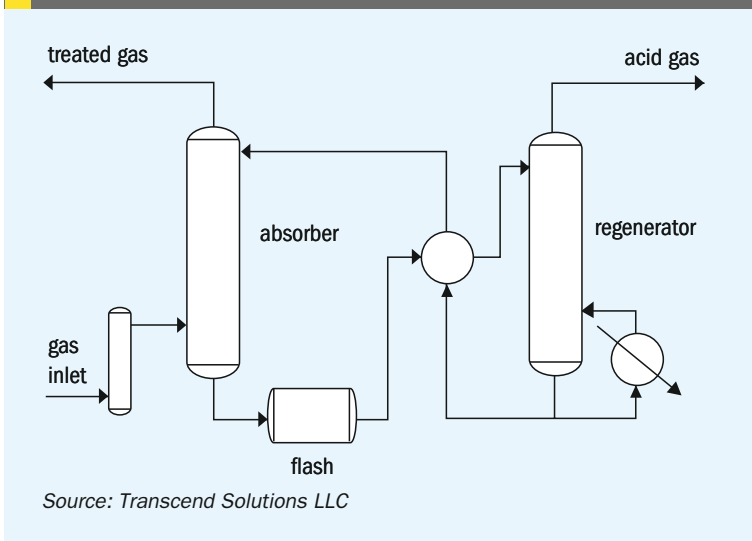
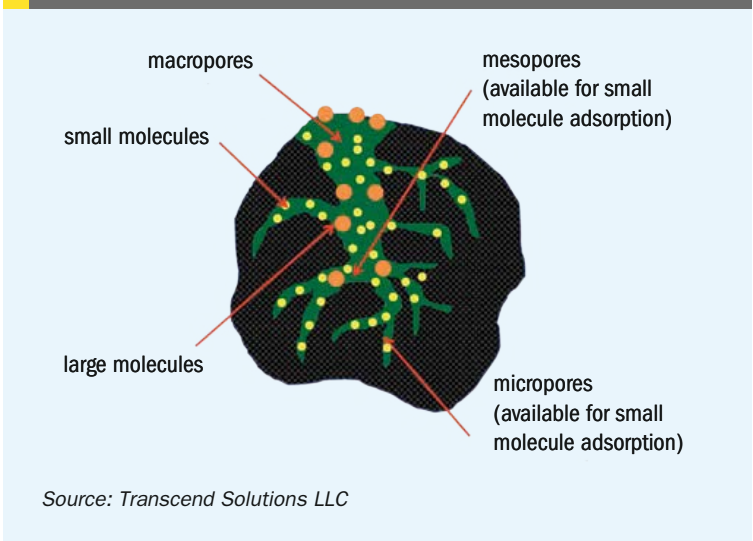


Fig. 2: Activated carbon pores and adsorption site



are where the bulk of the adsorbed pore surface resides.

Carbon capacity

The most common measures of the capacity of activated carbon are the iodine number and the carbon tetrachloride (CTC) number which are used for liquid and gas phase adsorption respectively. The iodine numbers are reported in terms of milligrams of adsorption per gram of carbon. An iodine number of 1,000 indicates that the carbon can adsorb up to 1,000 mg or 1 g of contaminant per gram of carbon. The CTC number represents the uptake of carbon tetrachloride on a percent basis, so that a CTC value of 50 indicates that the carbon adsorbed 50% of its weight in carbon tetrachloride, or 500 mg/g. The molasses number is a measure of the capacity of the mesopore capacity of the carbon to adsorb larger molecules (generally larger than 2 nm). This figure is typically in the 200 mg/g range.

The iodine atom has a van der Waals radius of 198 pm (0.2 nm) and is therefore expected to be able to fill up the entire microporous space in the activated carbon, for liquid phase adsorption. The molecular diameter of typical hydrocarbons is much larger, for example:

Butane	0.4 nm
Octanes	0.5-0.7 nm

In comparison to iodine (0.2 nm), a heavy oil molecule (C12+) in an amine will have a much larger molecular diameter, probably exceeding 1 nm. So, the iodine number represents a potentially unachievable upper bound to the adsorption capacity of the carbon for heavy oil from amine. For

that reason, the molasses number should be used for larger molecules to achieve a more accurate measure of available uptake. Note, however, that the actual uptake will always be dependent on the concentration in the external bulk phase, which further de-rates the actual adsorption capacity of the carbon. A rule of thumb is 10% weight uptake.

Carbon bed design for amine systems

Activated carbon is used in amine systems on either the rich or lean side. Activated carbon is used either in the form of canisters (6" OD x 36" L or 11" OD x 22" L), or fixed beds, in a kinetically suitable mesh size.

The typical residence time in a bed designed according to industry best practice will be at least 15 minutes. The residence time in a canister is generally shorter which is justified by the finer mesh material (allowing faster diffusion and adsorption kinetics) that is typically used, and the relative ease of canister replacement.

Due to the high residence time requirement, amine systems will only process a small slip stream (generally 5-15% of the total system flow) through their activated carbon beds. In the early days of amine treating (1930s), activated carbon was intended to remove amine degradation products, but today, activated carbon is primarily deployed for the removal of hydrocarbons.

The activated carbon adsorbent is intended to remove dissolved components from the amine system. This is illustrated in Fig. 3. Initially, the pores are filled with the amine, and then as hydrocarbons dissolve into the amine from the gas stream, the hydrocarbons diffuse through the macro- and mesopores and get adsorbed

on the interstices of the carbon according to the size of the molecule and the pore sizes available.

Fig. 4 shows what happens when the amine contains hydrocarbons above the solubility limit. In this case, a heavy oil dispersion or emulsion recirculates within the system. The carbon particle is very likely to be coated by the dispersed hydrocarbons, resulting in significant pore blockage, thereby reducing the available adsorption surface area.

Foaming in amine systems is attributable to solids, hydrocarbons and surface-active agents. The presence of solids and emulsified hydrocarbons are commonly correlated with foaming incidents in the amine system. Foaming incidents also tend to agitate settled hydrocarbons and solids from the tower internals, exacerbating the original incident.

Amine system example

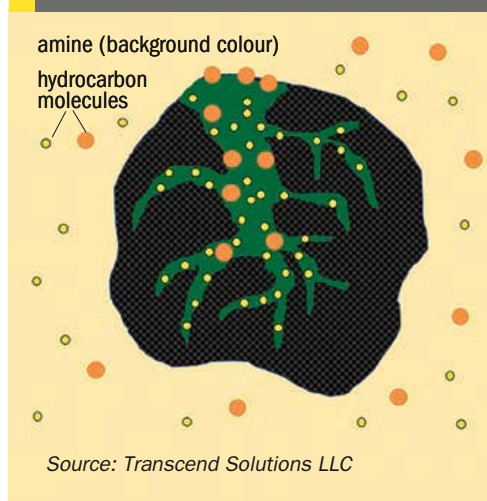
For the purpose of understanding the efficacy of carbon adsorption in an amine system, we will consider a case of an amine system used to treat a sour gas stream. The process parameters are listed below:

- gas flow rate: 400 million std ft<sup>3</sup>/day;
- gas operating pressure: 900 psig;
- average molecular weight of treated gas: 22;
- gas molecular flow rate: 1,060,000 lb-mol/day;
- CO<sub>2</sub> content: 5%;
- H<sub>2</sub>S content: 5%;
- amine system flow rate: 1,000 gal/min;
- amine system volume: 180,000 gal.

Given these parameters, and a typical molasses number, we can estimate the



Fig. 3: Schematic of adsorption



total adsorption capacity of activated carbon in an amine system:

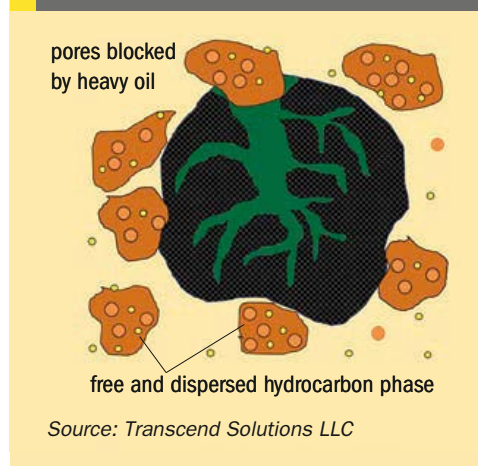
- amine slip-stream flow rate (15%) to carbon bed: 150 gal/min;
- carbon bed volume: 300 cubic feet;
- carbon bed weight (typical density of 30 lb/cf): 9,000 lb;
- available uptake of large molecules (molasses number = 200): 1,800 lb;
- available uptake of small molecules (iodine number = 1,000): 9,000 lb.

It is reasonable to assume that the incoming gas contains 2-10 ppmw of hydrocarbon aerosol that can get picked up by the amine. This translates into a hydrocarbon ingress of >200 lb/day. In addition, some vaporised hydrocarbon is also picked up by the amine. An especially significant amount of vaporised hydrocarbons will be picked up if there are aromatic species in the inlet gas, or if the gas treating solvents have an affinity for the aromatics.

A typical amine may be expected to have a solubility limit of approximately 100 ppmw which results in the recirculating amine in our example carrying up to 150 lb of hydrocarbon (180,000 gal x 8.3 lb/gal x 100/1,000,000). The hydrocarbon solubility capacity of the amine (150 lb, in our example) is generally lower than the ingress of aerosolised (200+ lb/day) and vapour hydrocarbons (variable). If the incoming hydrocarbon is not removed (by the carbon bed, in the regenerator), then the hydrocarbon will start condensing into a separate phase that will recirculate around the system. Some of this hydrocarbon will gravitationally separate in the flash tank, but much of it will recirculate as a stable emulsion.

The condensed hydrocarbon may not necessarily be visible as a separate phase

Fig. 4: The impact of free hydrocarbons on pore blockage



in an amine sample bottle. The human eye is only able to resolve droplets larger than 20-micron, and due to pump action and heating and cooling in an amine system which break droplets into smaller ones, the hydrocarbon droplets are generally not detectable by the naked eye. In addition, droplets of a very small size, i.e., below approximately 20-micron, settle very slowly and will remain suspended for a long time. A sample in a glass bottle may appear hazy, but due to the limited depth of the bottle, the human eye may not even be able to detect the presence of a haze.

### Rich-side carbon

If the carbon bed is on the rich amine, all the dissolved hydrocarbon in the amine will be immediately available for adsorption onto the carbon. This means that the 200+ lb/day of hydrocarbon entering the system will be available for adsorption by the carbon bed. Since the carbon bed operates on only 15% of the amine flow, the balance of the hydrocarbon will recirculate, free to be stripped in the stripper, to affiliate with solids and form a shoe-polish-like substance which may settle in dead zones, on heat exchange surfaces or in mass transfer equipment. The heavy hydrocarbons that do not boil off in the regenerator, will recirculate and the amine will reach the solubility level in a matter of days after start-up.

If we assume that the amine is saturated in hydrocarbons at a solubility level of 100 ppmw, the upper limit of the total hydrocarbon adsorbed by the carbon is approximately 180 lb/day (150 gal/min x 1,440 min/day x 8.3 lb/gal x 100 ppmw (HC)). Given the carbon capacity of between 1,800 lb – 9,000 lb of hydrocarbon adsorption, the carbon will be spent

in 10-50 days. This assumes that there is no free hydrocarbon fouling the carbon. The 10-day estimate (based on the molasses number) is a likely applicable because much of the soluble hydrocarbons (C6+, 0.5 nm+) will be larger in size than the iodine atom (0.2 nm).

If the amine has emulsified hydrocarbon, as is common, it is very likely that the carbon particles will be coated by the hydrocarbon, thereby introducing a significant mass-transfer resistance to hydrocarbon adsorption, i.e., the carbon is essentially spent at that condition. The use of carbon adsorbents on the rich amine section is particularly subject to fouling by free hydrocarbons because the ingressing hydrocarbons will not have had an opportunity to be stripped from the amine in the regenerator prior to contacting the carbon. If we assume that the available carbon capacity is reduced due to pore blockage by free and dispersed heavy oil to 30%, that means that the carbon capacity is now 600-3,000 lb. This suggests that the carbon is spent in 3-15 days. Most primary gas treating amine systems (i.e., not including tail gas amine systems) are contaminated with recirculating emulsified heavy hydrocarbon, so it is most likely that the carbon in these systems is spent in approximately three days!

Obviously increasing the slipstream, and the carbon bed size can help extend the available run life of the carbon; but the root cause solutions must involve (a) reducing the quantity of hydrocarbons challenging the carbon bed; and (b) reducing the likelihood of emulsified hydrocarbons that can foul the carbon.

### Lean-side carbon

If the carbon is located on the lean amine all the light hydrocarbons (C7 and lower) will be stripped out in the regenerator. This reduces the level of hydrocarbons in the amine system. The remaining hydrocarbon in the lean amine will be heavier (C8+), with a higher viscosity, and a lower solubility level.

Therefore, carbon beds on lean amine streams can expect to be faced with emulsified and dispersed hydrocarbon to a greater extent. In addition, the higher boiling hydrocarbons can expect to have lower adsorption capacity in the carbon. As a result, the likely run life will be in the 3-10 day period defined by the lower limits of the carbon capacity depending on whether hydrocarbon emulsions are present.

### Activity indication

Many owner/operators decide to replace their activated carbon on pressure drop. Pressure drop is a measure of solid contaminants building up on the carbon bed and is not a measure of available adsorption capacity of the carbon. A practical test for residual carbon activity is to conduct an amine foam test at the outlet of the carbon bed. If the carbon bed is not spent, and the amine is free of recirculating solids, there should be a significant difference between the inlet and effluent in foam heights and foam stability. However, since carbon can remove anti-foam, foaming tendency can be a non-specific test.

### Utility of carbon in amine systems

Carbon beds still serve a very useful purpose in amine systems. When designed and operated well, they can effectively remove surfactants, certain degradation products and even low levels of soluble hydrocarbons. However, to be effective, the carbon needs to be replaced when spent, not on a preventive maintenance schedule. In addition, their efficacy can be greatly extended if they are protected from free, dispersed or emulsified hydrocarbons and if the incoming heavy hydrocarbon load is reduced.

### Advanced alternatives – liquid-liquid separation – removing emulsified hydrocarbons

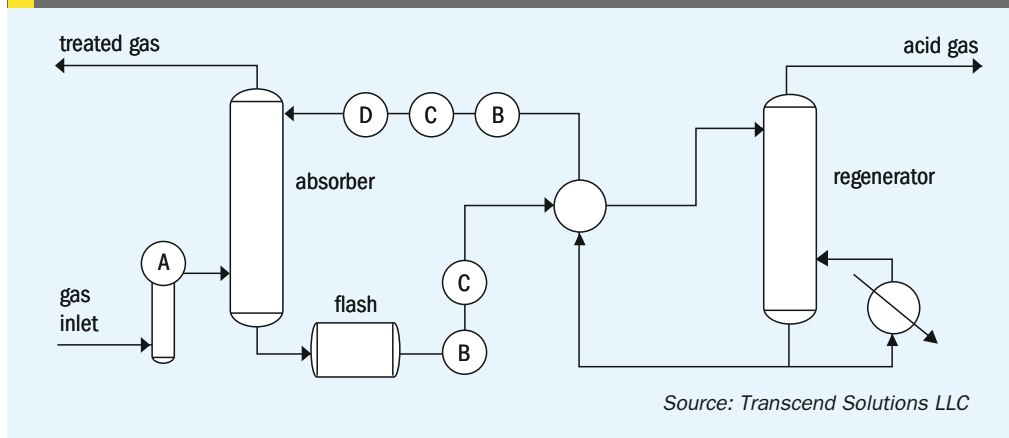
The presence of emulsified hydrocarbons has a significant impact on carbon capacity due to the pore blockage challenge. This paper assumes that 30% of the carbon capacity is still available, but it is very likely that this is a very optimistic estimate, given how common it is to have carbon beds contaminated with a layer of free oil. A good approach to improve carbon bed performance involves the deployment of a high efficiency emulsion separator prior to the carbon bed. Transcend Solutions provides its Envision™ EHR technology specifically designed for emulsified hydrocarbon removal from amine systems.

The emulsion separator is preferably used to treat the entire amine flow to remove emulsified hydrocarbons, thereby protecting downstream mass transfer columns, and reducing the burden on the carbon bed. Fig. 5 shows a sample of amine with and without emulsified hydrocarbons, illustrating the capability of the Envision™ technology. The emulsion separator may be located on the rich or the lean side of

Fig. 5: (Left) Amine with emulsified hydrocarbons (Right) Amine after treatment with Envision technology



Fig. 6: Amine system – preferred location of hydrocarbon and solids removal



the amine loop. The advantages of locating it on the rich side include removing hydrocarbons immediately after the flash tank, preventing fouling of the exchangers or the regenerator, reducing hydrocarbon load in the amine acid gas stream, and ensuring that the lean amine will not have emulsified hydrocarbons. Locating the carbon bed downstream of the emulsion separator on the rich or lean section of the amine system is enough to ensure that the carbon will not encounter emulsified hydrocarbons that will shorten its adsorption capacity.

However, if owner/operators are concerned about rich-side installation of a liquid-liquid separator, the system can be installed on the lean side before the carbon bed. It is preferred that 100% of the amine stream is treated which will also protect the downstream columns and other equipment in addition to protecting the carbon bed. However, if capital economics dictate that only slip stream treatment is affordable, an emulsion separator immediately upstream of the carbon bed will allow the carbon to have a longer run life.

Using a liquid-liquid separator is ultimately a solution to a symptom (of hydrocarbons in the amine system), rather than a root cause solution. The root cause solution would be the prevention of hydrocarbon emulsification in the amine system in the first place. However, the amine side solutions installed in amine systems can be economically justified if the gas phase treatment is more expensive due to pressure and metallurgy, or if, as in a refinery, there are dozens of absorbers feeding a single amine regeneration unit.

### Advanced alternatives – aerosol-gas separation – removing hydrocarbons before the amine unit

The root cause of the problem that carbon beds are expected to solve is the ingress of hydrocarbons into the amine system. These hydrocarbons are most commonly aerosolised sub-micron contaminants. Some vapour phase hydrocarbons can end up in the amine depending on the



treating solvent, but for the most part the offending contaminants that cause foaming and fouling in the amine loop are present in the inlet gas as an aerosol. These aerosols may be compressor lube oils, heavy aromatic naphtha from corrosion inhibition programs, hydrocarbons from hydroprocessing unit separators, etc. In any case, the sub-micron contaminants are often not stopped by conventional separators that are applied.

It is essential to have a high efficiency aerosol separator. The gas treating industry conventionally uses horizontal-filter separators to keep liquids out of the amine system. These systems have inherent flaws that limit their efficiency at removing liquids from gas streams. More importantly, they are unable to remove the low-surface tension, sub-micron aerosols that afflict amine treating systems. Transcend Solutions provides its Ensur™ technology specifically designed to remove these sub-micron aerosols. If the liquid aerosols are stopped before the amine absorber column, the only hydrocarbons that can be picked up by the amine are those that exist in the vapour phase of the

gas to be treated. For example, the vapour pressure of heavy hydrocarbons is very low (for example, dodecane has a vapour pressure of <20 Pa), so they are present only in ppb levels in the inlet gas.

Recommended best practices

Carbon beds are used in amine systems ostensibly to remove hydrocarbons for the purposes of foaming and fouling prevention. Foaming is caused both by the presence of emulsified hydrocarbons and solid particles. The root cause and industry best practices include (as shown in Fig. 6):



- high efficiency aerosol separation on inlet gas (A);
- high efficiency, solids removal from rich full-flow or lean slip-stream (B);
- high efficiency, emulsion separation rich full-flow or lean slip-stream (C);
- carbon bed located downstream of emulsion separator (D).

Summary

This article evaluated the capacity of a conventionally designed carbon bed

to remove the kinds of hydrocarbons that challenge it. We were able to show that even under ideal conditions, carbon beds most likely only have 10-50 days of available capacity for hydrocarbon removal. Also, if there are emulsified hydrocarbons present in the amine stream (which is the most common situation) then most likely the available capacity will decline to last about three days. Conventionally designed carbon beds are therefore wholly inadequate to maintain the fluid quality of an amine system.

This limited available capacity is often-times not recognised by owner/operators, so the carbon beds may be scheduled for replacement every 6-12 months, even though their useful lifetime had long since passed. We propose technology to extend the run life of the carbon bed, by protecting it from free, dispersed or emulsified heavy oils; thereby allowing carbon adsorption to operate to its maximum extent. In addition, we propose the use of high efficiency sub-micron aerosol removal to protect amine systems from heavy oils in the first place.



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# Copper smelter provides district heating in Hamburg

Copper plays a central role in today's transition to a low-carbon economy and Aurubis, the world's leading provider of non-ferrous metals, has been at the forefront of implementing low-carbon energy solutions. With operational safety paramount and several conditions needed to coincide, shifting operating conditions to allow energy recovery from the sulphuric acid plant of a copper smelter for public district heating is no trivial task. **H. Hintze** of Aurubis AG and **T. Weber** of Smart SCOPE GmbH describe this brownfield project from its conception to its realisation.

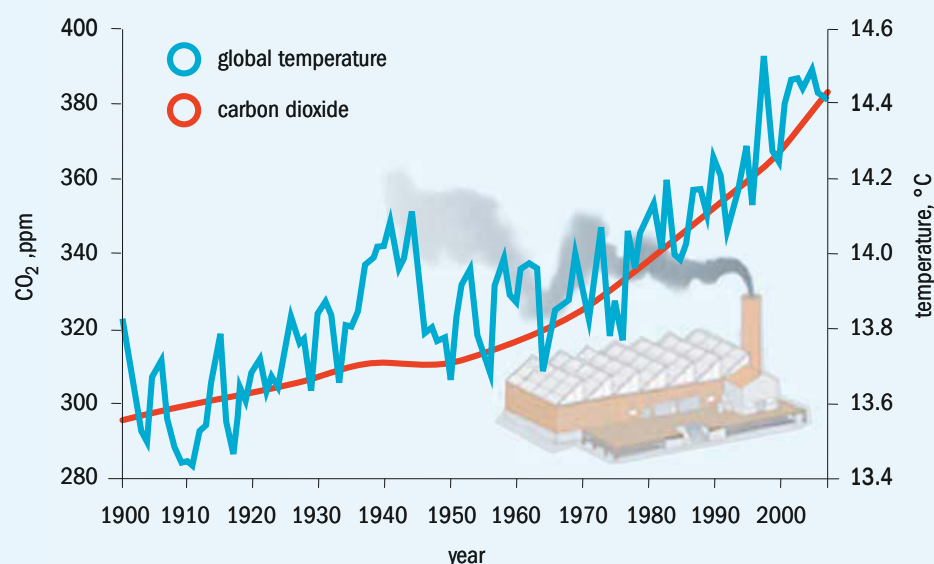
The correlation between the increase in atmospheric carbon dioxide concentration and temperature change is widely recognised around the world – as the concentration of carbon dioxide (CO<sub>2</sub>) has increased, the global average temperature has generally increased too (see Fig. 1).

The majority of politicians believe in the governmental scientists who try to model global and local climate and are looking closely at CO<sub>2</sub> production and the potential negative effects it has on climate change. This focus has led to local action plans to lower CO<sub>2</sub> production. As part of the 'Flagships of Energy-Efficient Waste Heat Use' project, the German Energy Agency selected copper producer Aurubis AG and energy service provider energcity Contracting Nord GmbH, for a flagship project showcasing for the first time how an entire district can be almost completely supplied with industrial heat.

The new Hamburg district Hafencity East will contain 12,000 new inhabitants and 45,000 office jobs. The Government of Hamburg contracted energcity to provide energy-efficient district heating to Hafencity East. Utilising industrial heat from existing installations does not create additional CO<sub>2</sub>. As Hamburg's goal is to significantly decrease CO<sub>2</sub> emissions within the next years, there is broad political consensus to develop the use of industrial heat.

The close proximity of the Aurubis Hamburg copper smelter (see Fig. 2) to the

Fig. 1: The main driving force to reduce CO<sub>2</sub> emissions



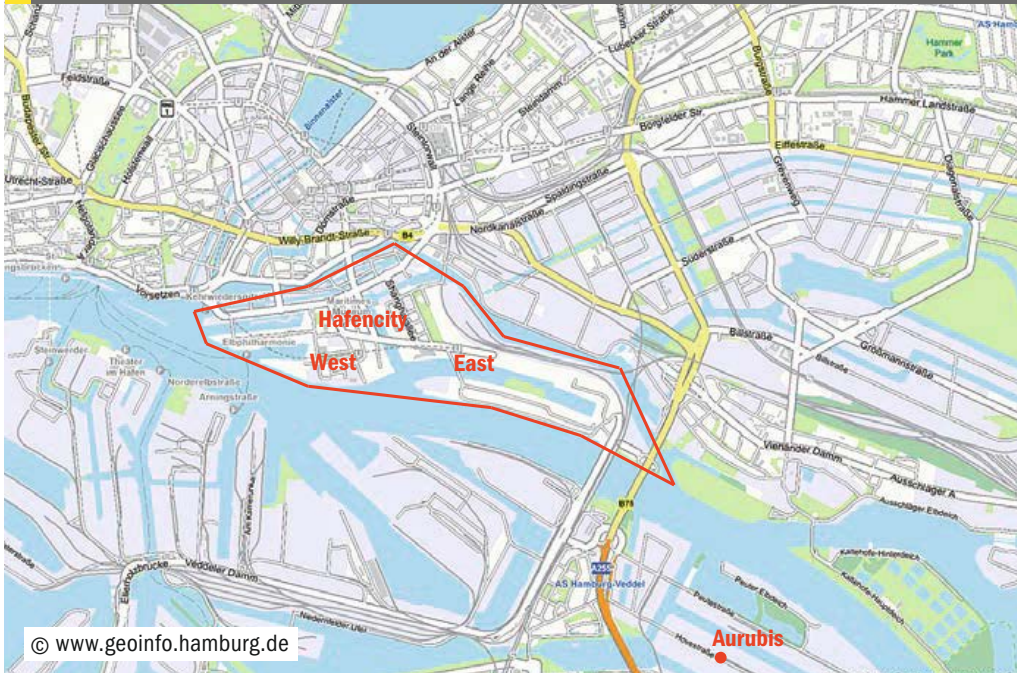
new Hamburg district made it possible to supply industrial heat from one of the sulphuric acid plants. Heat is extracted when sulphur dioxide gas, a byproduct of copper smelting, is converted into sulphuric acid. It has not been possible to use this heat energy until recently. A total of 160,000 megawatt hours of waste heat is available from this one line for heating purposes. Three quarters of the amount will be used to provide district heating for 6,000 Hamburg households, with the remaining quarter being used by Aurubis for internal processes. Some 32,000 tons of carbon

emissions can be eliminated in this way – 20,000 t/a as a result of the utilisation of waste heat in the Hafencity district, and 12,000 t/a by using the industrial waste heat in the plant itself (replacing the natural gas previously used to produce steam). In Hafencity East alone about 4,500 t of CO<sub>2</sub> will be saved every year by 2029.

Aurubis has invested €17 million in converting the plant, which includes moving the heat pipeline to the plant boundary. 30% of this cost is funded by the German Federal Ministry for Economic Affairs and Energy.



Fig. 2: A new district in the middle of the city of Hamburg, Germany



Enercity has built a new heat transport pipeline as well as a heat plant and storage capacity to balance the fluctuations in industrial heat volume, investing around €16 million, with approximately 30% being provided by the European Regional Development Fund.

In former times the batch operation mode of the Pierce Smith converter (PS converter) in the copper smelter resulted in big shifts of operation of the sulphuric acid plant. The acid plant went from operating at full capacity one minute to operating only to maintain autothermal operation the

next. This batch mode of operation made it unsuitable as a potential source of energy/heat supply for district heating. The situation changed in the year 2000 with the introduction of parallel operation capability of the PS converters. The new mode of operation resulted in much steadier heat production, a very important prerequisite when considering the supply of industrial heat from a copper smelter. Evaluation of the operation data showed the heat of one of the three intermediate absorption towers would suffice to deliver enough heat to the new district. To reach the required

temperature of the hot water supply, the operating temperature of the sulphuric acid of the absorption circuit would have to be enhanced by about 50°C. This required a complete redesign of the intermediate absorption tower system.

Feasibility study

A feasibility study was carried out to investigate the potential energy recovery on the acid side as well as the impact of an increased operating temperature on the gas system and the SO<sub>2</sub> conversion. The study was carried out by Bayer Technology Services (BTS) who created a detailed and very precise Aspen model around the intermediate absorption tower, pre-designing the new tower and surrounding equipment and providing the data needed for tendering.

The Aspen model described the real plant operation data very well – see the comparison of the real data in red and the predicted data of the model in green. The model showed a negligible influence on the SO<sub>2</sub> conversion, meaning no alteration on the gas side (heat exchanger adaption) was needed (Fig. 3).

The energy balance indicated the generation of a usable 16-20 MW of heat at the intermediate absorption tower, depending on the operating conditions – primarily the smelter throughput. This corresponds well to the amount of energy required for the district heating.

Fig. 3: Aspen model validation of the intermediate absorption tower

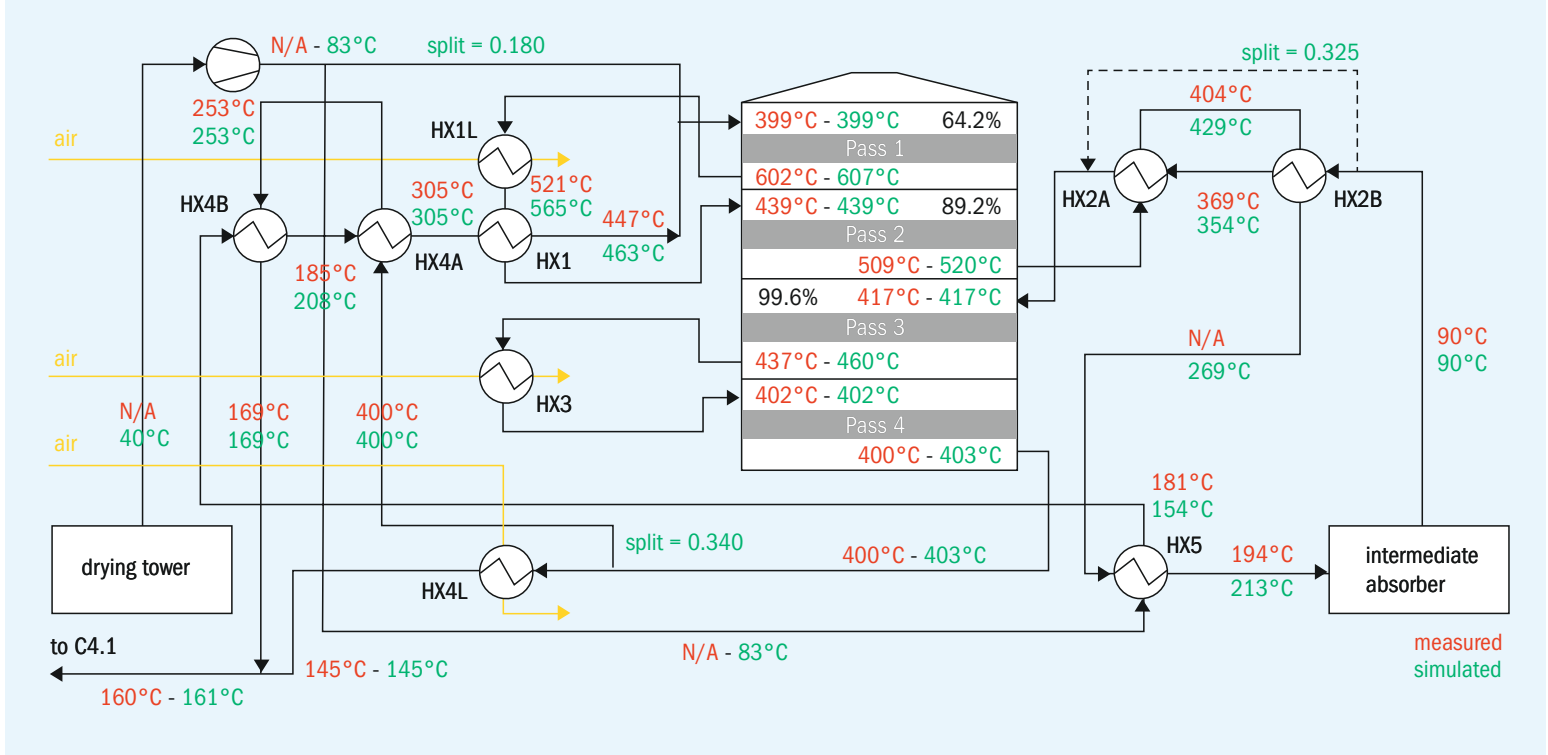
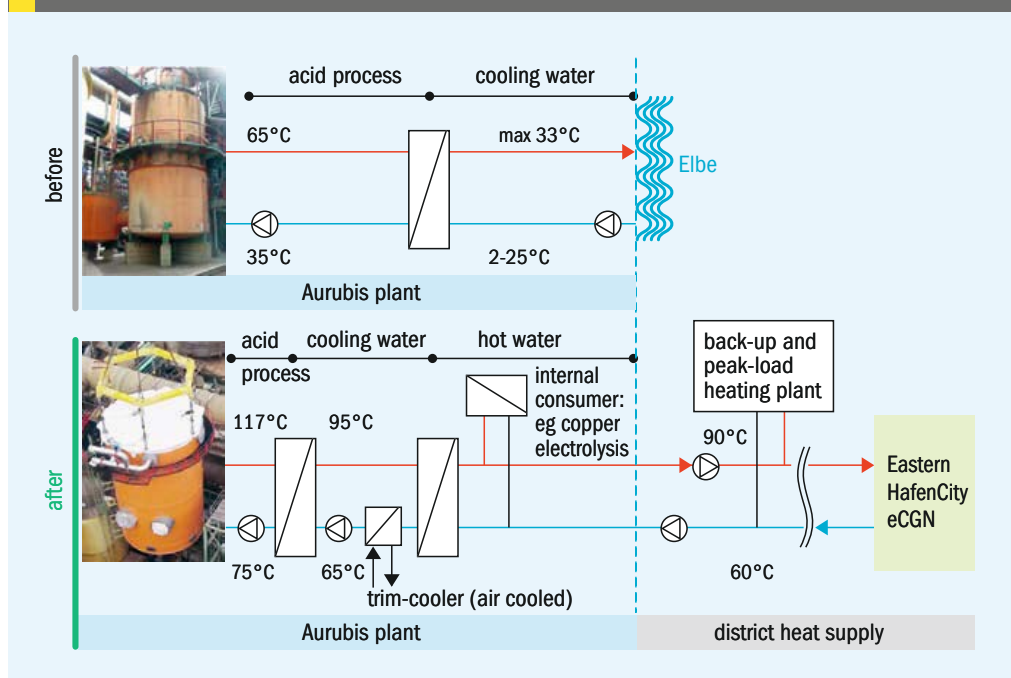


Fig. 4: Change of intermediate absorption tower system



The intermediate absorption tower system of sulphuric acid line one used water from the river Elbe as cooling water for the acid circuit. The heat was removed at a low temperature level, preventing it from being economically feasible to make use of it, as the water outlet temperature is restricted at 33°C. In order to be able to utilise the heat for district heating use, a hot water temperature of 90°C is required. An intermediate cooling water circuit needs to be applied to assure proper separation of the district heating system and the acid system and to suit the cooling needs of the acid plant according to the operation of the smelter. This new "hot" cooling water circuit cooling the acid

requires a temperature of at least 95°C, resulting in an acid temperature of about 120°C. Compared to the "old" system this means a 50°C increase of the acid operation temperature, forcing the project to fund the exchange of the entire intermediate absorption tower system to meet the requirements of the exponentially increased corrosion potential.

Eight state-of-the-art plate heat exchangers manufactured by Alfa Laval, mostly made from special Hastelloy materials, have been installed to handle the difficult operating conditions. The innovative solution is much more complex than a "normal" heat exchanger, but pays off after a short period because it guarantees

a long lifetime and minimal maintenance, which in turn means a significant medium and long term reduction of waste heat recovery costs.

The new system has the additional environmental benefit of no longer emitting any cooling water into the river Elbe. The change of the intermediate absorption tower system is sketched in Fig. 4.

With safety paramount, before deciding to operate at a significantly higher sulphuric acid temperature it was important to prevent any possibility of creating dangerous amounts of hydrogen. The key point is to keep the acid pressure higher than the water pressure. To avoid a driving force in case of a heat exchanger leakage occurring together with a power failure, it was decided to keep the water temperature below the boiling point at ambient condition, restricting the working temperature of the cooling water to below 98°C. In this way no system inherent driving force exists to move the water into the acid side in significant amounts. Taking these preconditions into account, a safe and responsible operation can be assured.

As there are two more sulphuric acid lines which could be upgraded in the same way to provide hot water, the pipe that connects the district heating system to the hot water supply was designed to have a sufficient diameter to accommodate all three lines. A suitable route for the pipe has been found, taking into account the river Elbe crossing and other difficulties. Using this route the connection of the pipe to the main district heat system of Hamburg is only 500 m.

Fig. 5: Complete model of gas side of sulphuric acid line one

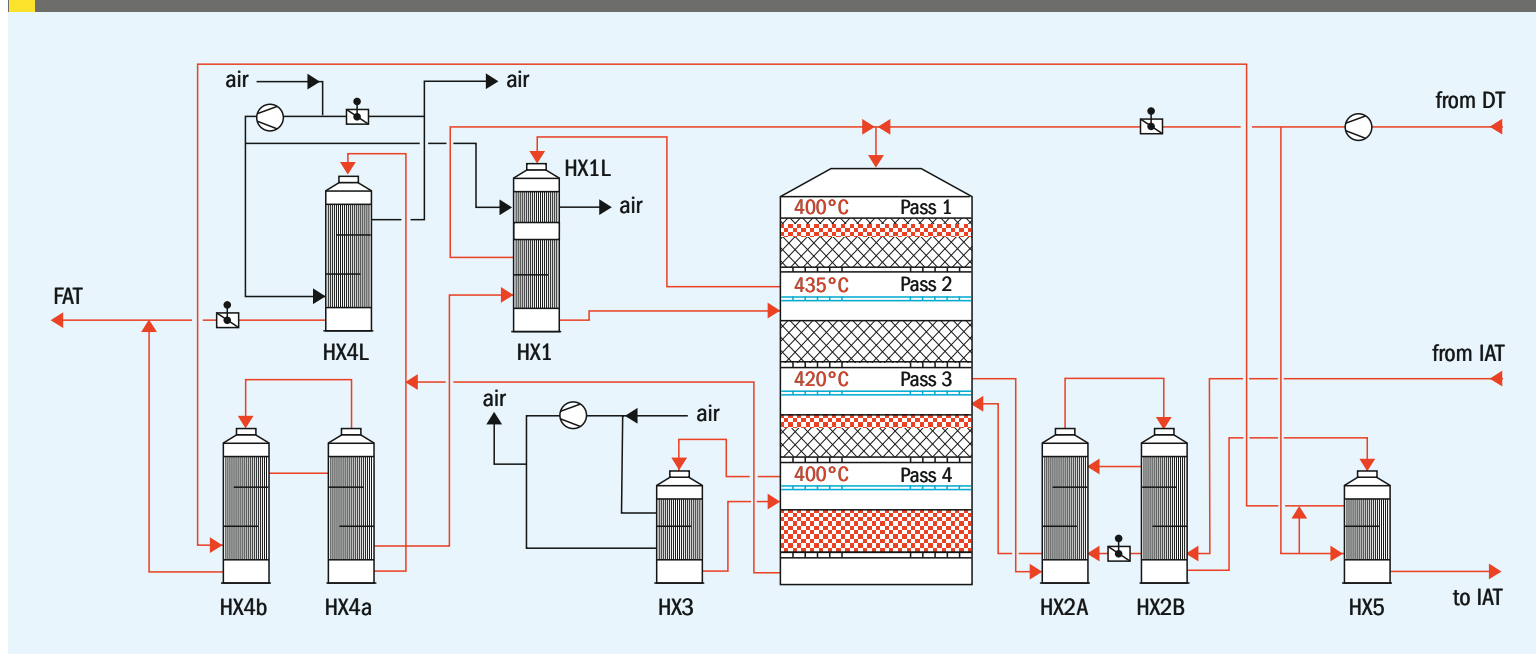




Fig. 6: Tower brick lining work



Fig. 7: Lifting the new tower in to place



Very important for using the energy of a smelter's production is the backup unit operated by the partner enercity to take care for production shortages that can happen at very short notice.

## Engineering

After the decision had been taken to execute the project, the detailed planning phase started. As the engineering partner company BTS was dissolved in 2016, the work has been continued by the company Smart SCOPE, which has become the new home for the core experts of the former BTS sulphuric acid competence centre. To continue the project with the same people that were involved right from the beginning was the best solution, so Smart SCOPE was awarded the engineering contract. Together with plant construction company Franken Apparatebau and Aurubis in-house civil engineering and electrical and controls engineering, the detailed planning started. Being a brownfield project, changing a central part of a running acid plant, required a lot of work by experienced specialists.

The shutdown time to replace the intermediate absorption tower, its pump tank, the acid piping, the heat exchangers and the hot water cooling circuit, as well as other tasks, was scheduled for 15 days only. In order to be able to keep to the timeframe, the new pump tank, the acid pumps, the acid/water heat exchangers (D205 Alfa Laval plate heat exchangers) and the connecting SX-piping were erected at a new location before the

shutdown started. The position of the tower itself could not be moved. Choosing a brick lined tower meant to planning for a very heavy lift of the new brick lined tower by the largest available mobile crane, as the brick lining needed to be applied in advance to save shutdown time.

To investigate the performance of sulphuric acid line 1 after refitting of the intermediate absorption tower system a complete Aspen model of line 1 has been set up (Fig. 5), in addition to the model around the intermediate absorption tower. This detailed and precise method showed the bottlenecks of the plant very well. Because of the improved heat removal a slightly higher SO<sub>2</sub> load can be processed.

## Commissioning

Five months prior to the beginning of the shutdown, the erection of the tower began.

Fig. 6 shows brick lining work by Steuler, starting at the bottom. The different layers are easy to distinguish.

Fig. 7 shows the lift used to fit the new apparatus. Franken and Steuler's proven technique to lift brick lined vessels ensures a safe and fast assembly.

Following the progress of the civil engineering work, the main parts such as the pumps and heat exchangers were placed and the corresponding acid piping was assembled.

Shutdown progressed according to schedule thanks to creative solutions e.g. Steuler removed the foundation of the old

tower and applied the surface protection for the new one in a very flexible way. As there was a FRP gas duct to be removed additionally, another company wanted to use the same space. The site fence has been opened alongside the construction site which needed extra security. There were many other minor and major tasks. Franken did a great job finishing on time. The start-up (as well as the shutdown) was supported by Smart SCOPE until the main systems were running. Smart SCOPE also supported the operators by providing detailed training for all shift personnel.

The district heating system was commissioned in parallel to the acid plant modifications.

The work was completed at the end of October 2018 and was marked by the official opening of the heat transfer by the mayor of Hamburg.

## The result

Thanks to this project, Hamburg's Hafencity East is the first entire district to be almost completely supplied with industrial heat. The Hamburg Aurubis plant has three production lines, each of which could provide 160 million kilowatt hours (kWh) annually. For the time being, one line is sufficient to supply Hafencity East, but there is hope that the other two lines will also be converted in the future. Using all three lines could supply nearly 500 million kWh of heat and cut around 140,000 tonnes of CO<sub>2</sub> each year.

# Co-production of liquid $\text{SO}_2$ and sulphuric acid

**M. Verri** and **A. Baldelli** of Desmet Ballestra S.p.A. describe design options for the co-production of liquid sulphur dioxide and sulphuric acid from elemental sulphur for the non-ferrous mining industry. Two industrial size integrated plants producing liquid sulphur dioxide and sulphuric acid are described. The first has been in operation since 2012 and the second is in the initial stages of erection.

The production of liquid sulphur dioxide from elemental sulphur, by cryogenic condensation from a gaseous stream, can be easily integrated or combined with a sulphuric acid production plant. A portion of the  $\text{SO}_2$ -bearing gas, which is fed to the first stage of the  $\text{SO}_2$ - $\text{SO}_3$  catalytic converter can be diverted to a unit dedicated to the condensation of the  $\text{SO}_2$  at low temperature (Fig. 1.)

After condensation, the off-gas leaving this unit still holds a residual amount of  $\text{SO}_2$ , which needs to be removed before release to the atmosphere.  $\text{SO}_2$  removal is carried out by sending back the off-gas to the first stage of the catalytic converter and therefore producing sulphuric acid.

Having fixed the required liquid  $\text{SO}_2$  production capacity, the amount of sulphuric acid which can be coproduced when designing a new plant varies from a minimum inevitable production, necessary to allow the operation of an acid plant, up to a large capacity modern plant.

The liquid  $\text{SO}_2$  unit is a stand-alone package, which can also be integrated into an existing sulphuric acid production plant with minor modifications subject to a revamping study.

## Cryogenic unit design parameters

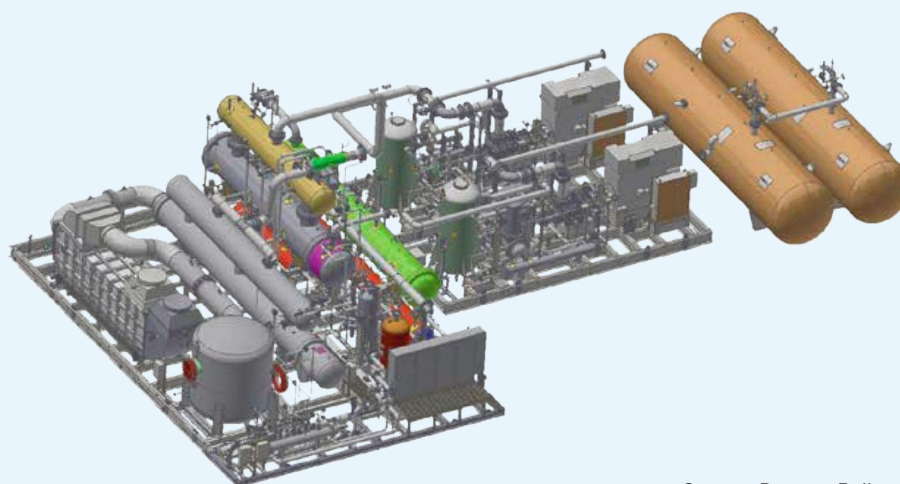
This article focuses on the identification of the most effective design parameters for the  $\text{SO}_2$  cryogenic condensation unit, which can be integrated in a sulphur burning acid plant with capacity requirements typical for the copper/cobalt mining industry.

The cryogenic process is based on the condensation of  $\text{SO}_2$  vapours and is therefore related to the vapour/liquid



*Sulphuric acid plant with integrated liquid  $\text{SO}_2$  production.*

**Fig. 1: 3D view of a 200 t/d liquid  $\text{SO}_2$  production unit**



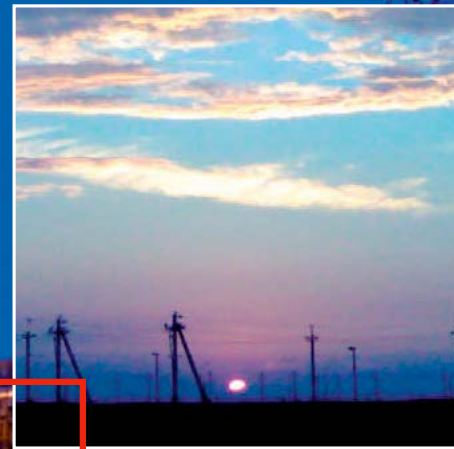
*Source: Desmet Ballestra*



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Table 1: Comparison between two liquid SO<sub>2</sub> packages designed at -65°C and -45°C respectively

Liquid SO <sub>2</sub> package	A	B
<b>Characteristics of machinery</b>		
Condensation temperature	-65°C	-45°C
Condenser pressure	1.2 bar(a)	4 bar(a)
Cryogenic package	Two stages (cascade) system, with separate fluids NH <sub>3</sub> , R23	Two stages (cascade) system, with NH <sub>3</sub> as mono fluid
HP and LP compressors	Screw type, oil injected HP stage compression ratio: 8.2 LP stage compression ratio: 12.2	Screw type, oil injected HP stage compression ratio: 6.2 LP stage compression ratio: 4.5
SO <sub>2</sub> gas booster	Single stage, centrifugal blower  Head: 0.2 bar LV motor	Two stages, integrally geared gas compressor with inter-refrigeration  Head: 3.5 bar HV motor
<b>Major utilities consumption</b>		
Water for cooling	1,710,000 kcal/h	2,940,000 kcal/h
Electric power		
Cryogenic package HP stage	513 kW (LV)	372 kW (LV)
Cryogenic package LP stage	513 kW (LV)	240 kW (LV)
Gas booster	160 kW (LV)	1,950 kW (HV)
Total power	1,186 kW	2,562 kW
<b>Pros and Cons</b>		
Operation	A variable frequency driver is used to manage the gas flow variations, allowing for energy savings	The multistage, engineered gas compressor requires a gas bypass to manage the flow variation which may be required by the process
Maintenance	Two fluids shall be managed as refrigerants	The gas compressor requires more maintenance and specialised technical service
Capital (based on machinery cost, not installed)	Baseline	30% more expensive (due to the complex gas compressor)
<i>The design case "A" provides not only an important capital saving but allows for about 1400 kW lower power consumption, 70% lower cooling duty and provides more operation flexibility and less maintenance.</i>		

equilibrium behaviour of the SO<sub>2</sub>. The SO<sub>2</sub> condenser operating temperature and pressure can have a strong impact on both the capital and operating costs of the unit and needs to be selected via optimisation in the conceptual design phase.

Design basis

The cryogenic unit is fed with a portion of the gaseous stream coming from the sulphur burning section of a sulphuric acid plant. The design is based on a standard sulphur furnace capable of operating with 10-14 vol-% SO<sub>2</sub>.

The higher the SO<sub>2</sub> concentration in the feed gas to the SO<sub>2</sub> unit, the lower the energy consumption and the better the efficiency of the unit. However, integration with a sulphuric acid plant is practically limiting the SO<sub>2</sub> concentration to 14 vol-%

with standard sulphur furnace designs. Concentrations of up to 18% are possible with major upgrades in the furnace design, but with such a high SO<sub>2</sub> concentration NO<sub>x</sub> production could be high due to the higher combustion temperature and post dilution with dry air is necessary to achieve the optimal oxygen level at the converter inlet.

Given a required SO<sub>2</sub> production capacity, the amount of gas fed to the cryogenic unit is related to the SO<sub>2</sub> removal capacity of the cryogenic condenser.

Taking advantage of the integration with an acid plant, the exhaust gas is returned to the first pass of the SO<sub>2</sub>-SO<sub>3</sub> catalytic converter. Since the uncondensed SO<sub>2</sub> is not vented to the atmosphere, a very low SO<sub>2</sub> residual concentration (volume parts per million) in the exhaust gas is not required.

It was found that 3.2-4 vol-% residual SO<sub>2</sub> concentration is an optimum range, allowing for the use of operating conditions that do not require very sophisticated equipment and machinery and provides the most effective operating cost.

Condensation temperature and pressure

The SO<sub>2</sub> condensation temperature is a key parameter which has a strong impact on the design of the cryogenic unit. According to optimisation studies this temperature should be minimised. A temperature of -65°C was selected to condense SO<sub>2</sub> vapours inside the tubes of a heat exchanger, which are submerged in a refrigerant fluid evaporating at constant temperature slightly above the SO<sub>2</sub> freezing point (-75.5 °C).



Condensation at  $-65^{\circ}\text{C}$  requires the use of a two-stage (high and low pressure) cryogenic package, working with two fluids (for low and high temperature stages) having separated circuits. This is a standard package available from different vendors operating in the refrigeration business. The minimised working temperature has a minor impact on capital expenditure and power consumption, as shown in Table 1 which compares two different condensing temperatures.

The condenser can also be operated at  $-65^{\circ}\text{C}$  and 1.0-1.4 bar(a) pressure to achieve 3.2-4% uncondensed  $\text{SO}_2$  in the exhaust gas coming from the condensation unit.

A standard blower is used to circulate the gas through the liquid  $\text{SO}_2$  unit. The blower head is set to the minimum amount required to withstand the gas circuit pressure drops, providing an optimised total electric power consumption of the liquid  $\text{SO}_2$  unit.

### Understanding the optimisation parameters

Fig. 2 shows the behaviour of the  $\text{SO}_2$  vapour-liquid equilibrium, providing the calculated amount of uncondensed  $\text{SO}_2$  in the exhaust gas as a function of the condenser pressure at three different condensation temperatures.

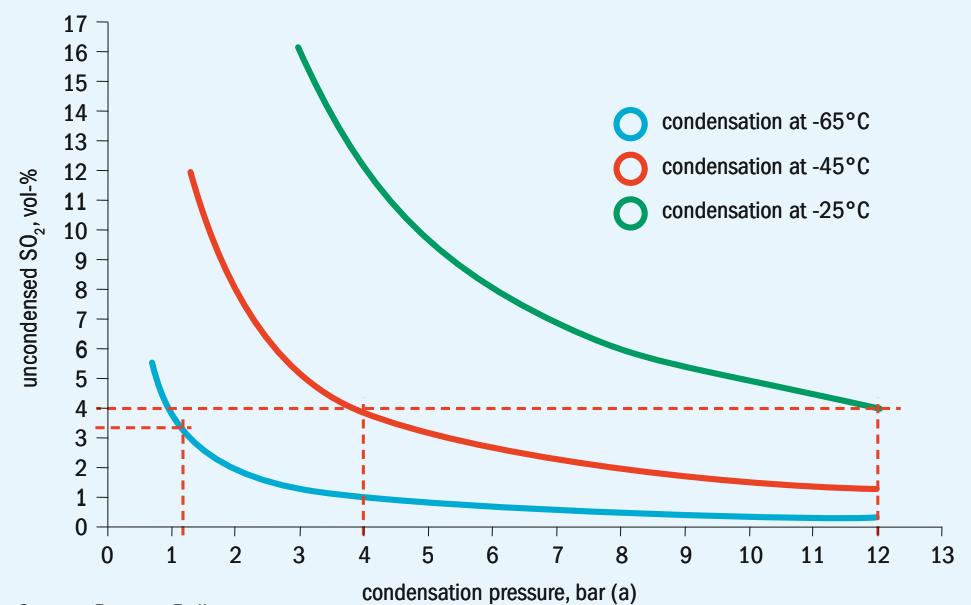
By increasing the condensing temperature from  $-65^{\circ}\text{C}$  to  $-45^{\circ}\text{C}$  the two-stage cryogenic unit can be optimised to have a single type of refrigerating fluid with less power consumption and slightly lower capital expenditure.

The  $\text{SO}_2$  condenser is operated at either  $-45^{\circ}\text{C}/4 \text{ bar(a)}$  or  $-25^{\circ}\text{C}/12 \text{ bar(a)}$  to limit the amount of uncondensed  $\text{SO}_2$  in the return gas to 4 vol-%.

Operation at a higher uncondensed  $\text{SO}_2$  concentration (e.g. 8 vol-%) would require practically double the amount of feed  $\text{SO}_2$  gas to match the targeted production capacity. In this case it is still required to condense  $\text{SO}_2$  at either  $-45^{\circ}\text{C}/2 \text{ bar(a)}$  or  $-25^{\circ}\text{C}/6 \text{ bar(a)}$ .

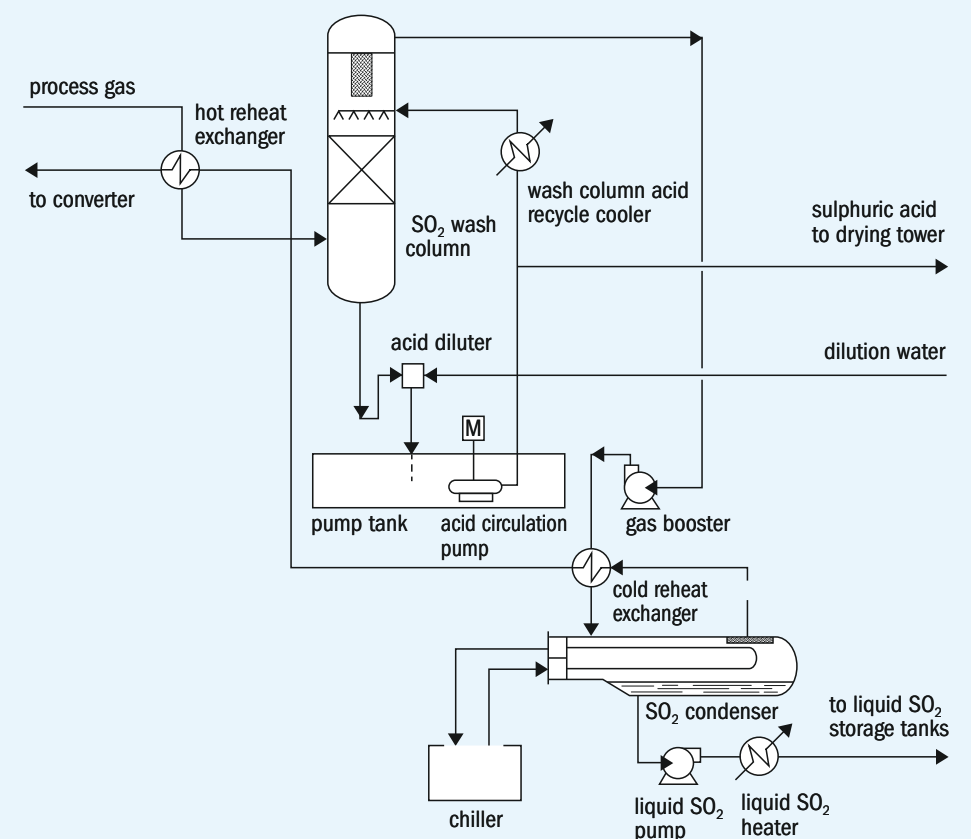
Operation at close to atmospheric pressure is not possible at  $-45^{\circ}\text{C}$  or at  $-25^{\circ}\text{C}$ , with a feed gas concentration of 10-12%  $\text{SO}_2$ . Working at a higher temperature, compared to  $-65^{\circ}\text{C}$ , a compressor is needed to achieve the required gas compression ratios. This machine can be very complicated and the associated costs in terms of capital and power consumption are a dramatic change from a standard single stage centrifugal blower.

Fig. 2: Behaviour of the  $\text{SO}_2$  vapour-liquid equilibrium



Source: Desmet Ballestra

Fig. 3: Process flow diagram of the liquid  $\text{SO}_2$  production unit



Source: Desmet Ballestra

Table 1 provides a comprehensive comparison between two liquid  $\text{SO}_2$  packages designed at  $-65^{\circ}\text{C}$  and  $-45^{\circ}\text{C}$  respectively. The data provided refer to a plant with the following design basis:

- production capacity: 900 t/d as 100% acid plus 100 t/d as liquid  $\text{SO}_2$ ;
- standard sulphur furnace, operating at 10-12%  $\text{SO}_2$  concentration;

- double conversion double absorption (DCDA) plant;
- catalytic  $\text{SO}_2$ - $\text{SO}_3$  converter with standard  $\text{V}_2\text{O}_5$  catalyst and 3+1 configuration
- standard inter pass absorption tower with common pump tank;
- liquid  $\text{SO}_2$  cryogenic unit, capable of running from minimum to maximum capacity without affecting the acid production.

**Fig. 4: Process flow diagram of the sulphuric acid production plant**



## The SO<sub>2</sub> cryogenic unit

A portion of the SO<sub>2</sub> gas leaving the waste heat boiler of the acid plant (see Fig. 4) is diverted to the SO<sub>2</sub> plant. The gas is cooled in the hot reheat exchanger preheating the exhaust SO<sub>2</sub> gas returning to the acid plant.

A controlled quantity of dilution water is added to the column's tank to maintain the acid concentration at 98.5%. The acid

The SO<sub>2</sub> gas leaving the top of the tower is boosted by a blower, cooled in the cold reheat exchanger by the return gas and sent to the SO<sub>2</sub> condenser. Inside this unit part of the SO<sub>2</sub> gas is condensed using a refrigerant. Uncondensed SO<sub>2</sub> is returned to the acid plant with the exhaust gas, after preheating in the cold and hot reheat exchangers.

The condensed SO<sub>2</sub> is transferred to the liquid SO<sub>2</sub> storage tanks.

The liquid SO<sub>2</sub> unit can be considered as a stand-alone package, which can either be integrated into an existing or a new sulphur burning sulphuric acid plant.

The sulphur furnace of the acid plant shall be designed for 12-14 vol-% of SO<sub>2</sub> concentration at the outlet. This is feasible using the standard refractory material widely used for sulphur burning acid plants. The maximum amount of SO<sub>2</sub> which can be condensed from this stream (i.e. the total liquid SO<sub>2</sub> production capacity) is limited by the SO<sub>2</sub>/O<sub>2</sub> ratio required by the SO<sub>2</sub>-SO<sub>3</sub> converter catalyst.

The waste heat recovery which can be achieved by an integrated plant is affected by the amount of  $\text{SO}_2$  removed from the catalytic converter inlet.

An acid plant, designed for medium pressure saturated steam, will produce



less steam when liquid SO<sub>2</sub> is operated.

An acid plant, designed for medium pressure superheated steam, will produce steam at lower superheating temperature when liquid SO<sub>2</sub> is operated. This temperature reduction does not compromise the operation of an electrical power co-generation unit. However, an additional superheater recovering waste heat from the last converter stage could be foreseen to improve the steam superheating temperature, maximising the efficiency of a power co-generation unit if present.

In addition, a larger surface may be necessary for the cold interpass exchanger (CIP) and hot interpass exchanger (HIP). The increase of the heat exchange surface is related to the concentration of the SO<sub>2</sub> at the converter inlet, as well as to the residual sulphuric acid production.

As shown in the process flow diagram (see Fig. 4), the tie-ins between the acid plant and the liquid SO<sub>2</sub> unit are limited to very few lines, which are marked in red.

### Case studies

The first case study refers to a sulphuric acid plant and liquid SO<sub>2</sub> project, based on DuPont-MECS technology, for a metal mining complex started up in 2012.

Table 2 summarises the key plant parameters of this plant:

The plant was commissioned with liquid SO<sub>2</sub> production on-stream in mid 2012.

It is noteworthy that the elevation of the plant site is about 1,500 m above sea level and therefore the ambient pressure is only 0.854 bar(a). Despite the lower ambient pressure, the residual concentration of the SO<sub>2</sub> after the condenser when the plant is operated at full capacity is about 3.3 vol-%.

The sulphuric acid plant and the integrated production of liquid SO<sub>2</sub> have been in operation and successfully operated by the customer since start-up without any downtime related to the failure of key equipment or machines.

The second case study refers to a bigger sulphuric acid plant and liquid SO<sub>2</sub> project that is now in the early stages of erection. Table 3 summarises the key plant parameters of this plant.

Fig. 5 is a view of the plant from above showing the sulphuric acid plant, cooling towers for the acid plant and for the condenser of the turbogenerator, the turbogenerator building, the sulphur melter and storage for sulphur, liquid SO<sub>2</sub> and sulphuric acid.

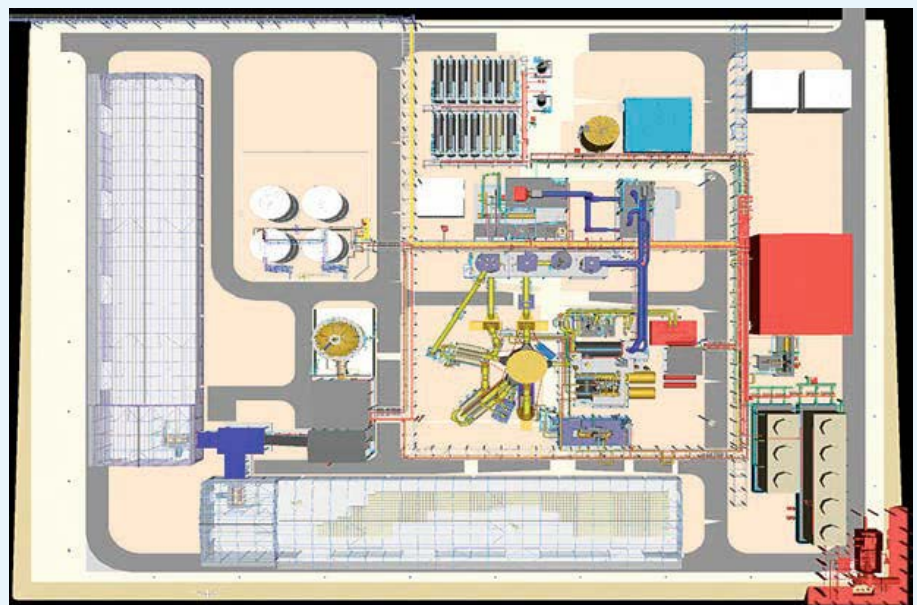
Table 2: Case study 1 key plant parameters

Plant capacity	362 t/d as 100% H <sub>2</sub> SO <sub>4</sub> and 90 t/d as liquid SO <sub>2</sub> Or, 500 t/d as 100% H <sub>2</sub> SO <sub>4</sub>
SO <sub>2</sub> -SO <sub>3</sub> converter catalyst	V <sub>2</sub> O <sub>5</sub> catalyst, 3+1 configuration 99.7% conversion
Waste heat recovery system	Co-produced steam at P = 25 bar(g), T = 250°C superheated • rate: 26.3 t/h when producing liquid SO <sub>2</sub> • rate: 28.4 t/h when producing sulphuric acid only
Liquid SO <sub>2</sub> unit	Cryogenic condensation at -65°C, operating pressure 1-1.2 bar(a)
Liquid SO <sub>2</sub> storage	Tank farm having 1,000 t total capacity

Table 3: Case study 2 key plant parameters

Plant capacity	1,900 t/d as 100% H <sub>2</sub> SO <sub>4</sub> and 200 t/d as liquid SO <sub>2</sub> Or, 2,200 t/d as 100% H <sub>2</sub> SO <sub>4</sub>
SO <sub>2</sub> -SO <sub>3</sub> converter catalyst	V <sub>2</sub> O <sub>5</sub> catalyst, 3+1 configuration SO <sub>2</sub> concentration 12.15vol-% – 99.7% conversion
Waste heat recovery system	Co-produced steam at P = 43 bar(g), superheated T = 405/415°C (with/ without liquid SO <sub>2</sub> )  rate: 115 t/h when producing liquid SO <sub>2</sub> rate: 119 t/h when producing sulphuric acid only
Electric power production	Condensing steam turbine  Power generated when producing liquid SO <sub>2</sub> : 26.5 MW Power generated when producing only acid: 28 MW
Liquid SO <sub>2</sub> unit	Cryogenic condensation at -65°C, operating pressure 1-1.2 bar(a). Two stages chiller designed to use non-hazardous ecological refrigeration fluids in both the stages of cooling.
Liquid SO <sub>2</sub> storage	Tank farm having total capacity 1,900 t of liquid SO <sub>2</sub>

Fig. 5: Sulphuric acid plant integrated liquid SO<sub>2</sub> production  
1,900 t/d H<sub>2</sub>SO<sub>4</sub> + 200 t/d SO<sub>2</sub>



Source: Desmet Ballestra

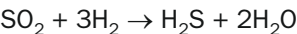
# Operation and performance of the Euroclaus® process

The Euroclaus® process is a well proven modification of the Superclaus® process to achieve higher sulphur recovery efficiencies. **B. Walton** and **G. Molenaar** of Sulphur Experts Inc., **O. Garcia** of Parkland Refining BC Ltd, **A. van Warners** and **T. Roelofs** of Jacobs Nederland B.V. provide a comprehensive overview of the Euroclaus® basics including process layout, catalyst chemistry, actual installations and performance capabilities. In addition, based on 15+ years of Euroclaus® performance testing, gathered plant data from the test work is presented and Euroclaus® performance reviewed. Various case studies are examined and discussed including the Euroclaus® installation at the Parkland Burnaby Refinery.

In the world of sulphur recovery, the Jacobs' Superclaus® process has proven to be a leading technology and continues to be widely applied in the industry to significantly reduce SO<sub>2</sub> emissions beyond that achievable with only conventional Claus technology. Since the commissioning of the first Superclaus® process in 1988, this technology has succeeded in meeting the needs of refiners and gas plant operators delivering high efficiency and operability at a reasonable add-on cost. The Superclaus® technology is able to achieve sulphur recovery efficiencies in the range of 99.0 to 99.4%. However, as more countries increase the required recovery efficiency closer to the 99.3 to 99.5+% range a modification was required that would allow the Superclaus® process the ability to meet these higher efficiencies. This modification was first introduced in 1999 and was called the Euroclaus® process.

The first official Euroclaus® process was built in 1999 at the Fortum Oil and Gas Company Refinery, now Neste, in Porvoo, Finland. This was a 120 t/d 3-stage sulphur recovery unit (SRU) and the sulphur recovery efficiency guarantee provided by Jacobs was 99.2%. This new process would capitalise on the component not con-

verted by the Superclaus® unit, namely sulphur dioxide (SO<sub>2</sub>), and thus increase the overall sulphur recovery efficiency (SRE) by limiting the amount of SO<sub>2</sub> entering the Superclaus® reactor (selective oxidation reactor). This is accomplished by the addition of hydrogenation catalyst in the bottom of the Euroclaus® reactor, which is the reactor preceding the Superclaus® reactor. The hydrogenation catalyst converts the bulk of the remaining SO<sub>2</sub>, after the Claus reaction, into H<sub>2</sub>S via the following pathway:



This reaction is not equilibrium limited and at the operating temperatures of a typical Euroclaus® reactor (180-230°C) could proceed to very low residual SO<sub>2</sub>. A schematic flow diagram of a typical Euroclaus® sulphur recovery facility is presented in Fig. 1.

There are currently 85 Euroclaus® reactors either in operation or planned for the near future in 58 different facilities around the world. This compares to the 238 Superclaus® reactors current and planned, in 143 different facilities. 46 of the Euroclaus® reactors are part of a 3-stage process, that is, one standard Claus reactor followed by a Euroclaus® reactor and then a Superclaus® catalytic stage. The remaining 39 Euroclaus® reactors are

integrated into a 4-stage process wherein there are two standard Claus converters/reactors ahead of the Euroclaus® and Superclaus® reactors. The worldwide distribution of facilities operating a Euroclaus® unit is presented in Fig. 2.

### Sulphur recovery efficiency

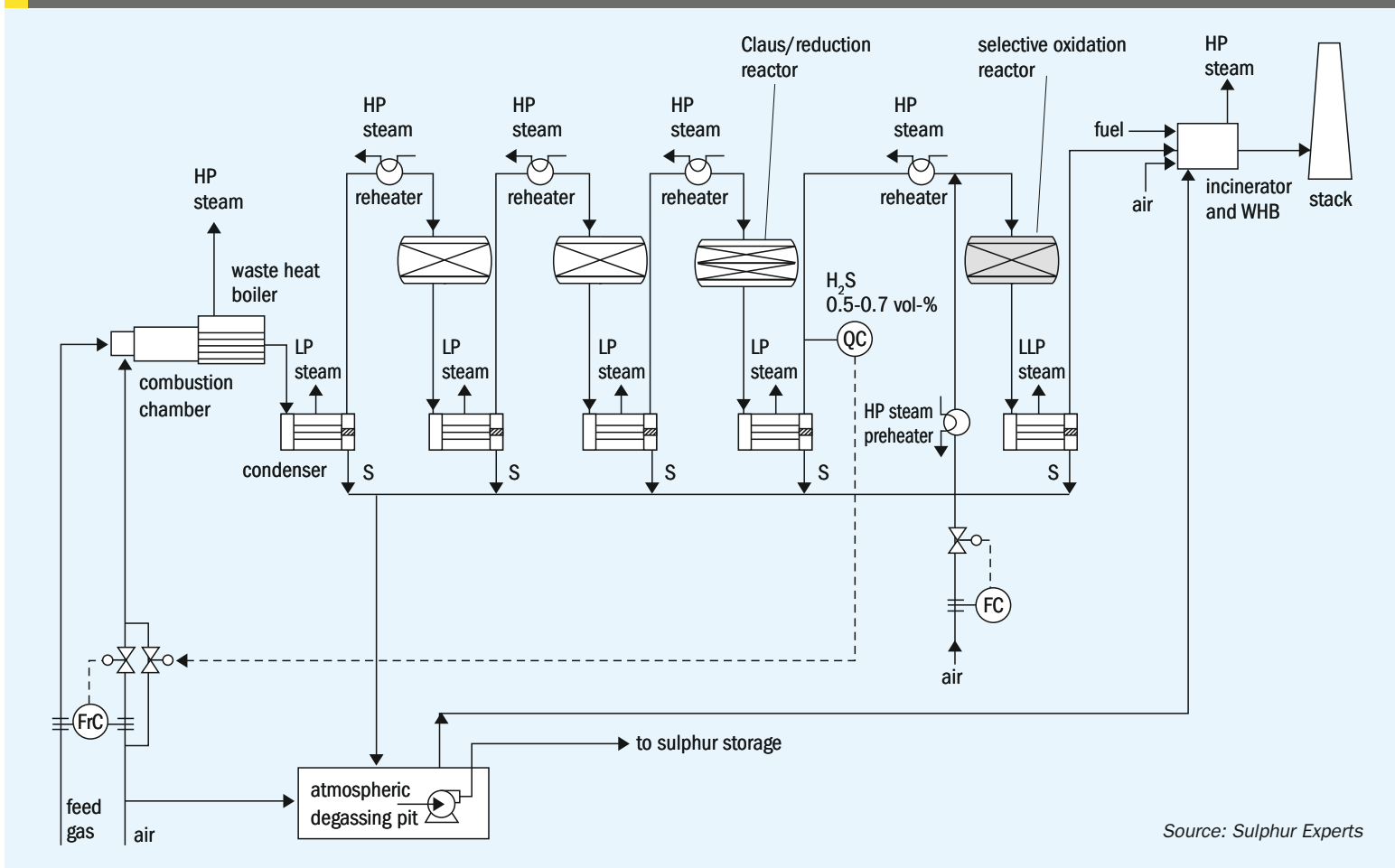
The SRE guarantee values for the Euroclaus® process for both 3- and 4-stage units are presented in Table 1. The guarantee value is the legally binding minimum SRE which the process licensor assures the customer that the process technology will achieve upon completion and handover of the unit(s).

While other industries use this SRU technology, only the oil and gas industry was considered relevant for the scope of this paper. Therefore, when controlling for the type of industry (oil and gas only), the averages look slightly different, as shown in the middle row of the Table 1.

As stated earlier, the guaranteed SRE is the minimum SRE given by the process licensor. However, in practice the actual (measured) SRE may be different. Sulphur Experts' test data were used to compare the guaranteed SRE against the measured SRE. The comparison is presented in Table 2.



Fig. 1: Typical 4-stage Euroclaus® process flow diagram



Source: Sulphur Experts

Test data indicate that the average SRE expected for a 3-stage Euroclaus® unit is 99.29%, compared to an average guarantee of 99.17%. The average tested SRE for the 4-stage Euroclaus® unit was 99.50% against an average guarantee value of 99.26%. This indicates that on average it can be expected that the measured SRE is 0.1 to 0.2% higher than the guarantee values. It should be noted that the majority of the test data reflect catalyst that is < 1 year old. The same data indicate that performance could exceed 99.50%.

Process description

Euroclaus® reactor catalyst

A typical Euroclaus® reactor will be loaded with a minimum of three types of catalyst: alumina, cobalt-molybdenum (CoMo)-type hydrogenation catalyst, and titania catalyst. A simplified catalyst loading diagram is presented in Fig. 3. Other catalyst, such as an oxygen scavenging catalyst as the top layer, may also be installed in a Euroclaus® reactor, depending on the specific SRU configuration. Catalyst volumes will vary with the type of catalyst but there will be approximately 47-75 vol-% alumina catalyst, 10-20 vol% CoMo catalyst and

Fig. 2: World distribution of facilities with Euroclaus® units



Source: Sulphur Experts

Table 1: Average Euroclaus® SRE guarantee values

Guarantee	3 stages	4 stages
Average SRE guarantee*, %	99.16	99.15
Average SRE guarantee**, %	99.17	99.26
Highest SRE guarantee, %	99.30	99.50

\* All Euroclaus® units (oil and gas, petrochemical, fertilizer, steel, coal gasification)  
\*\* Only Euroclaus® units in the oil and gas industry  
Source: Sulphur Experts

Table 2: Measured average Euroclaus® SRE by performance test

	3 stages	4 stages
Average SRE*, %	99.29	99.50
Highest SRE*, %	99.56	99.76

\* Final condenser temperature ≤130°C

Source: Sulphur Experts

approximately 10-20 vol-% titania in a Euroclaus® reactor.

The small amount of installed CoMo catalyst in a Euroclaus® reactor, relative to the process gas volumetric flow, results in a higher gross hourly space velocity (GHSV) than the maximum normally recommended for Claus catalyst (1,000 hr<sup>-1</sup>). From Sulphur Experts test data the calculated

GHSV in a Euroclaus® reactor across only the CoMo catalyst has ranged from 3,000 to 10,000 hr<sup>-1</sup>. Translating this GHSV to the entire catalyst bed in the Euroclaus® reactor, this would equate to a GHSV of 300 to 1,000 hr<sup>-1</sup>. When designing a Euroclaus® reactor it is important to give proper consideration to the GHSV. Each facility may require a tailored approach for

both the CoMo and titania catalyst layers. The GHSV influences the reaction kinetics and is, as a result, essential in ensuring a high sulphur recovery efficiency.

Laboratory data comparing the role of GHSV on different layers of catalyst is presented in Table 3. The impact of GHSV on residual COS concentration is relatively weak. At lower GHSV, more COS will be formed in the hydrogenation layer. However, also more COS conversion will take place in the downstream titania layer, largely cancelling the effect of GHSV on residual COS.

The largest impact at lower GHSV will be the hydrogenation of sulphur vapour (Svp) to H<sub>2</sub>S across the CoMo catalyst as is evident in Table 3. This increases the load to the downstream Superclaus®

Fig. 3: Typical Euroclaus® catalyst loading diagram

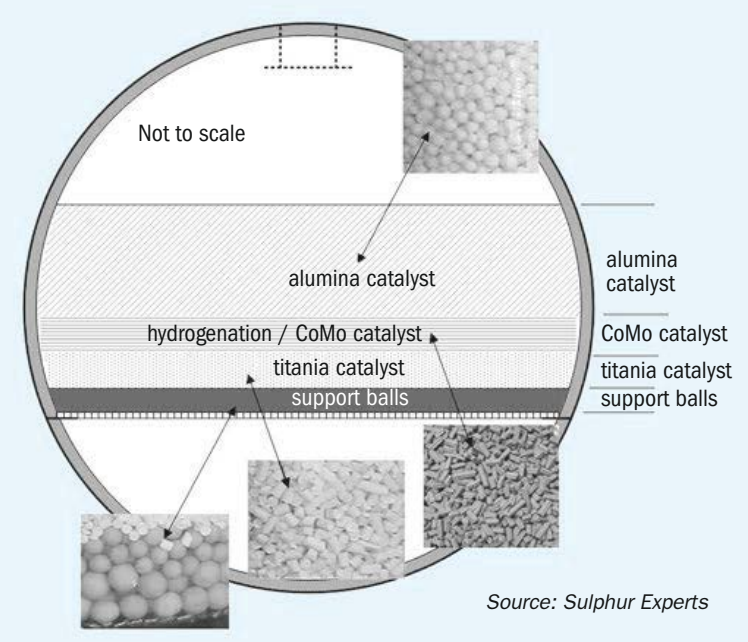


Fig. 4: SO<sub>2</sub> conversion across the Euroclaus® reactor

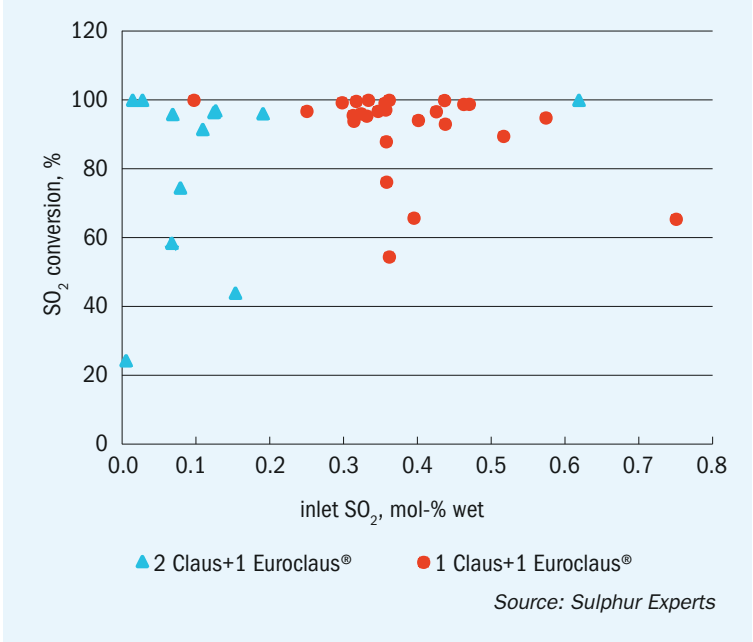


Table 3: Effect of space velocity on Euroclaus® catalyst performance

Component	Reactor in	Reactor out		
		80% alumina 20% glass pearls	20% O <sub>2</sub> scavenger 60% alumina 10% CoMo 10% glass pearls	20% O <sub>2</sub> scavenger 60% alumina 10% CoMo 10% titania
Space velocity 435 Nm <sup>3</sup> /m <sup>3</sup>				
H <sub>2</sub> S, ppmv	15,000	5,544	8,256	11,255
SO <sub>2</sub> , ppmv	6,000	1,053	273	55
COS, ppmv	0	7	1,308	44
Svp, ppmv S <sub>1</sub>	0	14,459	11,226	9,709
Space velocity 1,000 Nm <sup>3</sup> /m <sup>3</sup>				
H <sub>2</sub> S, ppmv	15,000	5,397	6,298	7,016
SO <sub>2</sub> , ppmv	6,000	1,036	607	312
COS, ppmv	0	15	594	135
Svp, ppmv S <sub>1</sub>	0	14,615	14,164	13,630

Source: Sulphur Experts





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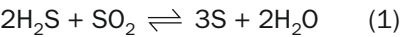
reactor and is an unwanted reaction because the conversion of H<sub>2</sub>S to sulphur in the Superclaus® reactor is only 85 to 90% efficient. A higher space velocity will limit the amount of Svp that converts to H<sub>2</sub>S.

However, at turndown conditions (low GHSV) in an actual SRU the tail gas analyser would control any increase in H<sub>2</sub>S from the Euroclaus® outlet by adding more air to the main burner to maintain the same H<sub>2</sub>S setpoint. This would result in a higher SO<sub>2</sub> concentration to the inlet of the Euroclaus® reactor. Laboratory tests indicate that at lower H<sub>2</sub>S/SO<sub>2</sub> ratios at the inlet of the Euroclaus® reactor, the hydrogenation of SO<sub>2</sub> and sulphur vapour slows down. In addition, more residence time would help convert the extra SO<sub>2</sub>.

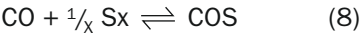
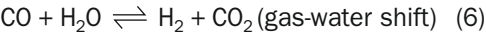
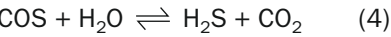
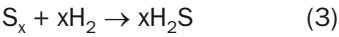
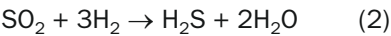
Therefore overall, the effect of GHSV on SO<sub>2</sub> is limited for fully active catalyst. The net result for the SRU will depend on the effect of the increased H<sub>2</sub>S load (if any) to the downstream reactor versus the lower SO<sub>2</sub> out of the Euroclaus® reactor.

Euroclaus® reactions

There are multiple reactions that occur across a Euroclaus® reactor. These reactions have been broken out in accordance with the layer of catalyst that will promote them. The Claus reaction is promoted mainly by the alumina catalyst (Al<sub>2</sub>O<sub>3</sub>) but also takes place over the other layers of catalyst:



The next layer of hydrogenation/cobalt molybdenum (CoMo) catalyst will promote these reactions:



Finally, there are the reactions taking place over the titania (TiO<sub>2</sub>) catalyst:

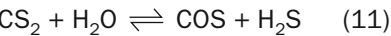
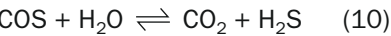


Table 1: Table 4: Process equilibrium constants for CoMo catalyst

Temperature	SO <sub>2</sub> hydrogenation (reaction 2)	Svp hydrogenation (reaction 3)
200°C	3.0 E19	4.4 E4
Source: Sulphur Experts		

The most important reactions are 2, 3, 8 and 9 in the hydrogenation layer and 10 and 12 in the titania layer.

The CoMo and titania catalyst are also Claus active, which help decrease any residual SO<sub>2</sub> and H<sub>2</sub>S. In The titania layer an increase of H<sub>2</sub>S is seen due to hydrolysis of COS (reaction 10) and SO<sub>2</sub> is reduced more than could be explained by the forward Claus reaction; it could be that reaction 12 is responsible for this effect.

Hydrogenation of sulphur species

The hydrogenation of SO<sub>2</sub> is strongly favoured across CoMo catalyst and typically an equilibrium amount of residual SO<sub>2</sub> would be predicted if the GHSV were sufficiently low. However, as identified in the earlier section on the Euroclaus® reactor catalyst, in a Euroclaus® reactor the amount of catalyst is relatively small and thus the SO<sub>2</sub> hydrogenation reaction will not proceed to equilibrium. In support of this, an analysis of the test data indicates that overall conversion efficiencies of approximately 90% or greater of the inlet SO<sub>2</sub> can be achieved across a Euroclaus® reactor in the majority of cases. This is the total of the SO<sub>2</sub> consumed in the Claus reaction plus that converted in the hydrogenation reaction. Test data is presented in Fig. 4 showing the SO<sub>2</sub> conversion over the entire Euroclaus® reactor as a function of inlet SO<sub>2</sub> concentration.

Sulphur vapour (Svp) hydrogenation is also strongly favoured across CoMo catalyst, however the complete hydrogenation of Svp is an unwanted reaction. H<sub>2</sub>S formation via sulphur vapour hydrogenation represents a potential efficiency loss as opposed to Svp that can be condensed and removed from the system.

Table 4 presents the process equilibrium constants (Kp) for reaction 2 as well as the Kp for reaction 3. As can be seen from Table 4, the forward reaction rates for both are highly favoured. For the Euroclaus® design, the catalyst activity and quantity, and thus the GHSV, must be considered in order to promote SO<sub>2</sub>

hydrogenation while still suppressing Svp hydrogenation.

COS formation

COS formation is an unwanted side reaction across Euroclaus® catalyst. The pathway of COS formation is outlined in reactions 7 and 8, and is mainly dependent on the inlet CO concentration as well as the reactor temperature. An analysis of the reaction kinetics would indicate that COS formation via reaction 8 is most likely responsible for the COS formation measured across the reactor. However, at bottom-bed temperatures between 180°C and 190°C the formation reactions (either reaction 7 or 8) are no longer contributing significantly to any COS formation. This can be observed in Fig. 5, whereby the COS increase is essentially non-existent at temperatures around 180-190°C and then starts to increase around 195°C.

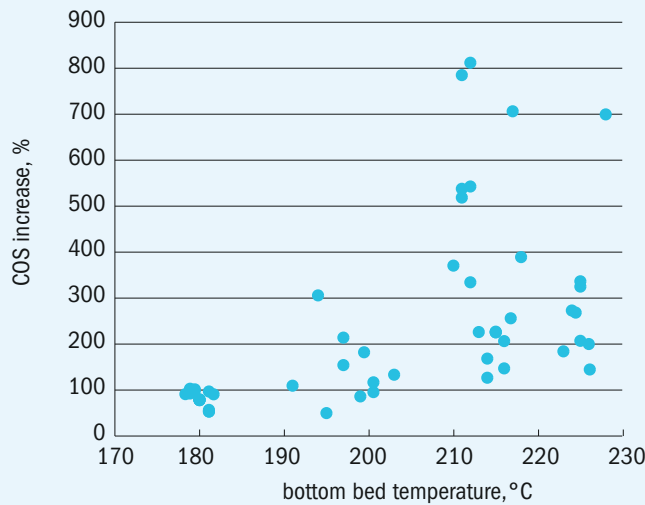
Sulphur Experts tests data has shown that COS can increase anywhere from 8% to 800% of the inlet COS amount. In general, the relative COS increase measured across the Euroclaus® reactor was higher at lower inlet COS concentrations. This has been presented in Fig. 6. For example, at the highest measured COS increase (818%), the COS inlet concentration was only 4 ppmv. Eliminating inlet COS values that were <20ppmv, and accounting for outliers, it is estimated that a COS increase of 5% occurs for every degree Celsius above 195°C. Lower operating temperatures resulted in less COS formation regardless of inlet CO concentration. If operating at a bottom-bed temperature of less than 190°C, then no COS formation may be possible. However, consideration should be given to ensure that the reactor is still operating above the sulphur dew point and that the SO<sub>2</sub> hydrogenation reaction is not inhibited at that temperature.

COS hydrolysis

Titania catalyst is included as the bottom layer of a Euroclaus® reactor to promote the conversion of the remaining COS into



Fig. 5: COS increase as a function of Euroclaus® bottom-bed temperature



Source: Sulphur Experts

Fig. 6: COS increase as a function of Euroclaus® inlet COS

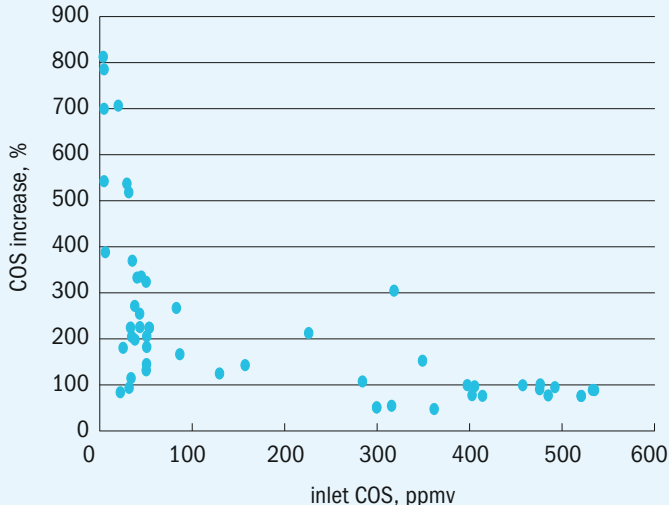
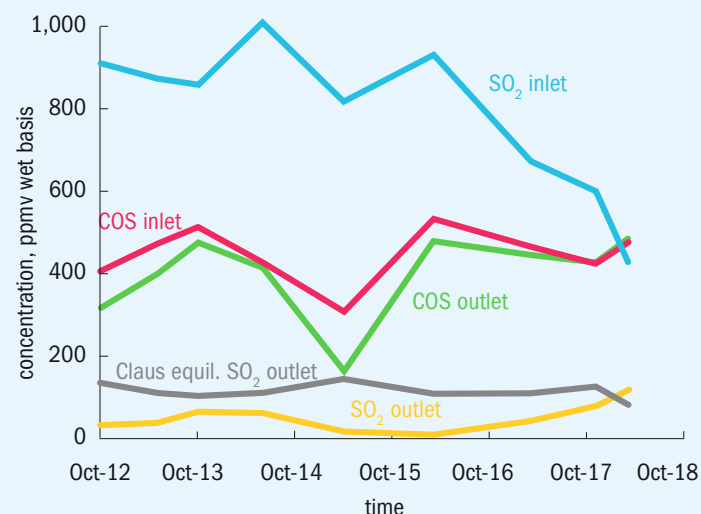
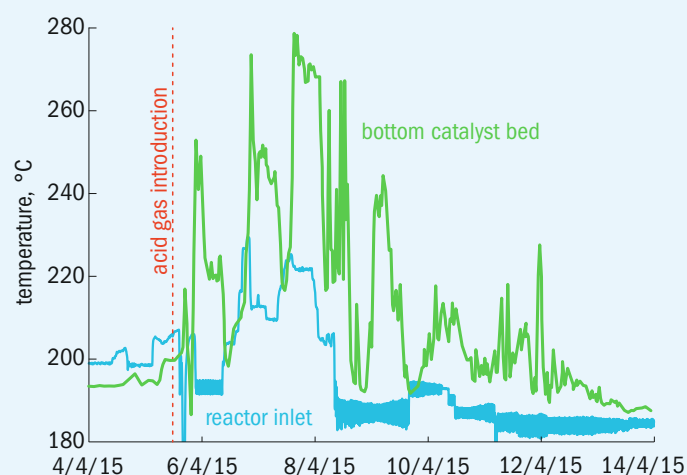


Fig. 7: Burnaby refinery Euroclaus® performance 2012-18



Source: Sulphur Experts

Fig. 8: Euroclaus® reactor inlet and catalyst bottom-bed temperature during SRU start-up



Source: Sulphur Experts

reactor in an SRU. The data presented in Fig. 7 for the seven years of operation all fall within this catalyst bed temperature range (176 to 182°C).

The main parameter for assessing the Euroclaus® catalyst (CoMo + titania) performance is the residual SO<sub>2</sub> measured at the outlet of the reactor. This residual SO<sub>2</sub> is compared to the theoretical SO<sub>2</sub> expected based solely on Claus equilibrium. Since 2012 the inlet SO<sub>2</sub> concentration to the Euroclaus® reactor was measured in the range of 450 to 1000 ppmv(wet). For that same time period, the SO<sub>2</sub> measured in the outlet averaged 78 ppmv while the concentration of SO<sub>2</sub> predicted to be in the outlet gas, based on Claus equilibrium conversion only, averaged 185 ppmv. Therefore, the estimated Euroclaus® SO<sub>2</sub> conversion (expected Claus equilibrium SO<sub>2</sub> minus measured value) averaged approximately 57% over the seven-year period. In comparison, a test of the new Euroclaus® catalyst installed in April 2015 shows that the Euroclaus® SO<sub>2</sub> conversion was 82% and 93% for test 1 and test 2, respectively. Over the entire bed (SO<sub>2</sub> in minus SO<sub>2</sub> out) the SO<sub>2</sub> conversion ranged between 96 and 99%.

With SO<sub>2</sub> falling to 50 ppmv or less in the outlet of the Euroclaus® reactor, the increase in sulphur recovery efficiency over the standard Superclaus® is estimated to be 0.03 to 0.06% which equates to a reduction in SO<sub>2</sub> emissions from the stack of approximately 6% for the Parkland Burnaby Refinery.

Apart from the hydrogenation reactions of the Euroclaus® CoMo catalyst there are

other side reactions occurring that reduce the catalyst efficiency, which become more pronounced as the catalyst ages or deactivates. One of these side reactions involves the production of COS across the CoMo catalyst, which is why titania is included as the bottom layer in this reactor.

The results for COS in and out as presented in Fig. 7 from 2012 to 2018 show that for the Burnaby Euroclaus® the amount of COS in the outlet is almost identical to the COS in the inlet of the reactor. The relatively low operating temperature of the Burnaby Euroclaus® catalyst bed is therefore most likely limiting COS formation. A more detailed discussion on operating temperature and COS formation is provided in the earlier section on COS formation.

Over the seven-year testing period, there is on average a slight reduction (12%) in COS across the Euroclaus® reactor. For example, during the May 2015 tests, with effectively brand-new activated catalyst, there was an overall decrease in COS concentration across the Euroclaus® reactor, at an operating temperature of 181°C, from 317 ppmv to 174 ppmv, which equates to a reduction in COS of 45%. In contrast, Fig. 7 shows that, with very similar reactor operating temperatures, the COS removal decreased to virtually zero from 2017 onward. This indicates an overall decline in either or both the titania and the CoMo catalyst activities and suggests that catalyst rejuvenation or replacement is required.

#### Euroclaus® start-up and catalyst activation

During the last turnaround in early 2015 all SRU catalyst was changed out.

The loading of the catalyst was supervised, and catalyst quantities verified as well as outages measured to ensure that each of the three catalyst layers were properly installed in the Euroclaus® reactor. Both the Euroclaus®/CoMo catalyst and the Superclaus® catalyst subsequently required activation.

During warm-up of the SRU and the introduction of acid gas to the main burner, the Superclaus® reactor was bypassed, which is common industry practice for this technology. As a result, the tail gas from the Euroclaus® reactor was routed directly to the thermal oxidiser and stack. During warm-up the Euroclaus® reactor temperature was maintained at approximately 195°C. As a precaution it is usually recommended that the CoMo catalyst temperature does not exceed 200°C while no H<sub>2</sub>S is present. During the SRU warm-up on natural gas, H<sub>2</sub> is present and this might impair catalyst activity at temperatures above 200°C. At these conditions CoO and MoO<sub>3</sub> may be reduced to their metal state (Co and Mo). A more thorough discussion on the CoMo catalyst can be found later in the article.

In Fig. 8 the inlet temperature and the catalyst bottom-bed temperature of the Euroclaus® reactor is presented for eight days of operation following the acid gas intake. It should be noted that only one of the multiple available thermocouple values was used in Fig. 8. The bottom thermocouple is placed exactly in the CoMo catalyst layer and therefore will directly represent exothermic reactions that might take place.



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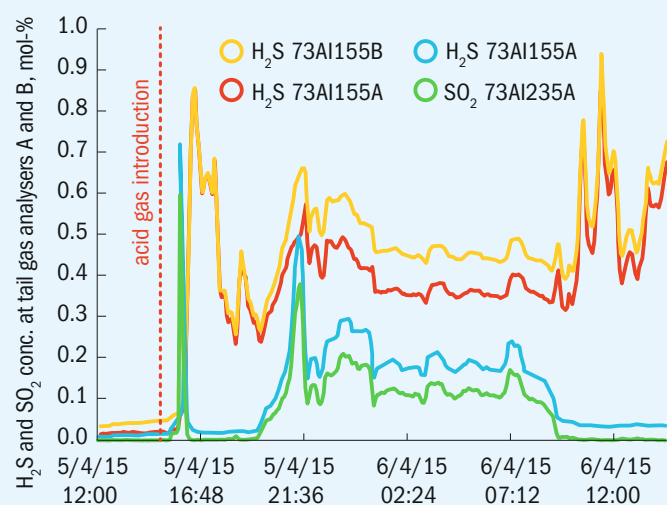
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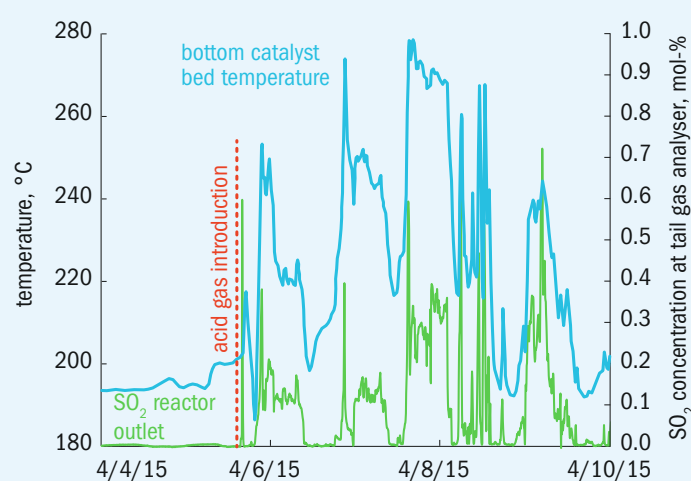
### SULPHUR

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Fig. 9: H<sub>2</sub>S and SO<sub>2</sub> in the outlet of the Euroclaus® reactor during first 24 hours of start-up

Source: Sulphur Experts

Fig. 10: SO<sub>2</sub> in the outlet of the Euroclaus® reactor and bottom catalyst bed temperature

Source: Sulphur Experts

Throughout the initial start-up and exposure of the CoMo catalyst to H<sub>2</sub>S, SO<sub>2</sub>, H<sub>2</sub>, and CO there is a proportionate increase in bottom-bed temperature, with a maximum temperature of 253°C seven hours after acid gas intake. Fig. 8 shows a steady inlet temperature of approximately 192°C shortly after acid gas introduction into the SRU. This temperature is held for approximately 12 hours while the bottom catalyst bed temperature stabilised at approximately 220°C. The inlet temperature was then increased to start the sulphiding of the CoMo catalyst. The objective was to maintain a bottom-bed temperature of 240°C for 12 to 16 hours. In reality, bottom-bed temperatures in the range of 270°C to 280°C were observed. Although this temperature does not present any risk of damaging the catalyst or the vessel, the increase in temperature negatively affects the Claus equilibrium, and with the downstream Superclaus® reactor in bypass, the increase in SO<sub>2</sub> emissions from the stack was significant. Thus, to remain within the allowable SO<sub>2</sub> emission limit, the inlet temperature to the Euroclaus® reactor was reduced several times to control the bed temperature.

After approximately 36 hours with the bottom-bed catalyst in excess of 240°C the inlet temperature was reduced to normal, 187°C. From Fig. 8 it is evident that even at the lower inlet temperature it took four to five days before the bottom-bed temperature was normal and showing just a differential temperature of several degrees Celsius over the catalyst bed.

Fig. 9 shows the H<sub>2</sub>S and SO<sub>2</sub> values in the outlet of the Euroclaus® reactor for the first 24 hours after acid gas introduction. The Burnaby SRU has two parallel tail gas analysers installed and the readings of both are presented in Fig. 9. The first observation is that as soon as acid gas is introduced into the SRU, both H<sub>2</sub>S and SO<sub>2</sub> are present almost immediately in the Euroclaus® reactor outlet. In Fig. 9 an SO<sub>2</sub> peak up to 0.6 to 0.7 mol-% is visible on both tail gas analysers right after acid gas introduction. H<sub>2</sub>S is also detected on both analysers and increases from 0.1–0.2 mol-% to 0.85 mol-% in the first 30 minutes while SO<sub>2</sub> decreases to close to zero over the first 20 minutes of acid gas operation.

Of significance in Fig. 9, in combination with Fig. 8, is that the evidence suggests that almost immediately upon H<sub>2</sub>S and SO<sub>2</sub> entering the reactor the catalyst is already active for the SO<sub>2</sub> hydrogenation reaction. Both the catalyst sulphiding reaction and the SO<sub>2</sub> hydrogenation reaction are exothermic with the latter one creating a significant amount of heat. Also, some of the sulphur vapour will react with H<sub>2</sub> to H<sub>2</sub>S over the activated CoMo catalyst.

After approximately four to five hours of acid gas operation, both H<sub>2</sub>S and SO<sub>2</sub> are present in close to a 2:1 ratio.

As can be seen in Fig. 9, both H<sub>2</sub>S and SO<sub>2</sub> values are stable for about eight hours. At that time the air to the unit was slightly reduced to increase the H<sub>2</sub>S in the tail gas to 0.5 to 1.0 mol-% as per the CoMo catalyst sulphiding procedures. Simultaneously, the inlet temperature to

the Euroclaus® reactor was raised as illustrated in Fig. 8.

Fig. 10 shows the bottom-bed temperature and the SO<sub>2</sub> measured in the outlet of the Euroclaus® reactor.

It is evident from Fig. 10 that for the first four days of operating the Euroclaus® reactor there is a strong correlation between the amount of SO<sub>2</sub> in the reactor outlet and the bottom-bed temperature. This correlation continued until the bed temperatures were reduced and were at normal operating temperature after eight days of operation, as can be seen in Fig. 8. These observations are enough to say that the hydrogenation reaction of SO<sub>2</sub> catalysed by the sulphided CoMo catalyst occurs almost immediately after acid gas intake.

This possible explanation is in good agreement with the fact that on several occasions during these first days of start-up it was observed that while increasing the air to the main burner, the H<sub>2</sub>S at the analyser remained the same, or in some cases increased, at the same time as the SO<sub>2</sub> increased. An example of H<sub>2</sub>S and SO<sub>2</sub> increasing simultaneously is provided in Fig. 9 on April 5 at approximately 21:30.

During these events a rapid increase in bottom-bed temperature was observed as illustrated in Figs 8 and 10. An explanation for these observations could be that with an increase in air to the burner more SO<sub>2</sub> is produced. SO<sub>2</sub> is then hydrogenated across the CoMo catalyst, which is a highly exothermic reaction creating the increased temperature rise. The H<sub>2</sub>S signal does not change, or increases, because the SO<sub>2</sub> is being converted to H<sub>2</sub>S.



Table 5: Euroclaus® case study 2 reactor inlet and outlet data

	Euroclaus® inlet	Euroclaus® outlet (theoretical)	Euroclaus® outlet
H <sub>2</sub> , mol-%	4.0684	4.0809	3.9555
Ar, mol-%	0.6522	0.6547	0.6537
N <sub>2</sub> , mol-%	56.8603	57.0309	57.0979
CO, mol-%	1.4231	1.4274	1.3975
CO <sub>2</sub> , mol-%	4.0014	4.0160	4.0361
H <sub>2</sub> S, mol-%	1.6413	1.0531	1.0680
COS, mol-%	0.0130	0.0097	0.0163
SO <sub>2</sub> , mol-%	0.3342	0.0368	0.0014
CS <sub>2</sub> , mol-%	0.0014	0.0014	0.0000
H <sub>2</sub> O, mol-%	31.0047	31.6897	31.7736
Temperature, °C	194	204	214

Source: Sulphur Experts

As a result, the key to maintain a desired bottom-bed temperature and to avoid high temperature spikes during Euroclaus® start-up is to ensure low levels of SO<sub>2</sub> in the tail gas, in the order of less than 1,000 ppmv (0.1 mol-%).

### Case study 2 (example of fully active Euroclaus®)

This refinery in Northern Europe contains four identical three-stage SRUs, each with one Claus, one Euroclaus® and a Superclaus® reactor. All reheaters are natural gas-fired in-line burners, and a thermal oxidiser is dedicated to each SRU. Sulphur Experts performed a test of this facility in 2012; the results for one of the SRUs is discussed here. This particular SRU processes a lean (low H<sub>2</sub>S content) acid gas feed and the Euroclaus® catalyst is less than one year old. The data from the test are presented in Table 5 together with the theoretical conditions for the outlet stream of a Claus-only reactor. The theoretical outlet is the gas stream predicted leaving a SRU reactor only considering the Claus reaction.

As can be seen from Table 5, the amount of residual SO<sub>2</sub> leaving the Euroclaus® reactor was 14 ppmv.

Based on Claus equilibrium predictions alone, the amount of SO<sub>2</sub> should have been 368 ppmv. This implies that the Euroclaus® CoMo SO<sub>2</sub> conversion was >96% and the overall SO<sub>2</sub> conversion is >99%. This would indicate fully active catalyst. There is some COS creation across the reactor, which should be expected given the bottom-bed temperature of 214°C. However, the COS formation is considered minimal and the

impact on the overall SRE was minor. The impact of the Euroclaus® catalyst on the overall SRE can be estimated by comparing the theoretical reactor outlet (Claus only) against the measured reactor outlet composition. In this case the presence of the Euroclaus® catalyst improved the overall SRE by 0.06%.

### Case study 3 (example of deactivated Euroclaus®)

A 4-stage Euroclaus® unit was tested by Sulphur Experts at a Northern European refinery. This SRU processes lean acid gas feed (52% H<sub>2</sub>S), co-fires with natural gas and the catalyst is approximately four years old. The test data are presented in Table 6.

Table 6: Euroclaus® case study 3 reactor inlet and outlet data

	Euroclaus® inlet	Euroclaus® outlet (theoretical)	Euroclaus® outlet
H <sub>2</sub> , mol-%	2.2635	2.2646	2.1259
Ar, mol-%	0.5929	0.5932	0.5948
N <sub>2</sub> , mol-%	50.9225	50.9461	51.0776
CO, mol-%	2.4290	2.4301	2.4205
CO <sub>2</sub> , mol-%	11.0653	11.0749	11.0217
H <sub>2</sub> S, mol-%	0.3747	0.2866	0.2138
COS, mol-%	0.0226	0.0183	0.0483
SO <sub>2</sub> , mol-%	0.1538	0.1074	0.0863
CS <sub>2</sub> , mol-%	0.0018	0.0017	0.0021
H <sub>2</sub> O, mol-%	32.1738	32.2770	32.4091
Temperature, °C	197	198	197

Source: Sulphur Experts

In case study 3 the amount of residual SO<sub>2</sub> leaving the Euroclaus® reactor was 863 ppmv, which represents an overall SO<sub>2</sub> conversion of only 44%. The Euroclaus® CoMo SO<sub>2</sub> conversion was <20%. The COS formation is relatively high at 212%, considering the temperature of 197°C.

Lowering the operating temperature of this reactor, if possible, should decrease any COS that is being formed across the CoMo catalyst. In addition, a higher H<sub>2</sub>S setpoint would help decrease any losses from unreacted SO<sub>2</sub>. Catalyst reactivation could also be considered.

### Optimised Euroclaus® catalyst activation and re-activation

The active sites of the CoMo layer in a Euroclaus® reactor are made up of both cobalt sulphide (CoS) and molybdenum sulphide (MoS<sub>2</sub>). Because the substrate of the CoMo catalyst is alumina (Al<sub>2</sub>O<sub>3</sub>)-based it is also considered an active site for reactions. However, when the CoMo catalyst is manufactured the metal sites are produced in their oxide forms, which are cobalt oxide (CoO) and molybdenum oxide (MoO<sub>3</sub>). For the catalyst to be made suitable for the hydrogenation/hydrolysis reactions, activation (i.e., sulphiding) must take place. This can be accomplished in-situ by using the H<sub>2</sub>, CO, and H<sub>2</sub>S present in the Claus process gas. The steps are slightly different than the typical sulphiding steps for tail gas treating unit (TGTU) CoMo reactors but can be grouped into three broad categories:

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- increasing the H<sub>2</sub>S content to the reactor;
- increasing the reactor temperature;
- maintaining conditions for a prescribed time.

It is important to note that in spite of the precautions taken during the conditioning period, the SO<sub>2</sub> emissions during the activation procedure will be higher than normal. The information discussed in this article also indicates that there is no benefit to sulphiding the Euroclaus® catalyst before activating the Superclaus® catalyst, especially if there are concerns with elevated emissions. There are two main disadvantages of performing the Euroclaus® sulphiding procedure with the Superclaus® reactor in bypass:

- the Superclaus® reactor is bypassed for a longer period, resulting in higher SO<sub>2</sub> emissions;
- the elevated temperature in the Euroclaus® reactor during sulphiding negatively impacts the Claus chemistry and therefore reduces the sulphur recovery efficiency and increases the SO<sub>2</sub> emissions.

Additionally, once the sulphiding procedure is finished the Euroclaus® catalyst bed does not cool down to normal operating temperature for many hours. This requires that the Superclaus® remains bypassed for even longer. Also, to prepare for the Superclaus® catalyst conditioning, the SRU must be controlled to a low H<sub>2</sub>S concentration in the tail gas and thus the SO<sub>2</sub> emissions will be high while the Euroclaus® catalyst remains hot. If SO<sub>2</sub> emissions are of concern during a Euroclaus® and Superclaus® start-up where catalyst activation is required in both reactors, the following steps are recommended:

**Step 1:** Introduce acid gas to the process with the Superclaus® reactor in bypass. Maintain the Euroclaus® catalyst bed at a temperature of 185 to 200°C.

**Step 2:** Simultaneously with the introduction of acid gas, commission the tail gas analyser and confirm the readings by means of gas analysis and/or Dräger tubes. Initially target an H<sub>2</sub>S setpoint of approximately 1.0 mol-%.

**Step 3:** Maintain the Euroclaus® reactor inlet temperature at 185 to 200°C and stabilise and control the H<sub>2</sub>S with the tail gas analyser. This usually takes four to eight hours after acid gas intake, but could be longer depending on upstream conditions and stability and how well the unit is being

controlled. Limiting the amount of SO<sub>2</sub> to less than 0.10 mol-% in the tail gas will reduce the risk of temperature excursions in the Euroclaus® reactor and the consequent increase in SO<sub>2</sub> emissions.

**Step 4:** Once the analyser is proven correct and the H<sub>2</sub>S concentration in the tail gas is stable, it is recommended to put the Superclaus® in service and activate the Superclaus® catalyst. This procedure will take several days.

**Step 5:** Once the Superclaus® catalyst is fully activated and H<sub>2</sub>S is being controlled at the desired setpoint, it is recommended to maintain the Superclaus® reactor in operation (not in bypass) and increase the inlet temperature to the Euroclaus® reactor to achieve 240°C in the bottom of the catalyst bed for a period of 12 hours.

The SRU SO<sub>2</sub> emissions will be higher than normal until the Euroclaus® reactor temperature cools to normal values following the activation process. To offset this, it is recommended that the H<sub>2</sub>S setpoint to the Superclaus® be increased, for example from 0.7% to 1.0%, to suppress the increase in SO<sub>2</sub>. However, a higher H<sub>2</sub>S setpoint will cause more H<sub>2</sub>S to react in the Superclaus® reactor and result in a greater exotherm. The Superclaus® inlet and catalyst bed temperatures will need to be optimised for optimum recovery efficiency.

If minimising SO<sub>2</sub> emissions during start-up is not a concern, then increasing the temperature in the Euroclaus® reactor as described in step 5 might be performed directly after step 2. Maintain a target of 0.5 to 1.0 mol-% H<sub>2</sub>S in the tail gas.

Euroclaus® operating guidelines

Step 1: Euroclaus® catalyst temperature

The following temperature guidelines for the Euroclaus® operator were developed from analysis of years of operating data and extensive operating experience.

Guidelines for one Claus reactor preceding the Euroclaus® reactor:

- Inlet temperature: 190 to 220°C such that outlet temperature is above sulphur dewpoint.
- Expected catalyst bed temperature differential 10°C (bottom minus inlet temperature).

Guidelines for two Claus reactors preceding the Euroclaus® reactor:

- Inlet temperature: 185 to 195°C.
- Expected catalyst bed temperature differential: 0 to 5°C (bottom minus inlet temperature).

The following must be considered when optimising Euroclaus® catalyst bed temperatures:

- Higher catalyst bed temperatures have a negative impact on Claus conversion in the Euroclaus® reactor. In addition, the higher temperatures will promote the hydrogenation of sulphur vapour in the CoMo layer.
- Higher catalyst bed temperatures have a positive impact on hydrogenation of SO<sub>2</sub> and hydrolysis of COS.
- With a bottom catalyst temperature greater than 190°C there is a net increase of COS over the Euroclaus® reactor, with significantly more COS production at increasing temperatures (210 to 230°C).
- With a bottom catalyst temperature less than 190°C there is usually a net decrease of COS over the Euroclaus® reactor.

From an operational perspective it is recommended to adjust the inlet temperature to the Euroclaus® reactor by 3 to 5°C increments, and to monitor the effect on performance. Changing the inlet temperature should only be considered when operating conditions are stable in the SRU. The performance can be determined by monitoring the SO<sub>2</sub> emissions or measuring the Euroclaus® reactor outlet gas composition.

Step 2: Performance Measurement by Analysis

The best determination of Euroclaus® reactor performance is with a detailed analysis of the process gas in the inlet and the outlet of the reactor. In particular, the SO<sub>2</sub>, H<sub>2</sub>S, COS, and CO concentrations will provide useful information with respect to the Euroclaus® activity towards the SO<sub>2</sub> and sulphur vapour reactions to produce H<sub>2</sub>S and in its ability to limit the amount of COS production.

The following three key guides can be used to interpret the gas analyses:

- Overall Euroclaus® SO<sub>2</sub> conversion. This is the total SO<sub>2</sub> conversion across the reactor. Normal conversion is in excess of 90%.
- Euroclaus® CoMo catalyst SO<sub>2</sub> conversion. This is the conversion of SO<sub>2</sub> beyond the expected SO<sub>2</sub> conversion based on Claus



chemistry only. Commonly this is in the 50 to 60% range but for newly installed and sulphided Euroclaus® catalyst, values in excess of 80% have been observed.

- COS production and/or conversion. COS formation is an unwanted side reaction across Euroclaus® catalyst and is dependent on the catalyst temperature and process gas residence time (GHSV). Maintaining a low enough catalyst temperature in the range of 190-195°C may limit any COS formation that may occur. This temperature should only be maintained if it is possible to do so considering the sulphur dew point temperature. Consideration should be given that the SO<sub>2</sub> hydrogenation reaction does not suffer at these colder temperatures. Estimations of the effects of COS formation and temperature indicate that for every degree Celsius above 195°C, a 5% increase in COS across the reactor should be expected.

If the interpretation of the gas analyses differs significantly from these guidelines, then it is probable that some catalyst deactivation has occurred, or that the Euroclaus® reactor

is not being operated at the optimum temperature. If necessary, a reactivation of the Euroclaus® catalyst could be considered, as outlined earlier.

### Acknowledgement

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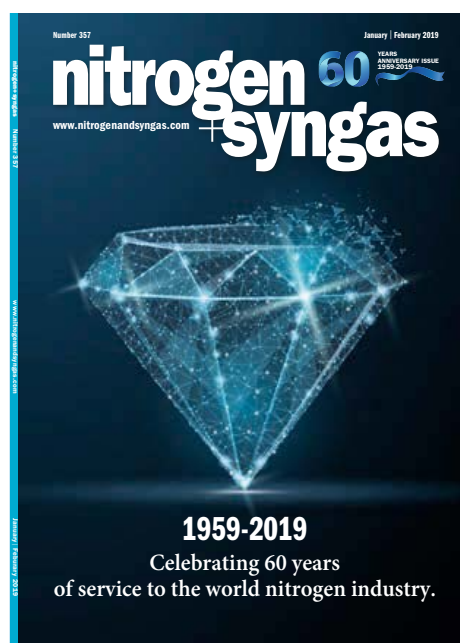
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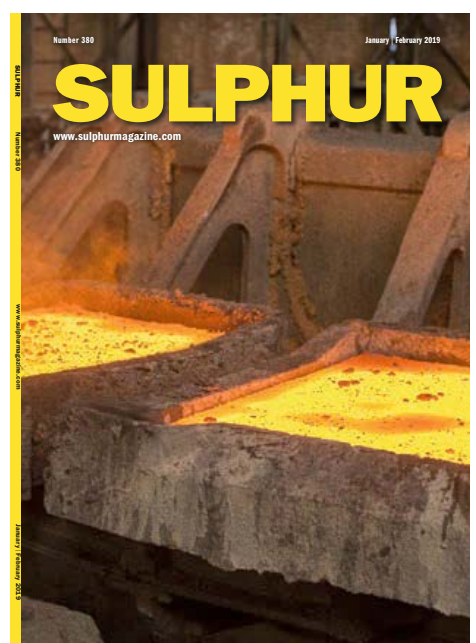
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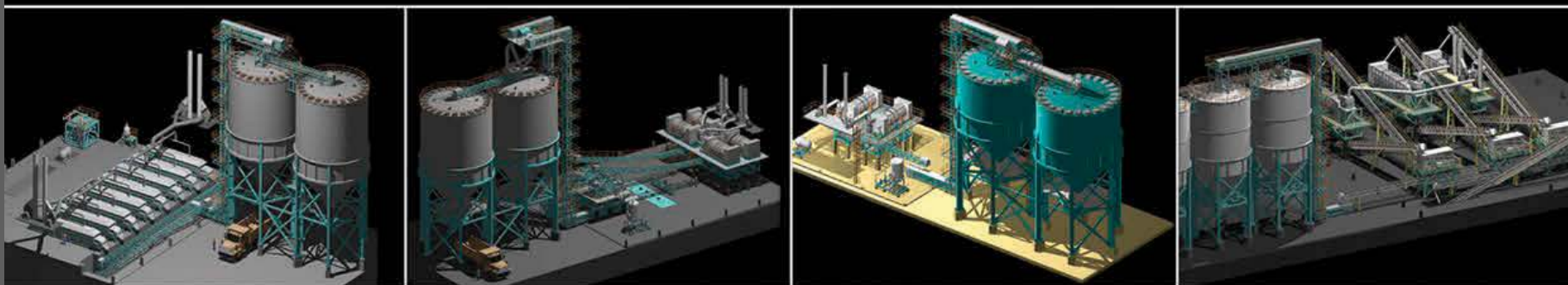
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