September | October 2016

Number 366



# Sulphur 2016, London Sulphur and acid in southern Africa Sulphur production in China Acid plant emissions

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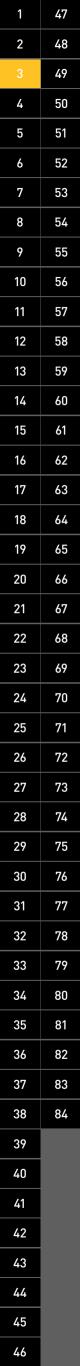
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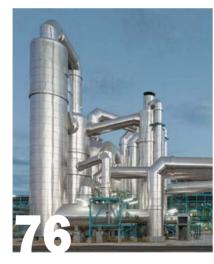


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Sustainable technology Dundee's new sulphuric acid plant.

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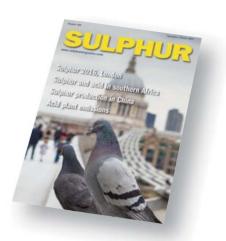
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## Acid test ahead for smelters



e've discussed before in this magazine the major shifts that are taking place in global sulphur markets, as Canada becomes slowly less relevant as the dominant world supplier and new capacity from the Middle East, especially Abu Dhabi, starts to change the dynamics of the market. But at the same time, no less seismic shifts are also happening downstream, in the world of sulphuric acid. The start-up in July of the third sulphur-burning acid plant at Moa Bay in Cuba as part of Sherritt's joint venture nickel leaching operation is only the latest symptom of this. Moa's new 2,000 t/d acid plant will consume up to 220,000 t/a of sulphur – welcome news for sulphur markets, to be sure. But of course that means that it will not be importing correspondingly less acid; Cuba has imported 500-550,000 t/a over the past few years. With global nickel prices in the doldrums, taking control of costs has been a major factor in Sherritt's decision, and the company claims that it can shave \$0.50/pound of nickel produced in terms of costs by running the sulphur burner, eliminating acid imports and generating power credits.

But the development comes at a time when a number of traditional markets for merchant acids seem to be drying up. In Namibia, the start-up of the new acid plant at the Tsumeb copper smelter has ended the country's need for acid imports, which stood at 135,000 tonnes in 2014, and could turn Namibia into a net exporter. In Morocco, the building of sulphur-burning acid plants as part of the huge processed phosphate expansion at Jorf Lasfar could also remove another million tonnes of annual acid demand. Acid demand is falling in Chile as well, with falling ore grades in mines supplying copper leaching plants, while last year's start-up of a 725,000 t/a acid plant in Turkey has also reduced demand there. In China, which has been a steady buyer of acid for many years, is now completing enough copper smelting capacity at the same time that demand for phosphate processing is slowing, that it seems set to become a new acid exporter over the next few years.

This is all bad news for smelters who currently sell their surplus acid onto the merchant market, mainly in Korea, Japan, Peru, Canada and Europe, as it seems that over the coming few years there may be an excess of acid chasing too few buyers. Of course buyers will buy if the price is low enough. At time of writing, f.o.b. acid prices were down to \$10/t in NW Europe and \$0/t in Korea and Japan, and it may be that a move into negative pricing may ultimately be required to persuade operators of sulphur burners - perhaps in India, China or Southeast Asia - to once more shut down their acid plants and start buying from the oversupplied merchant market again, as we saw most recently in 2014. But with sulphur prices also driven to low levels by oversupply, it's anyone's bet how low acid prices may have to fall this time to compensate.

Apere

Richard Hands, Editor

This is all bad news for smelters.

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## MARKET INSIGHT

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

## SULPHUR

## **Market recovery?**

Sulphur prices showed no signs of stabilising through July, eroding beyond expectations, but finally appeared to reach a floor in August. The main focus in recent months and main price driver has been lacklustre demand in the processed phosphates market and falling DAP prices. The global sulphur supply/demand balance has remained stable through 2016 to date, despite the start-up of the Shah gas project in the UAE. Integer expects a small surplus of sulphur for 2016, at under 1 million tonnes. New projects in oil and gas are expected to impact the global balance from 2017 onwards. However, in 2016, the Middle East is already set to become the largest regional producer of sulphur, overtaking North America in the rankings. This shift is now reflected in changing trade flows from the Middle East and will continue to evolve in the outlook.

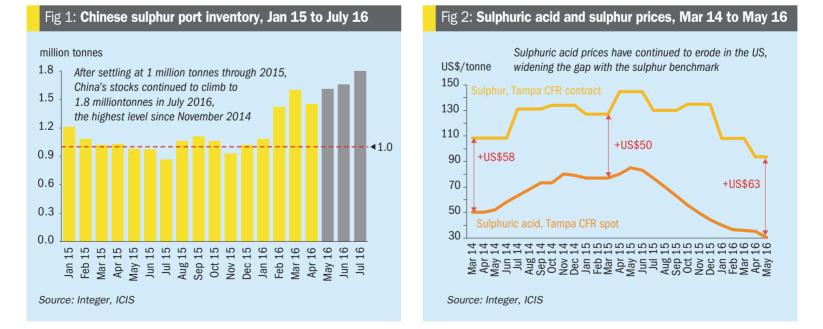
Middle East producers have signalled a more optimistic approach for September, with price postings reflecting increases across the board. In August, sulphur producers reduced contract prices as bears in the market on the demand side failed to dissipate. Prices dropped down into the mid-\$60s/t f.o.b Middle East on the back of pressure from end user markets. For September, Adnoc announced a \$7/t increase to \$77/t f.o.b. Ruwais for shipments to India. In Saudi Arabia, Aramco Trading posted its price at \$74/t f.o.b. Jubail, an \$8/t increase. Meanwhile, in Qatar, Tasweeq increased its September price by \$9/t from the August price to \$74/t f.o.b. The producer price increases led to an uptick in delivered prices in China and India, although it remains to be seen whether prices can hold and continue to recover. Uncertainty still prevails in the outlook for the remainder of the year as downstream markets have yet to see meaningful recovery.

China sulphur imports have been strong through 2016 so far, despite expectations of a possible slowdown from 2H 2016. January-July 2016 imports totalled 7.4 million tonnes, up by 12% year on year. Saudi Arabia has retained its ranking as number one supplier, despite the phenomenal growth in shipments from the UAE this year. Exports from Ruwais to China have more than doubled in 2016. Iran, Kazakhstan and Oatar have all lost market share in 2016, while Canadian volumes have remained strong to China to date, above 2015 and 2014 levels so far. Strong imports have also been reflected in the stocking strategy in 2016, with inventory at the major ports in China rising to over 1.8 million tonnes. Stocks have been decreasing slightly from this peak, down to 1.6 million tonnes in early September. Spot prices in China dropped into the \$70s/t c.fr in August, driven down by slow demand and ample stocks. Prices ticked up at the start of September to \$76-85/t c.fr but there is scepticism over how sustainable the recovery is likely to be.

Over in India, spot prices increased in early September, to \$80-83/t cfr, up from lows in the mid \$70s/t c.fr in July. Fresh demand is anticipated from end users IFFCO and FACT in September in purchase tenders. PPL issued a new tender, closing 2 September for 30,000 tonnes of sulphur for arrival end September/early October at Paradip, which was expected to test the upward momentum in pricing.

The main news on fresh sulphur demand for 2016 has been the start-up of Sherritt International's acid plant in Cuba and the continued ramp up of processed phosphates production in Morocco. Sherritt announced in July its acid plant had successfully started up for its nickel leaching operations, leading to expectations sulphur trade from Canada to Cuba would increase. Sulphur demand at the project will increase to 360,000 t/a once at capacity. A sulphur cargo was also heard booked from the Middle East. On the one hand, this is positive for the sulphur market but increasing sulphur demand will mean direct sulphuric acid imports will decline into Cuba, impacting European producers currently exporting acid.

Vancouver sulphur spot prices dropped in July and August, in line with global developments as the situation in Alberta normalised following the wildfires in Fort McMurray. Oilsands production is heard running at levels prior to the wildfires. Prices rebounded slightly on a notional basis at the start of September, follow-



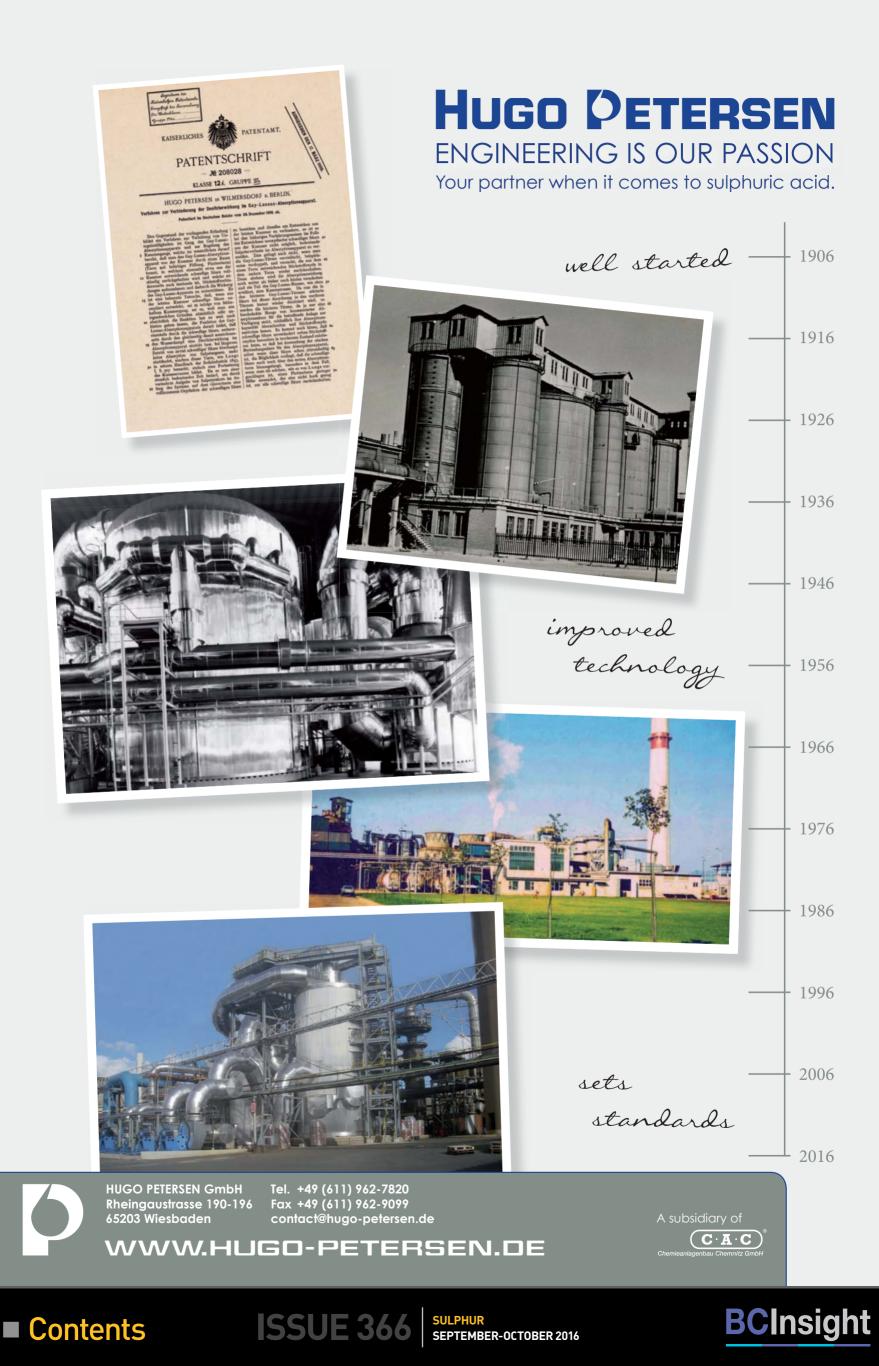
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ing the upward trend in the Middle East. Rail shipments to the US market were not impacted by the temporary tightness in Alberta, with January-June 2016 exports totalling 870,000 tonnes, down by only 20,000 tonnes.

Sulphur production in the US has continued to recover through 2016, following the production drop seen in 2015. In 1H 2016, output was 3% above year ago levels at 4.47 million tonnes. This trend is expecting to continue through the remainder of 2016. At the same time, exports from the US have been rising in 2016, up by 24% on 1H 2015 levels at over 1 million tonnes.

Brazilian sulphur imports in 2016 have dropped to date, with January-July imports down by 9% when compared with the same period in 2015. This reflects the slowdown in the country in demand and is expected to continue in the short term outlook. However, trade has been shifting in terms of supply sources, with the UAE taking a much largest market share this year. One Brazilian processed phosphates producer was heard experiencing production issues through August and into September, leading to a short term reduction in sulphur consumption.

#### **SULPHURIC ACID**

#### Stable outlook prevails

Global sulphuric acid prices have been on a more stable trend compared to sulphur, with prices continuing to firm in Northwest Europe for exports by a further \$5/t on two months earlier at \$5-15/t f.o.b. through August and early September. The pricing has been led by dynamics in supply, as smelter acid producers report comfortable or low inventories as regular offtake from contract holders remains healthy. At the same time, one European acid producer was heard facing production difficulties, further supporting a more balanced European market. KGHM/Poland is undergoing a maintenance turnaround, lasting 3 months and impacting exports from the country. Expectations are for a stable outlook on short term pricing from the region.

Chile remains a major weak spot in the market, with 1H 2016 imports dropping by 28% year on year. Integer previously estimated a deficit of 1.8 million tonnes for 2016, but based on import data for 1H 2016, this could be lower still, down to 1.7 million tonnes. Peru remains the main supplier for Chile, with trade increasing by 4% to date. Prices have dropped significantly in 2016 to the low \$20s/t cfr on the low end of the range. On the demand side, the Antucoya project began commercial production. Copper output is expected to reach 85,000 tonnes in 2H 2016. At the same time, cargoes for export have been heard, signalling short term surplus in the market.

Brazilian spot demand has been steady, with fresh tenders mostly leading to fixtures within the Latin American region. Timac, Yara and Mosaic were all in the market for tonnage, with two cargoes sourced from Chile and Mexico. In the first seven months of the year, acid imports to Brazil have dropped by over 21%, down to just 275,000 tonnes. Shipments from Belgium and Germany have declined, while tonnes from Spain and Mexico have increased. We anticipate stable pricing in Brazil in the short term and acid imports to continue to soften through the remainder of 2016.

Over in Asia, the surplus supply situation in the North East region has improved through July and August, with producers reported to be comfortable or tight. Prices firmed to above \$0/t f.o.b. South Korea/ Japan, signalling a more stable period in the market. Korea Zinc had a maintenance turnaround following an investigation into an acid spill. The roaster was expected to be down throughout August, further tightening availability from the producer. Exports from Japan have been healthy through 1H 2016, rising by 5% year on year. Exports to the Philippines for the Taganito nickel project decreased by 10% following the shutdowns and reduced consumption at the plant. Meanwhile, Japanese exports to India have grown significantly, up by over 77% on a year ago.

Key market China has continued to import acid above 2015 levels, despite the slowdown in the downstream markets, highlighting continued consumption and demand. Acid imports in 1H 2016 were up by over 30% year on year, with increased tonnage arriving from Japan, South Korea and Taiwan.

## **Price indications**

## Table 1: Recent sulphur prices, major markets

Cash equivalent	March	April	Мау	June	July
Sulphur, bulk (\$/t)					
Vancouver f.o.b. spot	80	75	80	80	70
Adnoc monthly contract	88	185	86	80	80
China c.fr spot	86	85	85	78	74
Liquid sulphur (\$/t)					
Tampa f.o.b. contract	95	70	70	70	65
NW Europe c.fr	143	143	116	116	106
Sulphuric acid (\$/t)					
US Gulf spot	45	45	35	35	35
Source: CRU					

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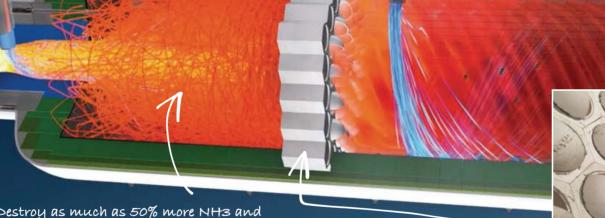
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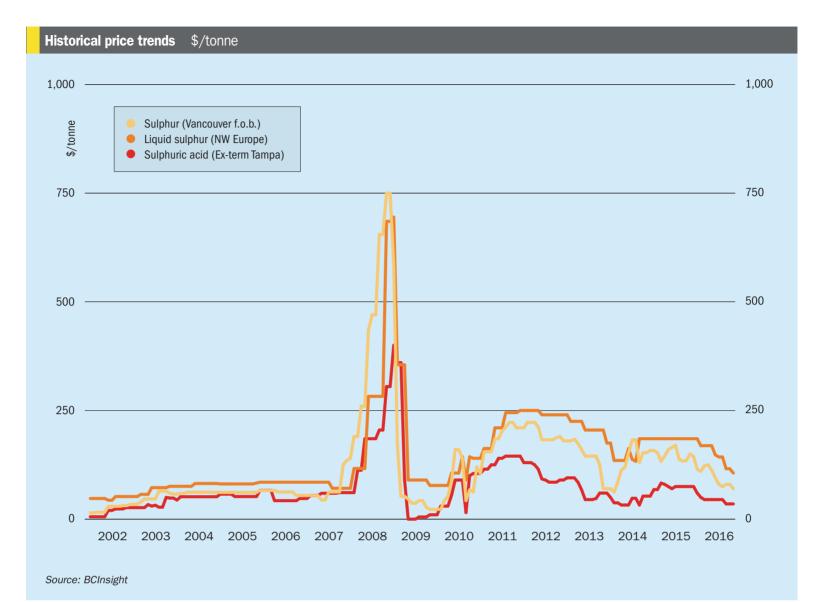


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## Market outlook



## **SULPHUR**

- **Outlook:** Sulphur prices are expected to tick up slightly and potentially stabilise as stocks in China continue to drop and demand emerges in India for the sugar season. However the upside is likely to be limited by developments in the phosphates market should DAP prices drop further, this may lead to any improvement in sulphur being short-lived.
- Any cutbacks in the phosphates market will be a key factor for the outlook

   on the one hand reducing sulphur consumption, but could also help to support DAP prices and having a positive impact on the sulphur market.
- Sherritt's new sulphuric acid plant will likely source sulphur from a range of producers including Canada and the Middle East
- The start-up of new supply projects in 2017 may impact trade and the global balance. In Qatar, the Barzan project is expected online next year and would add pressure to the market. The

Kashagan project in Kazakhstan is also pegged for start-up in 2017, although it remains to be seen if sulphur will enter the market upon ramp up

- India remains a key hotspot to watch for the remainder of 2016, as fertilizer imports are usually stronger in the latter part of the year. Healthy stocks in the country may limit any potential run up in pricing and demand for imported volumes
- The slowdown in investment in the energy sector and reduced project pipeline may lead to a slowdown in sulphur production growth in the long term outlook and a more balanced market is expected in this scenario
- **Outlook:** Sulphur prices are expected to see some recovery in the short term through September but uncertainty prevails in the downstream markets and may lead to market bears limiting price improvement.

## **SULPHURIC ACID**

• Sherritt's new sulphuric acid plant in Moa, Cuba started up in July and where

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displaced acid volumes from Europe will be placed as a result remains uncertain. This could lead to more competitive pricing in the market and remains a bearish factor in the outlook.

- Surplus acid from Mexico will be a factor for the spot market in the short term outlook, with potential to put downward pressure on pricing during tenders in Brazil
- Trade to key markets such as China and Morocco in the latter part of the year may continue to remain strong, supporting the upside to prices.
- European producers are expected to remain balanced in the short term outlook, although any reduction in volumes from Cuba may tip the balance going forward
- Outlook: Acid prices are like to remain stable, with potential to ease in the latter part of the year as supply normalises in Europe and Asia. The Asian export prices will be dependent on demand from China and any short term shortages of supply on the back of turnarounds.

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## **Sulphur Industry News**

## UNITED STATES INEOS buys Calabrian Holdings

INEOS Enterprises says that it has acquired 100% of the shares of Calabrian Holdings Corporation, which supplies technology sulphur dioxide and sodium based derivatives and technology across North America, for an undisclosed sum. The company has its main production site at Port Neches, Texas, where it is the largest producer in North America of SO<sub>2</sub>, with a capacity of over 200,000 t/a. The company is also building a new facility at Timmins in Ontario, Canada which will add an additional 35,000 t/a of capacity once completed at the end of 2016. INEOS says that the acquisition will add a North American dimension to the company's existing sulphur chemicals portfolio.

Ashley Reed, CEO of INEOS Enterprises said, "We are very pleased to have acquired this modern production facility in Texas and look forward to the completion of the Canadian facility late this year. The assets are ideally positioned to serve the North American market, with excellent cost position and logistical infrastructure. Additional synergy will be explored with our existing business in Europe."

Randy Owens, CEO of Calabrian Corporation said, "The Company has undergone significant transformation during SK Capital's ownership. INEOS' global infrastructure will allow the next phase of growth by accelerating geographical expansion and further advancing its technology strategy."

Amongst Calabrian's proprietary technologies is  $SO_2Clean^{m}$ , which allows in situ production of sulphur dioxide at what Calabrian says are lower operating costs than a conventional sulphur burner.

## **Refinery suffers SRU outages**

LyondellBasell's 263,000 bbl/d Houston refinery has returned to normal operation following two interruptions to operation, beginning with a power supply cut on August 10th which suddenly cut power to the refinery's sulphur recovery unit. The refinery was forced to turn down operations to about 50% and flare gas streams containing H<sub>2</sub>S for about 12 hours, resulting in the emission of an estimated 269 metric tonnes of sulphur dioxide and 2.9 tonnes of hydrogen sulphide, leading to worker evacuations and orders to shelter in place until the SRU could be restarted. The Houston Ship Channel was also shut for around 20 minutes to avoid exposing the crew of a ship on the waterway north of the refinery to any potential  $H_2S$  release. The refinery had only recently returned to full capacity following repairs to a coking unit damaged in a fire on April 8th - the coker did not restart until July 15th. A week after the SRU incident a neighbouring facility which exports process steam to the refinery was struck by lightning, resulting in a loss of steam pressure and a return to flaring for a brief period.

## Upgraded sulphur scavenger

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Oklahoma-based Chemical Products has developed an upgrade to its *SULFURTRAP<sup>®</sup>* sulphur scavenging media, *SULFURTRAP<sup>®</sup>-EX*.

The original spherical media have been modified into a new extruded pellet, which Chemical Products says offers extended bed life, leading to less frequent bed replacement and lower operating costs, while its high surface area and pore structure allow it to handle higher flow rates with shorter residence times in smaller equipment. The media also holds more sulphur and so is able to maintain outlet product specifications longer.  $H_2S$  concentrations of less than 1ppm can be achieved at loadings of up to 500 lbs./day over a broad range of process conditions.

## New software version

Optimised Gas Treating has released version 6.1 of its ProTreat analysis software to include a complete state-of-the-art sulphur plant package which can be fully integrated with upstream acid gas removal units, acid gas enrichers and sour water stripping, and with downstream quench towers and tail gas treating units. The new feature includes the ability to model sulphur plant de-gassing processes as well as thermal oxidisation. Sulphur dioxide has been incorporated as a rate component, allowing users to couple the thermal oxidiser/sulphur package with SO<sub>2</sub> scrubbing to model alternative tail gas treating processes such as MECS's DynaWave® and Wellman Lord. The sulphur plant package is being made available to all existing ProTreat customers free of charge until the end of December 2016.

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## **OMAN**

## Work begins on second refinery

Ground work has begun on a second refinery in the Duqm special economic zone (SEZ) in Oman. The 230,000 bbl/d refinery is being developed as part of the \$10.7 billion Sino-Oman Industrial City, a joint venture between the local authority and Oman Wan Fang LLC, a consortium of six private Chinese corporations, which agreed in May to establish this investment hub at a dedicated 1,200 hectare industrial park within the SEZ. A petrochemicals complex will also be built alongside the new refinery. A \$6 billion refinery also with a capacity of 230,000 bbl/d is already under construction elsewhere in the Duqm SEZ.

Ali Shah, chairman of Wan Fang Oman LLC, said that the company was in talks with Oman's Ministry of Oil and Gas to secure the gas requirements of some of the heavy petrochemical and industrial ventures envisioned at the park. "Heavy industries will require a great deal of energy for the production of petrochemicals derivatives, aromatics, methanol, feedstock for which we will provide through the establishment of a refinery in the SEZ.".

Chinese contractor Duqm Ningxia Construction Co is taking charge of site preparation at the SinOOman Industrial City, which will include tourist, commercial and healthcare components, together with roads, office and residential facilities. A number of gas-based facilities are planned, including a steel mill, aluminium smelter, tyre manufacturing factory, magnesium plant, urea scheme, and factories manufacturing cement, building materials and glazed glass.

## **MEXICO**

## Malaysian firm wins sour gas pipeline contract

SapuraKencana Petroleum Bhd has a secured a \$113 million contract to install a 36", 18 km sour gas pipeline in Mexico, the company's second contract win in the country. Work on the project began in August and will last until March 2017. The pipeline will link two gas platforms in Ciudad del Carmen, Campeche, Mexico. The scope of work comprises transportation and installation of pipelines, crossings, top side modifications and subsea works, including procurement and project management. The contract was awarded by state oil and gas company Pemex Exploracion y Produccion.

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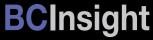
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## **First sulphur exports from Pajaritos**

In July the Pajaritos maritime terminal is reported to have made its first export of granulated sulphur, following the November 2015 completion of a sulphur forming unit at Cosoleacaque. The 10,000 tonne shipment accompanied 25,000 tonnes of calcium triple superphosphate on the Fourd Esmeral, destined for Uruguay and Argentina. Exporter Alfa y Omega says that it bought the sulphur from chemical company Fefermex, which operates the granulation unit. Fefermex in turn sources liquid sulphur from state oil company Petroleos Mexicanos (Pemex). Among anticipated customers for granular sulphur from the plant are expected to be Moa Nickel SA, which has recently completed a new sulphur burning acid plant (see Sulphuric Acid News) and which now has a requirement for 250,000 t/a of sulphur. The Fefermex granulation plant also has a capacity of 250,000 t/a of sulphur.

#### INDIA

## **Refinery upgrade for HPC-Mittal**

HPC-Mittal Energy Ltd (HMEL), part owned by steel tycoon L N Mittal, plans to shut its 180,000 barrel per day (bbl/d) Bathinda refinery in northern Punjab state for about 40 days in March 2017 to raise capacity. The refinery is 49% owned by state refiner Hindustan Petroleum Corp Ltd and 49% by Mittal Energy Investments Pvt Ltd. Crude processing capacity of the refinery's existing crude distillation unit will be raised to about 225,000 bbl/d, and the refinery sulphur recovery unit's capacity will increase from 600 t/d to 700 t/d as it seeks to increase the processing of cheaper sourer crude grades. The refiner will also increase the capacity of its vacuum gasoil hudrotreater to 3.5 million t/a from the existing 3 million t/a. The refinery's captive power plant, which has been running on gas and diesel, will be converted to run on petcoke from the refinery.

#### Paradip told to cut sulphur emissions

The Paradip Oil Refinery has been told by the state pollution control board to submit an action plan for reducing emissions after complaints relating to aromas emanating from the plant from locals, a well as some reported respiratory issues and eye irritation. Indian Oil Co Ltd, owners of the refinery, has said that the facility has been emitting higher than anticipated levels of sulphur dioxide because many downstream systems are still in commissioning, and will not be completed until January 2017.

## **SAUDI ARABIA**

#### **Contracts signed for Fadhili gas project**

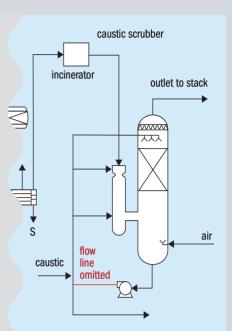
A signing ceremony was held on July 20th for four more contracts relating to the Fadhili gas plant project. Saudi Aramco executives were joined by personnel from Larsen & Tubro Ltd, responsible for offshore facilities, Saudi KAD Contracting Co. responsible for downstream works, Saudi Electric Co. and Engie Group PLC for a combined heat and power plant, and Mohammed I. Al Subeae & Sons Investment Holding Co. for a residential camp. These join 10 other major EPC and other contracts previously awarded.

Fadhili is a \$13 billion greenfield development 30km west of Jubail in the east of Saudi Arabia's eastern province intended to process both onshore and offshore sour gas and feed it into Saudi Arabia's Master Gas Gathering System to cope with increased energy demand. Scheduled to be completed by the end of 2019, the project will process 2.5 billion cf/d of gas, including an estimated 2 bcf/d of non-associated gas from the Hasbah offshore gas field and 500 million cf/d of gas from the Khursaniyah onshore field, producing 1.5 bcf/d of sales gas and 4,000 t/d of sulphur. The gas plant will have maximum sulphur recovery of 99.9% via tail gas treatment. The operator plans on adding a helium recovery plant and a CO<sub>2</sub> recovery unit for reducing future emissions. A 1,500MW co-generation power plant will also be con-



The HPC-Mittal refinery.

#### Correction



In the July-August 2016 issue of *Sulphur* there was an omission from the diagram (Figure 3) at the top of page 53. A flow line was omitted and should have been included as shown above in red. Our apologies for any confusion caused.

structed by a joint venture of Saudi Aramco and Saudi Electricity Company.

Tecnicas Reunidas was awarded two turnkey contracts including detailed engineering, procurement and supply of equipment and materials. It will also provide services for construction of the plant and assistance during the commissioning. Petrofac has been selected to perform EPC of the sulphur recovery plant. The scope of work includes construction of six sulphur recovery trains and associated facilities for the sulphur and heavy-duty oil handling, loading, unloading and storage, sour water stripper, flare system and wastewater treatment plant.

## CHINA

## K+S buys Chinese magnesium sulphate producer

K+S Group is to spend more than €10 million purchasing Huludao Magpower Fertilizers (Magpower), a Chinese producer of magnesium sulphate fertilizers. The German potash producer said the acquisition was an important step forward in its expansion into Asia. The exact purchase price was not disclosed although a statement from K+S did confirm it was for a "euro amount in the low double-digit millions range".

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**BCInsight** 

Magpower is one of China's largest producers of synthetic magnesium sulphate (SMS), a product used for industrial purposes and as a fertilizer for oil palm, soybean and sugar cane. The purchase provides K+S with the ownership of a modern 90,000 t/a SMS production plant "with an attractive cost structure" in Huludao City in the northeast Chinese province of Liaoning. The company believes the plant's capacity could be doubled to 180,000 t/a in future.

"We are bolstering our competitive position in the specialties area by means of this acquisition and can therefore better tap into the growth markets of South-East Asia," said Norbert Steiner, the chairman of K+S. "We see great sales potential for magnesium sulphate products to the agricultural sectors in China and South-East Asia which we can't service adequately from our German sites."

The SMS produced by the Huludao plant will add a new and effective water-soluble type of magnesium sulphate to the company's current product range. SMS products have a positive effect on root development, water absorption, yields and plant quality parameters, according to K+S.

## **CANADA**

## SemCAMS receives environmental approval for sour gas plant

SemCAMS, a subsidiary of SemGroup® Corporation, has announced that it has received Alberta Energy Regulator approval for its planned 200 million cf/d Wapiti sour gas plant. As well as sour gas, Wapiti will process 20,000 bbl/d of condensate. With producer concerns over the long term reliability of acid gas injection in the area, the Wapiti gas plant will be able to send the acid gas to SemCAMS' existing K3 and KA sour gas plants via existing infrastructure. SemCAMS says that this will provide a reliable long term option for the acid gas, and negotiations are underway with multiple producers in the area over in long term processing arrangements. Indeed, SemCAMS says that its final investment decision is expected upon execution of one or more of those agreements.

"With the engineering and licence approval now in hand, we are excited about moving this project to the next phase. SemCAMS has a long and successful history of safely operating sour gas plants, and we are looking forward to expanding that expertise in the Wapiti area and to Montney producers with this new facility," said David Gosse, SemCAMS' vice president and general manager.

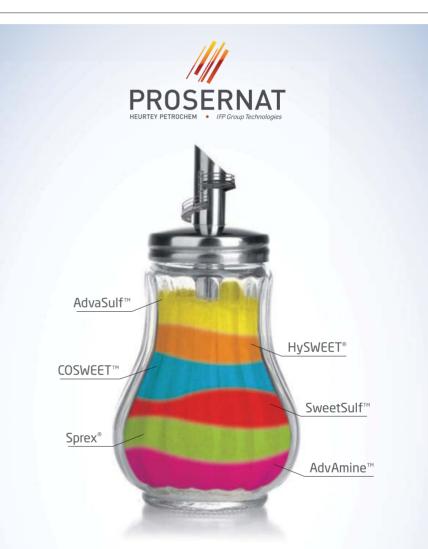
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## RUSSIA

## License awarded for new Caspian development

The Russian government has issued the license for the Tsentralnaya (Central) Oil and Gas Company, a joint venture between Lukoil (25%), Gazprom (25%) and Kazakhstan's KazMunaiGaz (50%) – to develop the Central field in the Caspian Sea, around 150km southwest of Aktau and 400km south of Astrakhan, on the Russian side of the sea. The license allows for prospect-

ing, exploration and production of hydrocarbons without an auction for a period of 25 years. The geological exploration stage will last seven years, according to Natural Gas Europe. Lukoil estimates that the region has at least 90 million tonnes of oil and 500 billion cubic metres of sour gas. Russia and Kazakhstan have also signed a production sharing agreement and Kazakhstan is also reportedly looking towards Russian participation in its offshore Khvalynsk field by late 2016, where there are a further 320 bcm of gas, 18.4 million tonnes of condensate and 240 million tonnes of crude oil.



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**BCInsight** 

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## **ALGERIA**

## Indorama to invest in large scale phosphate production

The Algerian government has signed a \$4.5 billion deal with Indonesia's Indorama Corp to develop a phosphate mine and downstream phosphoric acid and diammonium phosphate (DAP) capacity in the country. Algeria has extensive phosphate reserves, the third largest in the world after Morocco and China, but has lagged behind neighbouring Morocco and Tunisia in developing them. Ten years ago the government was developing a major phosphate project with Pakistan's Engro as a potential investor, but put the plans on hold in the wake of the 2008 financial crash. It looks as though this may be a revival of the first phase of that project.

Indorama signed the deals with state-owned phosphate companies Asmidal and Manal. They include a 49-51% joint venture between Indorama and Manal to develop a new phosphate mine in the eastern province of Tebessa. Indorama,

Asmidal and Manal will also build a phosphate processing plant in Souk Ahras, near the Tunisian border, to produce phosphoric acid and di-ammonium phosphate (DAP). Finaly, Indorama is also looking at a joint venture with Asmidal near the coastal town of Skikda to produce ammonia and ammonium nitrate.

So far no capacities have been given by the project developers. The original plan called for three phosphate complexes, each processing two million t/a of rock from mines in the Bled el Hebda deposit, and each involving 4,500 t/d of sulphuric acid, 1,500 t/d of phosphoric acid and 3,000 t/d of DAP production. However, according to Reuters Algeria's Industry and Mines Minister Abdesselam Bouchouareb has talked of Algerian phosphate output reaching 10 million t/a when the new projects is completed, up from 1-1.5 million t/a at present.

## TOGO

## Strikes hit phosphate industry

Togo's phosphate industry was shut down for 72 hours in August by a strike of workers at Societe Nouvelle des Phosphates du Togo (SNPT). The dispute, over pay and working conditions, affected the Hahatoe mine 40km north of Lome, and the Kpémé processing plant. Phosphates are one of Togo's major resources, and in the late 20th century accounted for 40% of government revenue. However, annual production has declined from 3.4 million t/a in 1990 to just 800,000 t/a in 2009 because of lack of investment in facilities. The government began a \$300 million stimulus package in 2010 with a five year plan to boost production, based on modernisation of existing facilities, and output has risen to 1.2 million t/a according to CRU. There are also plans to open new mines, and a \$1.4 billion Chinese investment project aiming to produce 5 million t/a of phosphate rock to feed fertilizer and phosphoric acid production by 2020-21. Nevertheless, staff wages and working conditions have remained a bone of contention since 2013, and the employees have threatened more action if the company does not take steps to meet their demands.

#### CUBA

## Start up for third acid plant

Sherritt International says that that the third acid plant at the Moa Joint Venture in Cuba, in which it owns a 50% interest, is in

commissioning and has begun producing sulphuric acid. The 2,000 t/d plant was operating at approximately 900 t/d in late July, with full performance testing scheduled over subsequent weeks. The project was concluded within the established construction timeline and on budget at \$65 million. It was Moa Nickel's first capital project to be fully financed by a Cuban financial institution.

"We are pleased to complete this expansion project and to see it start up successfully on time and on budget," said David Pathe, president and CEO, Sherritt International. "The third acid plant delivers significant cost savings, and reduces fuel consumption. The safety record during construction and commissioning was a 0.48 Lost Time Injury rate with over 1.2 million exposure hours and speaks to the high standards upheld by the Cuban construction workforce."

At full operation, the acid plant will reduce Moa's net direct cash cost of nickel production by an estimated \$0.50/ lb, according to Sherritt, with the savings derived from an elimination of third-party sulphuric acid purchases and reduced fuel oil purchases. Initial benefits will be realised in 4Q 2016, with the full impact expected in 2017.

#### INDONESIA

## New partners sought for Weda Bay nickel project

The Weda Bay nickel project in Indonesia, currently in the hands of France's Eramet after buying out its project partners Mit-

subishi Corp and Pacific Metals for \$110 million earlier this year, is now looking for new investment partners. The project was previously put on hold because of the downturn in the nickel market, but Eramet believe that the nickel market will be in deficit of up to 50-70.000 tonnes this year, and that prices are likely to recover from their current \$9,800/t to around \$14-17,000/tonne, making Weda Bay viable again. Eramet chairman and chief executive Patrick Buffet told a news conference in Tokyo; "we think there are very few deposits of this quality.".

## **CB&I** to license acid alkylation unit

CB&I has been awarded the license and engineering design of a grassroots alkylation unit by Indonesia's PT Pertamina. The unit will use CB&I's CDAlky sulphuric acid alkylation technology and Haldor Topsoe's wet gas sulphuric acid (WSA) technology as part of the upgrade of Pertamina's refinery unit V in Balikpapan, East Kalimantan, Indonesia. CB&I says that CDAlky is an environmentally-friendly alternative for obtaining high-octane, premium gasoline because it eliminates the need for human contact with sulphuric acid, reducing overall maintenance, chemical cost and environmental impact for refineries.

"CB&I is pleased to have been selected as the alkylation technology licensor for the project. We have previously licensed technologies to Pertamina, and we look forward to our continued partnership with them," said Daniel McCarthy, president of CB&I's technology operating group.

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## **UNITED STATES**

## Veolia buys Chemours' sulphur products business

Chemours Company, a supplier of titanium technologies, fluoroproducts and chemical solutions, has sold its sulphur products business, part of its chemical solutions segment, to Veolia North America for \$325 million in cash. The sale is part of a strategic realignment of the company, particularly its chemical solutions portfolio, according to Chemours, which has involved selling its aniline facility in Beaumont, Texas, cost improvement at its methylamines business in Belle, West Viriginia, and the shutdown of its reactive metals business in Niagara Falls, NY. The sulphur products business, with approximately \$250 million in revenue, offers sulphuric acid products and services to a range of industries in North America. It provides spent acid regeneration and sulphur gas recovery services, non-fuming sulphuric acid and higher value sulphur derivatives.

## Jacobs buys Bayer acid technology

Jacobs Engineering says that it has acquired all rights to Bayer AG's BAYQIK quasi-isothermal sulphuric acid converter and other associated technology, for an undisclosed sum. Jacobs has secured full patent rights and all associated technical, market and commercial information related to the technology. Bayer is offering its transitional services to ensure a seamless transfer of the business to Jacobs. Jacobs says that BAYQIK will help it to efficiently convert process gas with high sulphur dioxide concentrations, reinforcing the company's sulphuric acid portfolio and allowing it o offer technology to both high and low strength SO<sub>2</sub> market segments.

#### **Elemental sulphur from leaching**

Reno-based Itronics Inc. says that its pilot scale FeLix, SuLix leaching system is now producing dry sulphur powder. The company recovers valuable chemicals from waste streams, including photographic developing fluids and mining waste. The current pilot leaching programme is aiming to produce commercially saleable silver bullion from a mixture of its internally generated silver concentrates and electronic scrap (ground up computer circuit boards). The leaching now produces four products: silver concentrate; a high iron content liquid ingredient for use in fertilizer; a high sulphur content liquid ingredient for use in fertilizer, and dry sulphur powder. About 75% of the feed material to the leaching process is now being recovered for use as ingredients for the manufacture of GOLD'n GRO fertilizers. All of the silver in the leach process feed materials is retained in the concentrates being delivered to the refinery, along with gold, palladium, and platinum.

"Production of elemental sulphur by our new leaching technology is an exciting development for our investors," said Dr. John Whitney, Itronics president. "It improves the efficiency of our processes without a significant increase in cost and creates an opportunity to formulate new products. Also, the inclusion of measurable gold, palladium and platinum in our silver concentrates is a potential benefit to Itronics."

#### EGYPT

## Chinese to invest in phosphoric acid plant

Egyptian state phosphate producer Phosphate Misr has signed a memorandum of understanding (MoU) with several Chinese mining firms to build a phosphoric acid plant, at an estimated cost of \$1 billion. Phosphate Misr operates phosphate mines in the Abu Tartour region, 650km south of Cairo, where output is 2 million t/a of phosphate rock at 28% P<sub>2</sub>O<sub>5</sub>, according to Integer Resources. However, Egypt has historically had no downstream phosphate processing industry, and all of its rock is currently exported. The Chinese firms will take part in the construction phase as well as financing the project, according to Phosphate Misr's vice chairman, Abdul Rahman Ahmed. No capacity for the acid plant or associated sulphuric acid capacity has been released as yet.

#### Two more phosphoric acid plants

Prayon Technologies, says it will provide the license and technical consultancy for two new phosphoric acid plants due to be built in Egypt as part of the NCIC Ain Sokhna Fertilizer Complex on the Gulf of Suez. Prayon's scope of work comprises provision of technical expertise, process engineering, support for detailed engineering, operator training, and support for commissioning, start-up and performance tests. Prayon will also deliver critical equipment, including tilting pan filters, reaction agitators, scrubbers and separators. The plants, part of what is claimed to be the largest fertilizer plant in Egypr, are scheduled to be completed in 2018. Each will have a capacity of 600 t/d  $P_2O_5$  of phosphoric acid. Prayon says that it will work together on this project with its

longstanding engineering partner Desmet Ballestra, based in Milan.

"Prayon Technologies is delighted to have been selected by NCIC for this new project", said Marc Collin, director of Prayon Technologies. "We had already successfully managed a phosphoric acid plant project for the NCIC Group in Egypt back in 2009 and we are keen to once again demonstrate how our expertise and equipment make the difference."

## SENEGAL

## Another offtake agreement for Baobab

Phosphate developer Avenira says that it has signed another offtake deal for phosphate from its Baobab project in Senegal, which is currently in start-up. Gadde Bissik Phosphates Operations SUARL, the Senegalese subsidiary of Avenira, signed the export rock phosphate supply agreement with private Egyptian trading company Polyserve Import Export and Trade. Under the three-year offtake agreement, Polyserve will purchase 120,000 t/a of rock phosphate from the project's production, with the term extendable at the option of both parties. Avenira, which owns 80% of the Baobab project, has previously signed offtake agreements with Swiss trading company Actatrade and Dubai-based Getax Agrifert DMCC, bringing the total committed tonnage to 360-480,00 t/a. Avenira says that it is continuing to seek further offtake commitments to cover the balance of planned annual production. Total production at Baobab will be 500,000 t/a in the first phase.

Avenira managing director Cliff Lawrenson said: "securing this additional agreement further demonstrates that there is good demand for quality rock phosphate product, as well as showing the market's confidence in the Baobab project's ability to produce and deliver a desirable product."

The company says that it has begun wet commissioning at Baobab, with saleable product expected within weeks.

#### MALAWI

## License granted for hydrochloric acid process

Mkango Resources Ltd says that it has secured a two-year licence for a technology to produce high strength (up to 30%) hydrochloric acid from calcium chloride feed streams using sulphuric acid. The technology, applicable in rare earths processing has been developed by Dr. Thomas Feldmann and Professor George Demopoulos

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of McGill University in Montreal, Canada.

Mkango's processing flowsheet for the Songwe Hill rare earths project incorporates a hydrochloric acid leach step, producing calcium chloride in solution. The HCl is be regenerated using the calcium chloride feed stream, supplemented with additional calcium chloride, together with sulphuric acid produced from sulphur at a plant on-site. The company is also investigating production of a gypsum by-product for sale in Malawi and elsewhere.

William Dawes, chief executive of Mkango, said: "this technology is not only applicable for Songwe but potentially for other primary carbonatite hosted rare earths projects. We are also interested in evaluating the technology's use in other industrial applications where high strength hydrochloric acid is required."

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#### Funding secured for cobalt project

Broken Hill Prospecting Ltd (not to be confused with BHP...) has raised A\$746,000 through a share purchase plan to advance its Thackaringa Cobalt Project near Broken Hill, New South Wales. The company says

that test drilling will begin in September on the project, where assessments put the total resource of 35.7 million tonnes at 0.084% cobalt. The cobalt deposit at Thackaringa is contained in a pyritic rock, which adds the possibility for co-production of sulphuric acid from mining activities, according to a statement by BPL. The funds raised will be used to undertake drilling a programme to verify mineral resources, alongside a metallurgical testing programme, as well as marketing studies on cobalt and sulphuric acid production and development of business models to explore processing options for the ore.

## MYANMAR

#### Amnesty seeks relocation of acid plant

Amnesty International has urged the government of Myanmar in Naypyidaw to immediately relocate a sulphuric acid plant close to Kankone village, as it is posing serious health and environmental problems in the locality. The Moe Gyo Sulphuric Acid Factory, completed in 2007 in the Sagaing region of northwest Myanmar is reported to have caused respiratory, skin and eye problems to the local villagers because of fugitive emissions, as well as damaging soil and crops in the area. The facility was the subject of an investigation committee led by Aung San Suu Kyi in 2013, which found that it had been built without necessary permission from local authorities. The company that runs the factory is owned by the Myanmar military.

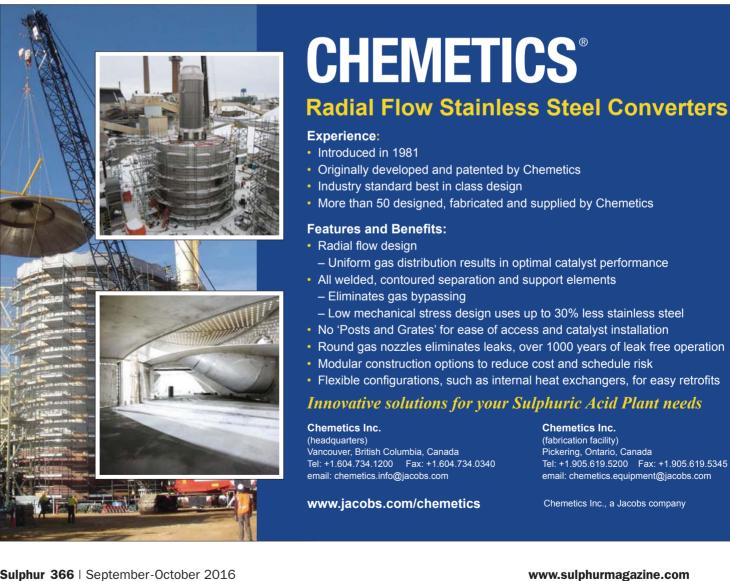
#### TUNISIA

## **Protests halt CPG phosphate** production

Tunisian phosphate rock mining company CPG (Compagnie des Phosphates de Gafsa) has suspended all production at its three main sites due to job protests, Reuters reported on 30 August.

CPG's production has been badly hit by protests and strikes first triggered by the 'Arab Spring' uprising which began in Tunisia. The country produced 8.26 million tonnes of phosphate rock in 2010. But this fell to 4 million tonnes last year, with 1.86 million tonnes produced during the first six months of 2016, according to Tunisia's energy ministry.

The renewed protests will be an early test for the new government of Youssef Chahed.



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**BCInsight** 

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The Sulphur Institute (TSI) has announced the selection of **Ms. Kerry Kurowski**, CMP as Senior Manager, Meetings, Member Relations, and Office Services. Robert McBride, TSI president and CEO, remarked, "We look forward to Kerry's meeting planning experience and her additional skills which will enhance programs and operations."

Ms. Kurowski has worked in the events industry since 2002 having previously been employed in a similar capacity at The Biscuit & Cracker Manufacturers' Association. She is a Certified Meeting Professional and earned a bachelor's degree from the University of Maryland. Ms. Kurowski also serves as the Director of Communications for the Professional Convention Management Association Chesapeake Chapter.

Copper North Mining Corp. has announced the appointment of **Rebecca Moriarty**, CPA, CA as chief financial officer. Mrs. Moriarty is a Chartered Professional Accountant with over 16 years of experience related to the mining industry. She previously spent 11 years at PricewaterhouseCoopers LLP working with public resource companies. She earned her BSc in Geology from Queens University in Kingston, Ontario and later returned to obtain her accounting credentials. Copper North has also announced the resignation of **Julien François**, her predecessor as CFO. The Company thanked Mr. François for his service as chief financial officer since Copper North's inception in 2011.

Fertilizer Canada's board of directors has appointed **Kathy Jordison** of Yara Canada LP as chair for a two-year term.

"Kathy has been a valued member of our board since 2013, and during that time the association has benefitted greatly from her leadership and expertise," said Garth Whyte, president and CEO, Fertilizer Canada. "As we implement our new strategic plan, Vision 2020, Kathy will bring immense value to the association drawn from her nearly 20 years in the industry."

Jordison is vice president, asset development at Yara Canada LP. She has worked in fertilizer since 1998, joining the Belle Plaine nitrogen plant soon after it began operation. She has an extensive background in the management of nitrogen production, sales and the transportation of dangerous goods by rail and truck. She holds an Honours BA from the University of Toronto and an accounting certificate from the Saskatchewan Institute of Applied Science and Technology. In addition to her service to Fertilizer Canada's board of directors, Jordison has been Chair of The Fertilizer Institute's Transportation Committee.

"The fertilizer sector – and the world in which it operates – is evolving," said Jordison. "I look forward to working with the members and staff at Fertilizer Canada to implement the new strategic plan, and make effective changes to benefit the fertilizer industry."

Jordison succeeds **Steve Biggar**, assistant vice president, fertilizer and energy products at Richardson International Ltd. Biggar, who has served as Chair since August 2015, will continue his service to the industry as a member of Fertilizer Canada's Board of Directors.

"On behalf of the Board and the staff, I would like to thank Steve for his exceptional leadership and service as Chair, guiding Fertilizer Canada through the development of our Vision 2020 strategy," said Whyte.

## Calendar 2016

## SEPTEMBER

#### 12-16

Brimstone Sulphur Symposium, VAIL, Colorado, USA Contact: Brimstone STS Ltd, 6547 South Racine Circle, Suite 1600, Centennial, Colorado 80111, USA Tel: +1 909 597 3249 Fax: +1 909 597 4839 Email: mike.anderson@brimstone-sts.com Web: http://brimstone-sts.com/symposia/ vail/vail-registration-page/

## **OCTOBER**

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3rd Middle East Sulphur Plant Operators Network Forum (MESPON) 2016, ABU DHABI, UAE Contact: UniverSul Consulting Tel: +971 2 645 0141 Email: info@universulphur.com Web: www.universulphur.com/mespon

Gas Treating & Sulphur Recovery Workshop, HOUSTON, Texas, USA Contact: Optimized Gas Treating Email: ralph.weiland@ogtrt.com Tel: +1 281 970 2700

#### NOVEMBER

## 7-10

CRU Sulphur 2016 Conference and Exhibition, LONDON, UK Contact: CRU Events Chancery House, 53-64 Chancery Lane, London WC2A 1QS, UK Tel: +44 20 7903 2167 Email: conferences@crugroup.com 14-16

European Refining Technology Conference (ERTC), LISBON, Portugal Contact: Eliot Morton, GT Forum Tel: +44 20 7316 9832 Email: eliot.morton@gtforum.com

## 2017

## FEBRUARY

## 26 – 1 MARCH

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

## MARCH

## 12-15

Phosphates 2017, TAMPA, Florida, USA Contact: CRU Events Tel: +44 20 7903 2167 Email: conferences@crugroup.com

AFPM Annual Meeting,

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

Web: www.afpm.org

## 26-30

SOGAT 2017, ABU DHABI, UAE Contact: Dr Nick Coles, Dome Exhibitions Tel: +971 2 674 4040 Email: nick@domeexhibitions.com

## **APRIL**

TSI World Sulphur Symposium, DUBLIN, Ireland Tel: +1 202 331 9660 Email: sulphur@sulphurinstitute.org Web: www.tsi.org

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# Sulphur and sulphuric acid in Southern Africa

Sub-Saharan Africa's rapidly expanding mining and mineral industries produce and consume significant volumes of sulphuric acid, but the region remains a large net sulphur importer.



Increasing acid capacity: installing the new acid plant at the DPM Tsumeb smelter, Namibia.

ub-Saharan Africa's oil and mineral wealth has attracted considerable inward investment by overseas companies. While the recent stall in the commodities market has put back many plans for new investments, especially in the central copper belt of Zambia and the Democratic Republic of Congo, environmental improvements to smelters are generating considerable volumes of new acid which are substituting for sulphur imports in some areas.

## **Regional sulphur sources**

Sub-Saharan sources of sulphur are extremely limited. The only significant producer is South Africa, at about 280,000 t/a. A good proportion of this comes from sulphur recovered from coal

and gas to liquids production at Sasol, but the rest comes from refining. The refining sector is relatively underdeveloped in southern Africa. There are only 19 refineries, with a total capacity of 1.4 million bbl/d, and most of these are small and relatively simple refineries with low upgrading capacity built many years ago in the decolonisation era, many of which have been forced to close as a result of low refining margins, small local markets, high operating costs and poor yields. Only South Africa, with 490,000 bbl/d and Nigeria, with 435,000 bbl/d, have any significant capacity, and represent 70% of the region's refining capacity between them. Some 375,000 bbl/d is represented by just two refineries - Port Harcourt in Nigeria and Sapref in Durban, South Africa.

In consequence, Africa produces far more oil than it consumes. Nigeria, the largest economy in Africa, is the region's dominant oil producer, with a daily output of 2.4 million bbl/d in 2015, and the country is the fifth largest exporter of oil in the world. However, it has only four refineries - at Kaduna, Warri and two at Port Harcourt - and operating rates have been very low in recent years - as low as 20% according to some figures. Added to this, Nigerian crude is relatively sweet, and local fuel sulphur standards are such that there is no significant sulphur output from Nigerian refineries. Angola produces 1.8 million bbl/d of oil and has only one fullscale refinery.

While the South African refineries have been modernised, they are not without their own troubles, and in January this year Chevron announced its intention to sell its 75% stake in its 110,000 bbl/d refinery in Cape Town. Sasol is said to be considering buying the stake. Outside of South Africa, the only other refinery in the region with any significant sulphur recovery capacity is the China National Petroleum Corp refinery at Khartoum, Sudan.

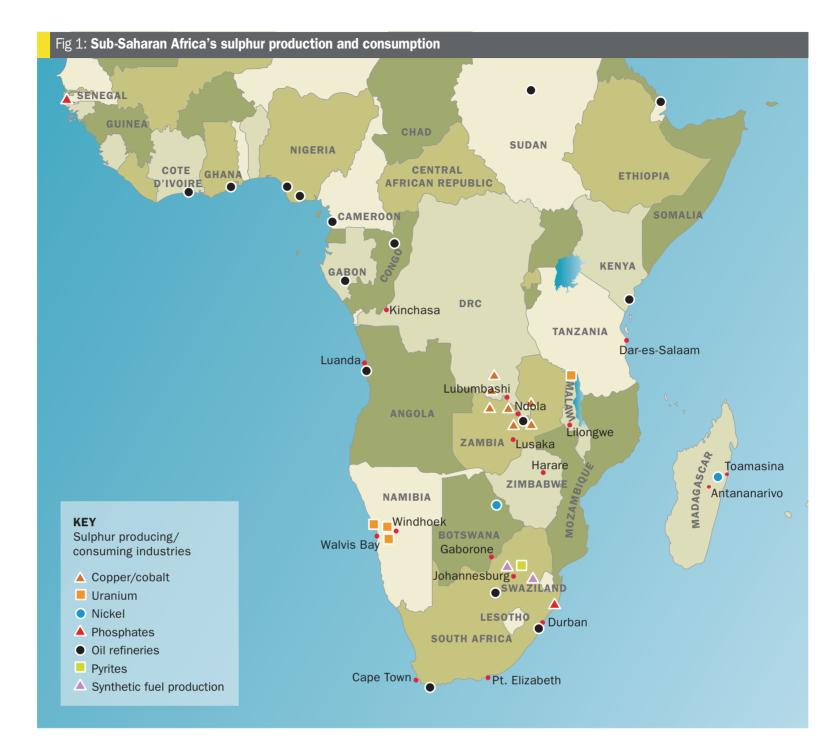
## New refining capacity

The situation could be poised for significant change, however. On the one hand, several of the fastest growing economies in the world are in Africa, and as the region develops, so is transportation use. By 2030, it is expected that there will be 34 cities in Africa with a population of over 3 million, up from 16 today, and vehicle ownership is rising. South Africa has just over 100 cars per 1,000 people; Nigeria has 30, compared to a world average of around 120. This in turn is leading to

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rapidly rising dependence on imported fuel, and it has been suggested that sub-Saharan Africa is ripe for development of additional new refining capacity, allowing the region to benefit from reduced import/ export charges, import charges and lower subsidy payments, and creating skilled local jobs.

Furthermore, fuel quality standards are rapidly tightening. The African Refiners' Association (ARA) is committed to moving to what it describes as an 'AFRI-4' sulphur standard; 150 ppm sulphur ('Euro-III') in gasoline and 50 ppm sulphur ('Euro-IV') in diesel by 2020. Some countries are moving in advance of this. The standards were adopted from January 2015 by the countries of the East African Community (Kenya, Tanzania, Rwanda, Burundi and Uganda), while South Africa is moving from its 500 ppm sulphur standard to 10 ppm ('Euro-V') in 2017. Considering that some countries are moving from 5,000 ppm or even 10,000 ppm permitted sulphur levels, this is a very significant reduction indeed.

These new standards and the surge in domestic demand are potential drivers for considerable new investment in African refining capacity. There are also, somewhat belatedly, signs of private sector involvement as well (previous refinery investment has almost all been by national oil companies). Alhaji Aliko Dangote, Africa's richest man and owner of the Dangote Group, is attempting to raise \$14 billion to build the first private refinery in Nigeria in the Lekki Free Trade Zone in Lagos State. The 650,000 bbl/d refinery would more than double Nigerian refining capacity, and is currently targeting a start-up date of 2019.

However, while Angola, Chad, Ivory Coast, Mozambique, Niger, South Africa, South Sudan and Uganda also have plans to build new refineries in-country, the run of low oil prices has made finding the financing much trickier. Uganda is planning a \$4 billion, 60,000 bbl/d refinery to process newly discovered oil reserves, but recently parted ways from Russian partner RT Global Resources Corp and has now invited participation from SK Engineering of South Korea. Tanzania's 200,000 bbl/d Noor Refinery project has made little progress in recent years, while Angola's Sonangol has retained Engineers

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India Ltd to undertake a feasibility study on its own 200,000 bbl/d Lobito refinery project now that costs have soared from \$5 billion to \$14 billion. Ghana is in the process of revamping its existing 60,000

bbl/d facility, but still has plans to add another 100,000 bbl/d. PetroSA, South Africa's national oil company, is still planning a 300,000 bbl/d refinery at Coega, 'Project Mthombo', but again has so far failed to find funding for it. South Africa is already having to

find \$2.7 billion to upgrade its four existing refineries to meet the new lower sulphur fuel standards.

If all of sub-Saharan Africa's existing refining capacity switched to the mandated lower sulphur targets by 2020, this would represent an extra 350,000 t/a of recovered sulphur across the region. However, with many of the refinery projects still uncertain, the best bet is currently that some tens of thousands of tonnes of extra sulphur will be being produced by that time, mainly from upgrades to existing facilities.

## The mining and metals industries

China's hunger for primary resources of all kinds has driven huge investment in mining and metal processing in Africa in the past decade, and this in turn has both generated and required large volumes of sulphuric acid. However, the slowdown in the Chinese economy and resulting crash in markets for copper and other base metals has also led to many mine closures and cutbacks.

#### Copper

Africa's 'copper belt' stretches across the southern Katanaga province of the Democratic Republic of Congo (DRC) and into northern Zambia. The area had been rapidly developing new copper capacity a few years ago, to feed Chinese demand. However, the slump in copper prices has hit the region equally hard. In particular, Glencore's decision to halt production at Katanga in the DRC and Mopani in Zambia removed 350,000 t/a of copper production. Eurasian Resources Group has cut 1,300 jobs at the five mines it controls in that country, and Trafigura has placed the Kapulo mine on care and maintenance. Copper production dropped in DRC in 2015 for the first time in five years, and fell

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below 1.0 million t/a,. It is forecast to fall still further this year – output is said to be down 14% for 1H 2016 year on year. Chinese interest remains, however, with over a dozen companies involved, and while

Sub-Saharan Africa's key developmental constraint is a logistical one.

% for 1H 2016 year on year. Chirest remains, however, with over companies involved, and while Freeport McMoRan may be getting out – selling its 56% stake in Tenke Fungurume – China Molybdemum has been willing to buy, for \$2.7 billion. Canada's Ivanhoe is

still targeting production at

its high grade Kamoa copper

development in 2018, with

production eventually slated

to reach 300,000 t/a.

In Zambia, copper output rose marginally to 711,000 t/a in 2015, and is projected to reach 750-800,000 t/a this year and up to 1 million t/a next year. New production is coming from the FQM Kalumbila mine, aka Sentinel, which is ramping up, and where output is eventually scheduled to reach 300,000 t/a. In spite of Glencore's temporary shutdown of Mopani, it is also refurbishing facilities there and expects to expand output, and improved power supply may also boost other existing operations.

On the acid side, a second acid plant was completed at Tenke Fungurume this year, bringing capacity at to 2,250 t/d (750,000 t/a) acid for SX/EW operations, and increasing sulphur demand. In Zambia, acid capacity at the Kansanshi copper smelter is over 3,000 t/d, allowing FQM to process additional oxide ores using leaching. In Namibia, the new acid plant at the Tsumeb smelter, now operational, has a capacity of 400,000 t/a of acid, some of which will be used locally for uranium leaching.

#### Nickel

Regional nickel production comes from two major sources. The first is the Phoenix nickel mine in Botswana, which Russia's Norilsk sold to local copper producer BCL in 2014 for \$330 million. BCL has been in considerable difficulties due to the low nickel price and in April 2016 announced a major rationalisation programme. The company operates the largest flash smelter in the world, but does not capture SO<sub>2</sub> at present. It ends up either in slag or is released to the atmosphere. Tightening environmental regulations are pushing BCL to convert this to sulphuric acid, but in the absence of local demand and with the cost of transportation to the sea for export deemed too high, the country is currently looking at possible fertilizer production locally.

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Not strictly Africa, but close offshore, is Madagascar's Ambatovy high pressure acid leaching (HPAL) nickel project. The plant produced 80% of its nameplate 60,000 t/a of nickel in 2015, according to the company. There are two huge sulphurburning acid plants each of 2,750 t/d at the site, which leaches the nickel, and at capacity would require 600,000 t/a of sulphur. The facility is losing money at current nickel prices, and Sherritt took a C\$1.6 billion writedown this year on its earnings as a result.

#### Uranium

Uranium mining is concentrated in Namibia. The country's main uranium project to date is Rio Tinto's Roessing facility, the longestrunning open pit uranium mine in the world, but output has been hit by falling ore grades and low prices and a fire, and output was only 1,200 tU308 in 2015. It is planned for this to rise to 2,000 tonnes in 2016. At peak production the facility consumes around 260,000 t/a of sulphuric acid, but this was only 150,000 t/a in 2014. Previously this was imported, but the company has signed a take or pay agreement with the Tsumeb smelter for a portion of the acid output from its new acid plant. Roessing is building storage tanks at Walvis Bay in case leaching requirements are not sufficient to use all of the acid supplied.

Other projects have been plagued by low metal prices. Canadian Forsys Metals, developing the nearby Valencia uranium deposit, has laid off most of its staff. French energy group Areva has placed the Trekkopje uranium mine on care and maintenance and says it has no plans to re-start it at present. Paladin Energy Ltd operates the Langer Heinrich uranium mine near Walvis Bay, which produced 1,150 t/a of uranium oxide last year, but production is to be cut next year and in any event this uses a caustic leach rather than an acid leach.

The one new project which does seem to have made progress is at Husab, near Walvis Bay in Namibia. This project is owned by Swakop Uranium, a subsidiary of the China General Nuclear Power Group (CGNPG), and uranium mining began in late 2015, although an on-site fire caused delays and a re-start did not occur until February 2016. This is an open pit mine with an acid leach process plant on-site. Production is scheduled to ramp up to 5,770 t/a of uranium oxide per year by 2017, possibly rising to 7,000 t/a, making it the

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second largest uranium mine in the world. The Husab ore-body is claimed to be the third largest uranium-only deposit in the world with measured and indicated reserves of about 140,000 tonnes. There is also a 500,000 t/a sulphur burning acid plant as part of the development, as acid availability from Tsumeb does not seem to be sufficient for the project.

There is also potential uranium production in Malawi, where the Kayelekera uranium deposit is operated by Australia's Paladin Energy Ltd. However, the mine there is currently on care and maintenance due to low uranium prices, and the 230 t/d (76,000 t/a) Outotec sulphur burning sulphuric acid plant is currently idled. Niger also has major deposits of uranium, and of higher grade than Malawi's, but development of the resources has been slow due to political instability and security concerns, and more lately by low uranium prices. The country produced 4,100 tonnes U308 in 2015 at Somair and Comina, co-owned by Areva NC and Office National des Ressources Minieres du Niger (ONAREM).

South Africa's uranium production has historically mainly come as a by-product of gold mining. The only dedicated uranium mine, Dominion, developed by (and later disposed of by) Uranium One, has been on care and maintenance since 2008.

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South Africa produces finished phosphates and DAP and phosphoric acid producer Foskor buys in acid from local smelters as well as operating 2.2 million t/a of sulphur burning acid capacity in three large trains at Richards Bay. Senegal is a major phosphates producer, and sulphur is imported to feed sulphuric acid production for phosphate treatment. Industries Chimique du Senegal (ICS) operates two large sulphur burning acid plants with a combined capacity of 1.8 million t/a of sulphuric acid. Production dropped to less than 50% when phosphate demand was crimped by the economic recession, but has bounced back again to about 70% in recent years.

The prospect of offshore development has been mooted in Namibia, but so far has come to nothing.

#### **Other metals**

Vedanta operates the only zinc leaching project in the world, in the southwest of Namibia. There is a sulphur-burning acid plant for SX/EW extraction, but Vedanta has indicated that the mine which produces the unique skorpionite ore is likely to close in 2018-19.

#### Logistics

Sub-Saharan Africa's key developmental constraint is a logistical one. Many of the metal deposits are a long way from ports. There are few rail lines, and those that do exist are often poor quality. Roads in remote areas are often little better than dirt tracks, made impassable by heavy rains. Even moving acid from Tsumeb to Rossing in Namibia has been complicated by shortages of rolling stock, while road tankers capable of bulk acid transport are in shorter supply and, as Steve Sackett of TradeCorp explained at last year's Sulphur conference, border delays between e.g. Zambia-DRC and South Africa-Zimbabwe.are already long, time consuming and expensive. Placing the two 400 tonne converters for the two 2,750 t/d acid plants at the Ambatovy site in Madagascar necessitated the construction of several bridges to get the large and unwieldy load to the site. Outside of the Republic of South Africa, port facilities are often not set up for large volumes of bulk

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chemical freight, especially dangerous cargoes like sulphuric acid. All of this complicates and makes more expensive large chemical processing complexes.

#### Sulphur balance

The region's major sulphur consumers are South Africa, Senegal and Madagascar, and all are major importers; domestic South African sulphur production is not enough to satisfy local demand. New refinery projects may add some sulphur production in the longer term in Nigeria and elsewhere. However, elsewhere large new additions to smelter acid capacity for environmental reasons are reducing the requirement for sulphur burning acid supply, in Namibia and Zambia. Poor transportation links make long distance acid transport unlikely, and force producers to consider other downstream uses. New sulphur demand may have to wait on an uptick in the commodity cycle, meanwhile.

The critical issue will be how the region absorbs large new volumes of smelters acid in Namibia and Zambia – up to 2.7 million t/a by 2018 according to some estimates. Namibia is looking at a surplus of 200,000 t/a, and Zambia of potentially up to 700,000 t/a. With logistics constrained, there seems to be nowhere for the Zambian acid to go except over the border into the DRC. But even a turnaround in the copper market that allowed more SX/EW capacity back on-stream could not absorb this, and smelters may either have to accept lower prices to displace current sulphurburning acid capacity, produce less metal, neutralise the acid, or find other uses for it.



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# New applications for sulphur in polymers

**Dr. Saeed Alhassan**, Assistant Professor and Director of the Petroleum Institute Gas Research Centre in Abu Dhabi presents the results of work on incorporating sulphur into polyethylene.



he story of sulphur in United Arab Emirates (UAE) is interesting not only because of the expected level of production, but also from the challenge in marketing these quantities and its impact on the sulphur market price. Currently, the UAE produces more than 6 million tonnes of sulphur per annum, which places the UAE among the top six producers in the world. Most of this production is exported, since the local uses for this element is minimal. With the expected increase in energy demand, followed by an increase in exploration and production of sour gas fields around the world, it is inevitable that the sulphur market might experience an excess supply situation that puts pressure on prices.

A similar situation existed in the 1970s when the environmental regulations related to lowering sulphur content in fuel led to a sudden increase in sulphur supply in Europe and North America. This increase stimulated interest in new sulphur applications, as evidenced by the organisation of a symposium focusing on new sulphur applications during the 167th American Chemical Society meeting in 1974 and the 173rd American Chemical Society meeting in 1977. These two symposia have helped in advancing different applications to market such as sodium sulphur batteries, sulphur concrete and sulphur asphalt. Additionally, other uses such as lithium sulphur batteries are coming back to academia and industry arenas because of their high energy density.

## **Sulphur polymers**

In recent years, the interest in sulphur applications has picked up again due to recent advances in sulphur inverse vulcanisation and the development of 2D inorganic materials like molybdenum sulphide, which is an analogue to graphene. To this end, at the Abu Dhabi Petroleum Institute we have also begun working on sulphur applications starting in 2011 as one way to deal with the impending sulphur issue in UAE. In our efforts, we developed composites that contain up to 50% by weight sulphur. The matrices used for these composites are both commodity plastics such as polyethylene and polypropylene and engineering plastics such as polyamide.

Adding secondary components to plastics is a well-established practice in the plastic conversion industry because such components provide specific functions, either as passive fillers or reinforcing agents. The former is achievable by using relatively inexpensive materials that can help in lowering the amount of plastic used, which is in this case more valuable. The latter is achievable by using higher value components such as nanoparticles, which are used to enhance either mechanical, thermal or optical properties of the finished product. When we use sulphur, it acts as both; a filler and as a reinforcing agent, depending on the processing conditions. We used it with low density polyethylene (LDPE), where it was extruded

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## Table 1: Summary of mechanical properties of LDPE and HDPE composites with sulphur

Sample	Sulphur content (by weight)	Tensile modulus (MPa)	Elongation at break (%)
LDPE	Nil	142 ± 8	64 ± 4
LDPE + sulphur	5%	162 ± 3	61 ± 4
LDPE + sulphur	10%	159 ± 6	60 ± 4
HDPE	Nil	673 ± 122	835 ± 54
HDPE + sulphur	5%	556 ± 40	$1,011 \pm 14$
HDPE + sulphur	10%	558 ± 26	1,110 ± 45

at temperature below the polymerisation temperature of sulphur, and hence elemental sulphur acts as a passive filler with some minor improvement in mechanicals properties.

In the case of high density polyethylene, we processed it at a temperature above the polymerisation temperature of elemental sulphur, and by doing so, the mechanical properties of HDPE have changed. The most interesting change is the improved elongation at break of HDPE with the addition of sulphur. It is known that HDPE possesses quite a large elongation at break (ca 800%), but what is surprising is that when sulphur is added, this elongation at break improves to ~1200% with the addition of 15% by weight sulphur. Figure 1 is a photograph of samples after mechanical testing, which show the extent of improvement in elongation at break for HDPE. This in effect can improve plastic toughness and hence open the door for more applications for the same. Table 1 shows a summary of key mechanical parameters for LDPE and HDPE composites with varying sulphur content.

From an economical point of view, these composites are an attractive means to both utilise sulphur as well as increase its value. Thermoplastics in general are traded above \$1000 per tonne compared to below \$100 for sulphur. Adding sulphur as either a passive filler or an active reinforcing agen, would retain the value of these composites or increase it. In both cases, sulphur is used in volume and would be sold as a added value product.

Additionally, we have developed a molybdenum sulphide foam monolith which can be used in separation and catalytic applications. Other applications are under study at our laboratories in the Petroleum Institute. Historically, the sulphur market has been consistent in reaching equilibrium in price and in supply/demand balance, and it is yet to be seen if the recent efforts in developing applications can make a difference. But doing nothing about this matter is not an option any more.





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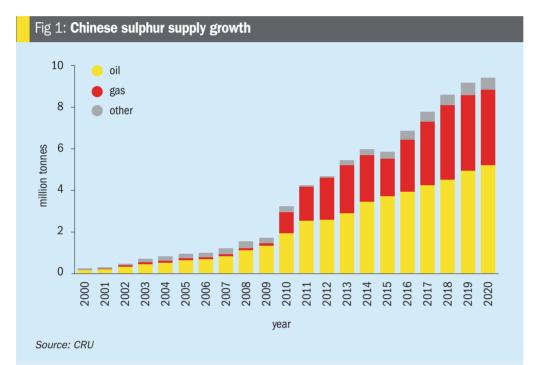
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# New sulphur production in China

The sour gas fields of Sichuan and new refineries on the east coast are generating increasing quantities of domestic sulphur for China. With demand from phosphates slowing, could this lead to falling Chinese imports of sulphur?



hinese sulphur production has risen rapidly over the past few years, from steady growth in refinery output and several large new sour gas projects in the southern province of Sichuan. So far, domestic demand, especially for phosphate production, has kept pace with this, and China has continued to be the world's biggest sulphur importer, averaging around 10 million t/a. But can that continue for many more years?

## **Unconventional gas**

China's gas consumption is the third largest in the world, even though it represented only 6% of primary Chinese energy demand in 2015, and this consumption is increasing rapidly as China becomes concerned about the impact of its coal consumption on air quality and carbon dioxide output. The country is moving towards capping total energy use in terms of coal equivalent as part of the 13th Five Year Plan (2016-2020), and that will involve more use of gas, rising to 10% of energy consumption in 2020. China will launch a national cap-and-trade scheme in 2017 that favours gas.

China has pushed unconventional gas production as a way of maximising its relatively meagre gas reserves. Production of tight gas, coalbed methane and shale gas have been rising, and will represent around 60% of gas output by 2020, split fairly evenly between the three. China has missed recent shale gas targets but in March and September signed two production sharing contracts with BP. BP predicts that Chinese shale could be producing 13 tcf of gas by 2035.

## Sour gas

The push for gas is also driving considerable investment in sour gas extraction, most of it in the southern province of Sichuan. Most of the fields were discovered in the late 1990s, and exploration and discovery continued throughout the 2000s. The first sour gas field to be exploited was Puguang, where there are 410 bcm of reserves with an  $H_2S$  content of around 15-17%. The Puguang sour gas processing plant, operated solely by Sinopec, became operational in 2012, and achieved its maximum capacity of 12 bcm/year in 2014. Sulphur output at Puguang is now over 2 million t/a and could reach over 2.4 million t/a at capacity.

The second major prospect, Yuanba, is of similar size to Puguang – estimates say 210 bcm – but extremely deep; the field is over 7.5 km down in places, and averages 6.7km deep. The  $H_2S$  content at Yuanba is lower than Puguang, at 5%, but the high pressure makes severe demands upon the equipment. The Yuanba development is targeting 3.4 bcm/year of gas, and the first phase began operations at the very end of 2014. Total sulphur output is expected to be 300,000 t/a.

More recently, production began at Chuandongbei, one of the few sour gas projects in China with foreign participation, in this case Chevron, who have a 49% stake in the project against China National Petroleum Corp's 51%. Total proved reserves at Chuandongbei are put at 175 bcm, with H<sub>2</sub>S content between 7-11%. Target production is 7.4 bcm/year by 2018, with gas from the Luojiazhai, Gunziping, Tienshanpo and Dukhouhe-Quikibei fields all being fed to central processing plants. The first of these, processing 250 million scf/d, came on-stream in January this year, producing 350-400,000 t/a of sulphur. At capacity, sulphur output from the entire project is expected to be up to 1.5 million t/a.

## **Refineries**

In addition to its sulphur output from sour gas production, China also has considerable sulphur recovery at refineries, and this figure is also growing steadily. Overall Chinese refining capacity has almost doubled in the past decade, from 7.7 million bbl/d in 2005 to 14.3 million bbl/d in 2015, according to BP. However, capacity utilisation has

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not grown as quickly, and throughput only reached 10.7 million bbl/d in 2015. As with many other industries, China has heavily overbuilt refining capacity and is facing a glut of refined products. The recent start-up of a 200,000 bbl/d refinery at Kunming has added to what is estimated to be 2 million bbl/d of excess capacity in spite of record exports of around 1 million bbl/d - up 45% on last year. Another 260,000 bbl/d refinery will start up in October at Anning. But in particular, there is concern about the plethora of so-called 'teapot' refineries - over 150 small, independent refineries which last year were allowed to import crude from overseas for the first time, and which have capitalised on the fall in oil prices by ramping up production and undercutting the giant state refiners like Sinopec, PetroChina and CNOOC. The teapots are now importing 1.2 million bbl/d of crude – about 15% of Chinese imports.

Chinese refineries have also been upgrading to cope with steadily tightening domestic standards for fuel sulphur levels- now down to 50ppm, and moving to 10ppm ('Euro-V') next year. China is also introducing a 0.5% sulphur limit cap for marine fuels used close offshore in its own Emissions Control Area (ECA). Sulphur output from Chinese refineries is thus continuing a steady rise, reaching around 3.8 million t/a in 2015, and forecast to climb to 5 million t/a by 2020.

## **Sulphur output**

Figure 1, based on CRU estimates, combines these figures for refining and sour gas production. Sulphur output from Chinese sour gas fields continues to rise rapidly, from just 80,000 tonnes in 2009 to over 2.0 million t/a in 2014, and is forecast to reach 4 million t/a by 2020 With additional incremental capacity from refining, China is on course to be producing nearly 9 million t/a of sulphur by this time. The 'other' figure represents sulphur recovered from thermal power plants and rarely exceeds 500,000 t/a.

## **Sulphur consumption**

Sulphur consumption in China is dominated by sulphuric acid production. China's acid production is supplemented by smelter acid – which has been growing rapidly – and pyrite roasting, but sulphur burning continues to be the largest slice of demand. Acid demand is mainly for phosphate fertilizer and other phosphate processing (63%),

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but the rapidly growing industrial sector consumes the remaining 37%. Diammonium phosphate is the most important phosphate fertilizer, and production has continued to grow rapidly, reaching 17 million t/a in 2015, up 6 million tonnes in just the past five years. Once again, China has overbuilt DAP capacity, and has turned into a major exporter to try and deal with the excess capacity within China, leaving it vulnerable to swings in phosphate prices. Chinese phosphate exports reached a record level in 2015, but that was in part due to a collapse in domestic demand, and China is a relatively higher cost producer compared to other major exporters. The Chinese government wants to keep rises in DAP use to 1% per year to 2020, and for it to be level after that, to cope with over-application of fertilizer. The betting is thus for lower Chinese production and exports going ahead in the current low phosphate price environment. In other sulphuric acid consuming industries like caprolactam, China is also struggling with overcapacity. Chinese sulphur consumption was 16.2 million tonnes in 2014, requiring 10.4 million tonnes of imports, can this level of imports be sustained in the face of lower or at least flattening demand and higher production?

## **Sulphur imports**

The rapid growth in Chinese sulphur-burning acid capacity has led to a rapid rampup in sulphur imports over the past two decades, reaching 11.8 million t/a last year, a 17% on 2014's figure, and representing over one third of all global traded sulphur. And in spite of predictions, Chinese sulphur imports have been strong through 1H 2016 so far, up another 12% at 7.4 million tonnes. However, there are signs that not all of this sulphur is reaching domestic consumers. Port inventories of sulphur in China have steadily risen and stood at 1.8 million tonnes in July, the highest level for a few years, and significantly above the average level of 1 million tonnes seen throughout most of 2015, although there were signs of a fall in more recent data. But looking towards the longer term, increases in Chinese domestic sulphur production look set to outpace increases in demand, and China's import levels may fall - perhaps by up to 2 million t/a to 2020. This will still make it the largest importer of sulphur in the world, but Morocco's rapidly rising demand could be closing fast by the end of the decade.



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# Sulphur 2016

CRU's Sulphur 2016 International Conference and Exhibition takes place in London at the Hilton London Metropole Hotel from 7 to 10 November. Participants at this event can expect informative presentations providing project updates, supply and demand forecasts, latest technological advances and best practice operational experiences.

ow in its 32nd year, the Sulphur Conference and Exhibition continues to be the leading annual event for the sulphur and sulphuric acid industry, regularly attracting more than 500 participants from around the globe. The comprehensive conference programme together with the extensive exhibition provide the ideal opportunity to meet industry experts and colleagues and to find out about the latest market trends and technological advances.

The commercial sessions on the first day of the conference feature presentations on market trends, project updates and supply and demand forecasts. The two day split stream technical programme that follows showcases the latest technological developments to improve efficiency and compliance and provides a high-level forum for engineers from the sulphur and sulphuric acid industries to share experiences and find solutions to operational problems.

Whilst retaining all the regular programme content, this year's conference programme also features some new additions. An interactive sulphur recovery troubleshooting clinic moderated by Elmo Nasato of Nasato Consulting will run in parallel to the annual sulphuric acid workshop run by Rick Davis of Davis & Associates. The topic of this year's sulphuric acid workshop will be advances in process control.

In addition, for the first time there will also be technical showcases presentations with 15 minute timetabled slots on the pre-conference workshop day.

# 2016 London

## Sulphur 2016 workshops

Three workshops will be held on Monday 7 November. Places are limited and will be offered on a first come first served basis.

In the morning, **Optimized Gas Treating** will be hosting a hands-on sulphur recovery workshop using process simulation software to gain a better understanding of several broad aspects of modern sulphur recovery. Topics covered will include:

- Thermal reaction: contaminant destruction (NH<sub>3</sub>, BTEX, hydrocarbons); CS<sub>2</sub>, COS, and trace sulphur; oxygen enrichment.
- Sulphur condensers: equipment design and rating; H<sub>2</sub>S/H<sub>2</sub>S<sub>X</sub>/SO<sub>2</sub> solubility; entrainment.
- Catalytic conversion: optimal operating temperature; catalyst selection; COS/ CS<sub>2</sub> conversion vs. Claus reaction; modelling SOR vs. EOR conditions.
- Sulphur storage, handling, and degassing: sulphur viscosity, product quality, H<sub>2</sub>S degassing
- Tail gas clean-up: effect of NH<sub>3</sub> and SO<sub>2</sub> on quench column and amine system performance; EOR design and operation considerations.

Running in parallel, **SNC Lavalin** will be hosting a workshop on project development and how to ease the pressure of raising capital. In today's fluctuating market conditions and capital constrained environment, economic viability and financing opportunities are of the utmost importance for businesses. The workshop will discuss various economic and operational advantages achievable by introducing multiple capital-raising approaches and specific financial models that have been proven by the development of many projects. SNC-Lavalin will also present an overview on the significant role that capital services have played on overall project development and achievements, sharing key lessons learned and case studies of how project financing has been developed for challenging projects and situations.

In the afternoon, **Shell** will host a workshop on the sulphur value chain. Royal Dutch Shell has managed sulphur for over 50 years and currently has over 800 reference points across the globe that demonstrates its expertise across the entire sulphur value chain. This halfday interactive workshop will make use of presentations, case studies, Q&A discussion and networking to provide a view on what Shell has to offer across the entire sulphur value chain, from sulphur recovery to sulphur management, including SO<sub>2</sub> emissions abatement.

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## **Commercial programme**

On Tuesday 8 November CRU's sulphur team and invited guest speakers will provide global outlooks on commodities, oil and gas, sulphur, sulphuric acid, phosphates, base metals, caprolactam, and dry bulk markets. In addition, there will be presentations on the importance of sulphur to food production, and its use in solar cells, wind turbines and electronics as well as a presentation on cybersecurity for the oil, gas and chemical markets.

## **Technical programme highlights**

The technical programme takes place over two days, 9-10 November. A selection of some of the topics that will be presented is outlined below:

Amine Experts will be presenting a paper on how to minimise the chances of catastrophic amine system failures. Equipment malfunction or unplanned shutdown of an amine system can have a devastating effect on a production company's profitability and an equally serious impact on the environment. The goal of this paper is to focus attention on the highest probability threats to a facility's operability and reliability based on the analysis of 300 cases of amine system failure investigated by Amine Experts over the last 18 years.

Aspen Technology will be discussing opportunities to reduce costs while meeting air regulations with integrated simulation for sulphur recovery and acid gas cleaning. Best in-class thermodynamics combined with flexible modelling of equipment enable more accurate and reliable results. Different applications call for different methods of calculating properties and some solutions now allow users to seamlessly transition between different property packages within the same simulation case. Aspen Technology has combined specialised property packages with modelling tools to produce the best solutions for modelling the acid gas removal and sulphur recovery units in the plant.

**Optimized Gas Treating** will be revealing several misconceptions that are commonly held by the industry with regard to ammonia destruction in the SRU reaction furnace. Over the years, much has been published on the pros and cons of single vs. 2 zone reaction furnaces for ammonia destruction but surprisingly, little quantitative data has been published. To quantify the results of each design, several case studies will be reviewed utilising a newly developed SRU simulation tool, which incorporates new kinetic data for the destruction of ammonia from recent work by Alberta Sulphur Research Ltd (ASRL). This model confirms that the pathway for ammonia destruction relies heavily on the oxidation of  $H_2S$ , using  $SO_2$  produced from this oxidation as the primary catalyst for ammonia destruction.

The most critical issue in the performance and operational life of a sulphur pipeline is the safe and reliable re-melt of solidified sulphur to re-establish flow. Pentair Thermal Management will be introducing a new and unique approach for an automated re-melt program for sulphur pipelines, to safely and reliably heat up solidified sulphur in the pipeline without the requirement for continuous operator assistance. State-of-the-art technologies such as continuous fibre optic distributed temperature sensing can be combined with other advanced pipeline instrumentation methodologies to gather key decision-making data. With recent developments in predictive modelling, transient analysis and improved software solutions, it is now possible to create a dynamic, real-time model for the solidified sulphur as it transforms through its phase change inside the pipeline.

**ASRL** will be suggesting and analysing **long term strategies for sulphur storage**. Utilisation of oil and sour natural gas has led to periods in which sulphur is produced in quantities in excess to demand resulting in storage of solid in block form. The longer the product stays in storage, the greater the expense that is incurred in limiting environmental concerns resulting from acid run-off and dust emissions. This paper will review factors which lead to dust and acid run-off and report on field work conducted by ASRL for long term storage of sulphur, either in underground or above ground sites.

Breen Energy Solution will be demonstrating the benefits of a **dewpoint mea**surement device for copper smelting and sulphuric acid manufacture. In a copper smelter an acid dewpoint monitor has been placed in the gas stream downstream of the ESP to measure the acid dewpoint and use it to optimise the air injection to maintain the balance between adequate  $SO_3$  for ESP performance while minimising downstream corrosion. In addition, in the sulphuric acid manufacturing process, there are many sections of the process where there exists a potential for moisture leakage, including the superheater, waste heat boiler and economiser areas. When there is a moisture leak of some kind, it leads to rapid downstream corrosion. A dewpoint measurement device can provide early detection of these conditions leading to a more reliable long-term operation.

Haldor Topsoe will be discussing how to optimise the profitability of sulphuric acid plants through better operating strategies and will focus on how the catalyst may be chosen and operated to improve plant profitability in a number of different ways. Campaign length can be improved, resulting in less downtime, turnaround costs and catalyst losses. Downtime and fuel consumption may be reduced by using the right catalyst and knowhow. Power consumption can be reduced by reducing plant and catalyst pressure drop, saving on energy costs. Finally scrubber chemical consumption can be lowered by improving the conversion over the converter, resulting in savings on both chemical costs and potential by-product disposal. The benefits of the proposed strategies will be illustrated using operational data from industrial sulphuric acid plants.

DKL Engineering will provide details on the first year of operation at Kansanshi's sulphuric acid plant which started production at Kansanshi Mining PLC's copper smelter in Solwezi, Zambia in March 2015. The sulphuric acid plant has performed reasonably well during this period with an average availability of about 96%. However, issues arose in the sulphuric acid plant that had not been evident during the design phase only becoming evident after operation of the plant for an extended period of time. Some of the biggest issues centred around the converter. Other areas where operating problems were encountered were the wet electrostatic precipitators, blower power consumption and preheater. This paper provides details on the problems encountered in the plant, the analysis of the problems and the solutions implemented.

Following the successful commissioning of a heat recovery system in Atlantic Coppers AC3 sulphuric acid plant, Atlantic Copper and Outotec will provide insight on the course of the whole project: Starting with the design process considering distinctive characteristics of removing heat from the gas side of a metallurgical acid plant to manufacturing and construction of the system with minimal impact on the operation of a smelter complex and ending with experience collected during commissioning and operation as well as improvements realised in the efficiency of the plant.

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#### 5 51 **South Korea's** 6 52 7 53 8 54 sulphuric acid industry 9 55 10 56 11 57 12 58 13 59 14 60 15 61 16 62 63 17 18 64 19 65 20 66 21 67 22 68 S-Nikko Copper Inc is expecting the start-up of its fifth purified sulphu-23 69 ric acid (PSA) plant in the second 24 70 half of 2016. Planned to meet growing domestic and overseas demand for PSA 25 71 from semiconductor manufacturers, construction began on the new plant in early 26 72 2015. The new facility is the first of two 27 73 new PSA plants that LS-Nikko is due to complete over the next 18 months, 28 74 with further production expansion under consideration should semiconductor 29 75 manufacturer clients continue to expand 30 76 output. Demand for semiconductors is expected to grow for another two years 31 77

at least. LS-Nikko started construction on its sixth semiconductor grade sulphuric acid plant earlier this year, and it is due for commissioning in the second half of 2017. Both of the new plants have a capacity of 20,000 t/a, and when complete will bring the company's capacity to 100,000 t/a.

"We believe the semiconductor market is bullish, so our company is investing to expand semiconductor grade sulphuric acid production," an LS-Nikko source said. "Samsung and the SK Group are both expanding their semiconductor manufacturing capacity in South Korea, that's why we are expanding our semiconductor sulphuric acid production as it's a single

grade. We supply it in 300kg drums and in ISO-tanks.

In addition to local market demand, LS-Nikko exports some semiconductor grade sulphuric acid, mainly to South Korean customers with overseas semiconductor plants. "We export about 20% of our semiconductor grade sulphuric acid to China," the source said. "It goes to Wuxi near Shanghai, where the SK Group has a semiconductor plant. Some of our semiconductor grade sulphuric acid production expansion will be for export as well."

The company is considering building a seventh 20,000 t/a PSA plant, though no decision has been taken. "Based on our current expansion phase we should consider starting construction of our seventh plant soon. In our current expansion phase we need to build one plant every year," the source said.

## History

LS-Nikko was orginally established as LG Copper, a wholly owned subsidiary of South Korea's Lucky Goldstar (LG) Group. LG Copper's ownership changed in 1999 when, following the Asian financial crisis, Nikko of Japan acquired a 49% shareholding in the company from the LG Group. Soon afterwards, in 2001, LG Copper's

David Hayes reports from South Korea, where major acid producer LS-Nikko Copper Inc. is expanding production of purified sulphuric acid (PSA) to meet rising demand from the semiconductor industry.

Left: The LS-Nikko smelter at Onsan.

name was changed to LS-Nikko Copper Inc. However, ownership of the company remains unchanged with Nikko holding 49% and LG Group retaining its 51% stake.

LS-Nikko's main business activity is the operation of its copper smelting plant at Onsan near Busan in the southeast of the Korean peninsula. Designed to produce 680,000 t/a of copper, the Onsan plant is South Korea's only copper smelter and is the country's second largest sulphuric acid producer, with an annual output capacity of 1.75 million tonnes of general industrial grade sulphuric acid and 60,000 t/a of PSA.

"Our copper production is mostly for the local market. We export some of the industrial grade sulphuric acid as we do not have copper mining in South Korea," the source said. "Our factory is in Onsan because it's the best place to import copper for smelting."

## Korea's acid production

South Korea currently has a total industrial grade sulphuric acid production capacity of about 4 million t/a, as well as PSA production facilities totalling about 160,000 t/a. In addition to LS-Nikko, Korea Zinc Co Ltd, which operates two zinc smelters in Onsan, is South Korea's largest general industrial grade sulphuric acid producer

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with a combined annual output of 580,000 t/a of zinc and 290,000 t/a of lead, along with about 2.1 million t/a of general grade sulphuric acid and PSA.

South Korea's other industrial grade sulphuric acid producers are all small fertilizer companies, among which only Dongbu Fertilizer Co Ltd is understood to be in production. Dongbu produces ammonium sulphate and formerly produced phosphoric acid using imported rock but now imports phosphoric acid instead. "Dongbu produces about 150,000 t/a of sulphuric acid. Other producers such as Cosmo Chemical are not producing now as they have stopped fertilizer production," the source said. "The other sulphuric acid producer was Korea Caprolactam, but they have closed their plant because of an oversupply of caprolactam."

In addition to its semiconductor grade sulphuric acid production facilities, LS-Nikko operates two industrial grade sulphuric acid plants in the Onsan copper smelting complex, with a combined capacity of 1.75 million t/a. The original sulphuric acid plant is capable of producing 650,000 t/a, while the second plant, which started up 20 years ago, is designed to produce 1.1 million t/a. A number of small plant expansions have been carried out on both plants over the years, the last being completed in 2011.

"We are producing general grade sulphuric acid at full capacity and we did so in 2015. The market for sulphuric acid is very bearish; it's bad now because of the low oil and metal prices," the source commented.

#### **Domestic demand**

South Korea's domestic market for general industrial grade sulphuric acid is about 600,000 t/a, according to industry figures, with demand remaining stable in recent years. Most local demand for sulphuric acid is to make industrial products including batteries and for water treatment, while a small amount is used as a food additive. LS-Nikko supplies about 300,000 t/a of general grade sulphuric acid to the domestic market each year, accounting for about 50% of local demand, while around 1.30-1.35 million t/a of the company's output is exported.

"In South Korea we have many sulphuric acid customers who are car battery manufacturers who supply locally and export, local water treatment companies; also, metallurgy companies supplying steel products and car wheels to the local market. Local export customers are making fertilizers for export, mostly to India," the source said.

## **Exports**

China is the largest export market for LS-Nikko's general grade sulphuric acid exports, taking about 50% of the company's total overseas shipments. "We have two customers in China, both are distributors. Our general grade sulphuric acid exports are used by fertilizer companies, water treatment plants and as food additives," the source said. "The Chinese sulphuric acid market is always expanding but their sulphuric acid supply also is growing, and faster than overall demand, so we expect that their imports will start to get smaller every year. We have exclusivity contracts with our distributors. We supply them through about five or six different seaports."

Australia is LS-Nikko's second largest export market. Most of the firm's sulphuric acid shipments are used for uranium mining. "We have two or three major customers in Australia including the second largest uranium mine which is Era Mine in northern Australia," the source said. "The Australian sulphuric acid market is very stable. Uranium prices are not so volatile so uranium production is stable."

Chile is another important market for LS-Nikko with most shipments being used for copper smelting. "We have many customers in Chile including Codelco. The market is bad there at the moment because of the low copper price," the source said. "Copper mines in Chile are working at 60-70% of their capacity, so sulphuric acid prices there are depressed as well."

Southeast Asia is another market for general industrial grade sulphuric acid, and one that is poised to grow in importance. Most of LS-Nikko's exports there are used by industrial customers, including battery makers, and for water treatment. "We supply Thailand, Indonesia, Malaysia and Vietnam, sometimes the Philippines," the source said. "Some of these countries' electricity supply is not so stable so many people own a battery to have their own power supply because of the unstable mains electricity supply."

LS-Nikko previously supplied the Coral Bay and Taganito nickel leaching plant operators under long term contracts but now supplies these clients on a spot order basis. Both the Coral Bay and Taganito projects are operated by Sumitomo Metal Mining Co of Japan. Most of the combined annual imports of about 1.1 million tonnes of.sulphuric acid used at the two plants are supplied by Japanese smelters. LS-Nikko supplied two sulphuric acid cargoes to the Philippines last year when supplies from Japan were interrupted last autumn.

"There was a fire last year at Pan Pacific Copper, our sister company, and the biggest copper smelter in Japan. They had a big fire last September and they stopped production until the end of December. They shut down for three months as the control room burned out and they had to order new equipment. They lost 300,000 tonnes of sulphuric production; some was for the local market but most was for export. Taganito did spot sulphuric acid orders and we negotiated two orders for 20,000 tonnes."

## **Opportunity in Indonesia**

Meanwhile, LS-Nikko is looking to expand sulphuric acid exports to Southeast Asia in future to offset an expected decrease in orders from China, where local production of general grade sulphuric acid is due to increase in future. "We will have to rebalance sulphuric acid supplies from China. There is more competition there, so we are looking for new markets," the source said. "In the near term the sulphuric acid market is not so good; it's bearish and there is oversupply. Competitors are increasing their capacity including Korea Zinc and Pasar, the copper smelter in Isabella in the Philippines. In the longer term we expect new fertilizer projects in Southeast Asia, also more demand in Mexico and Peru which are expected to open new copper mines using sulphuric acid leaching in 2018 and 2019."

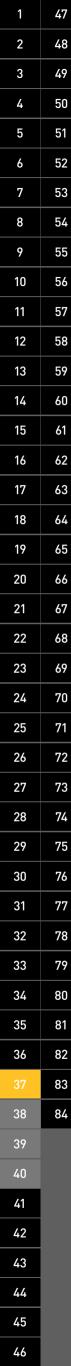
LS-Nikko is currently negotiating a supply contract with Indonesian fertilizer manufacturer, PIATC, which is an associate of state-run PT Petrokimia. The company is building an NPK fertilizer plant in Kalimantan which is estimated to require from 500-800,000 t/a of acid once production begins. In Malaysia, LS-Nikko is negotiating a supply contract with NPA Malaysia ,which is building an NPK fertilizer plant that is estimated to require from 300-400.000 t/a of acid. "There will be big new demand for sulphuric acid in Southeast Asia. These two NPK plants will start up in 2018 or 2019," the source said. "We are hoping to supply 100-150,000 t/a of sulphuric acid to Indonesia and we hope the same amount to Malaysia."

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## A twice yearly review contributed by Alberta Sulphur Research Ltd

# ASRI REVIEW

# Storage of solid elemental sulphur: will it be necessary? How best to do it?

**P.D. Clark**, Director of Research, Alberta Sulphur Research Ltd (ASRL) and **H.H.M. Wan**, **P.M. Davis** and **P. Alegre** of ASRL examine the results of long-term studies by ASRL into block storage of sulphur, and the best options if sulphur must be stored for very long periods.

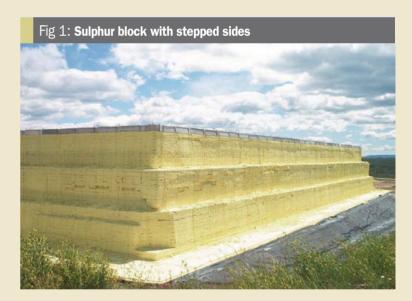
eriodically major producers of sour hydrocarbons, usually those tapping sour gas, have had to store sulphur when demand has fallen short of supply. In Alberta, up to 30 million tons was in storage in the early 1980s and lesser but still substantial quantities have accumulated at various times in France, Saudi Arabia and most recently in Kazakhstan. Sulphur demand is a complex matter involving global economic trends but, in the main, sulphur demand in the past has been largely controlled by its use in phosphate fertilizer production. Factors affecting demand are gradually changing as uses for other products are growing faster than the traditional uses like fertilizer. Reasons for these changes in sulphur use are beyond the scope of this article but, in summary, are linked to demand for sulphuric acid in providing basic materials, nickel and uranium for example, and for elements used in high-tech electronics. On the supply side, sour gas producers in Abu Dhabi, Turkmenistan and Saudi Arabia are set to obtain a dominant position in sulphur markets as these countries continue to exploit sour gas reserves. The rate at which such reserves can be brought on-stream will determine the extent to which the longpredicted sulphur surplus actually materialises. But, most likely, sulphur storage will be needed in the Middle East and elsewhere as the inevitable fluctuations occur in the world economy.

The goal of this article is to present a summary of field research that ASRL has conducted over the last 15 years on methods for long term block storage of solid sulphur. 'Long-term' is defined as in excess of 25 years, as experience has shown that a few simple maintenance measures enable safe and environmentally benign storage up to and, perhaps, over that time period.

#### **Current storage technology**

Solid sulphur is stored in blocks made by pouring liquid in 10 cm or so layers across a base prepared to withstand the mechanical stress imposed by a 20 m high sulphur block. It is important to isolate the sulphur from the sub-soil to prevent contamination of the sulphur during its eventual recovery. Base preparation consists of removal of topsoil, addition of gravel and compaction to the required density. Usually, a polymer liner is placed on the compacted base but both concrete and asphalt pads may also be used. Another function of the base is to isolate the sulphur from the sub-soil

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microbes which may cause acidification of the sulphur and contamination of the surrounding environment through release of sulphuric acid. Aluminium forms are used to contain the liquid sulphur until it solidifies and promote even distribution of the liquid. It is particularly important to construct a block with stepped sides to avoid collapse of the vertical walls (Figure 1). It is crucial to limit the depth of the liquid pour to allow complete solidification of each layer. In practice, the surface of the liquid layer freezes first so if the liquid layer is too thick, the insulating properties of that solid layer isolates the remaining liquid leading to build up of liquid pools over successive liquid pours.

Historically, individual blocks have contained as much as 2 million tonnes of sulphur and some have been kept in place for at least 20 years. As mentioned, thio-metabolising bacteria may acidify the surfaces of a block but, since these bacteria are killed above 50°C, each liquid pour sterilizes the new surface. However, on completion of the block, these airborne organisms will populate the surfaces down to a depth of about 3 cm. These bacteria receive

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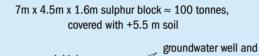
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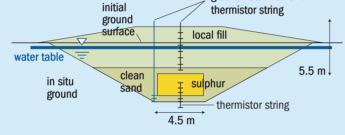
Fig 2: Molten sulphur is being poured to construct the underground sulphur block situated below the water table.



Fig 4: Schematic of the sulphur block below the water table

#### site #1 below water table





the necessary nutrients on the wind and grow rapidly in the 20-35°C temperature range. Water is, of course, also needed for bacterial growth but, even in dry climates, enough water seems to be retained in the porous structure of the sulphur to support rapid growth at certain times of the year. The sulphuric acid excreted by the micro-organisms is washed off the block by rain and snowmelt, requiring that run-off be collected and neutralised before discharge to the environment. Other factors which result in degradation of a sulphur block are freeze-thaw of water in the surface laver and heating-cooling cycles in summer, during which daily changes in surface temperature may be as much as 50°C to a maximum of 85°C. Both effects result in compressive force in the surface layer leading to surface deterioration in both cold and hot climates. The overall result is cracking of the surfaces and formation of sulphur dust which may be blown into the surrounding areas. Because oxidising microbes only grow at sulphur surfaces, accumulation of

sulphur dust at the top surface of the block accelerates bacterial growth rates such that the rate of acid production increases with time.

Most of the blocks that have been built have been reclaimed within 20 years so it is not clear what would happen over longer periods. Significant maintenance is required for sulphur blocks over a 20 year period, thus storage over longer periods would require ongoing investment to ensure adequate protection of the environment and also to maintain the sulphur quality. In the late 1990s ASRL initiated a program of field research with its members to determine "best practice" for long-term sulphur storage. The thinking in Alberta around 2000 was that sulphur from oil sands and continued sour gas production would 'submerge' the province in sulphur, but light, sulphur-free shale oil and gas in North America has changed that viewpoint. Now it is projected that Middle East and Central Asian producers will produce excess sulphur as they strive to meet their regions' energy

demands using sour methane. Blocks of sulphur may become common sights in Abu Dhabi, amongst other locations.

local clay fill

tocal

in situ

ground

sand fill

Fig 3: Construction of the underground sulphur block situated above the water table is almost complete.

Fig 5: Schematic of the sulphur block above the water table

site #2 above water table

 $7m \times 4.5m \times 1.6m$  sulphur block  $\approx 100$  tonnes,

covered with +5.5 m soil

4.5 m

#### **Underground storage**

water table 🗐

One suggestion was to store sulphur in subterranean excavations such as those produced in the course of recovering surface oil sands deposits. Where excavations are not available, it may be possible to simply cover the sulphur block in a large mound of gravel and soil. These scenarios were developed and studied by ASRL at the Syncrude Canada oils sands site (Figures 2 and 3). The design of these pilot sites (Figures 4 and 5) were such so as to have the sulphur submerged in water in one case, and above the water table in the other. The sites were monitored over a period of 6 years and then examined more carefully with partial recovery of sulphur in the 7th year. Interestingly, sulphur from the submerged site had become contaminated by organic debris from the multitude of organisms that had permeated the block with the water inflow. Despite

the generally cold conditions  $(4-7^{\circ}C)$ , both aerobic and anaerobic organisms had flourished over the relatively short timeframe of the project, and it was concluded that if sulphur was to be stored underground, it must be isolated from ground water. Otherwise, a plume of sulphide and sulphate would leach from the sulphur, leading to significant change, if not damage to the local environment. Very importantly, the sulphur would become unusable without purification.

groundwater well and

5.5 m

thermistor string

clean sand

thermistor string

When sulphur from the partiallyburied but dry block (Figure 3) was examined it was found to be in pristine condition (Figure 6). The sand and soil used to build the mound was dry below 50 cm and the topography of the mound was such that rainfall and snow melt had shed down the sides of the small hill, preventing little if any water reaching the sulphur. The top surface of the final soil layer of the mound had become completely vegetated, thus acting as a trap for rainfall during the summer months. Furthermore, winter temperatures of -40 to -15°C had resulted in

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Fig 8: Hail damage – plastic covered block



freezing of soil and subsoil down to at least 0.5 m, another reason why water did not penetrate to the sulphur surface. As a consequence, micro-organisms did not penetrate to the sulphur with the result that it remained uncontaminated.

From a practical viewpoint, a commercial scale block of sulphur covered in a mound of sand and sub-soil may not be possible as not only would a large investment be required to obtain and place the materials, a land surface area at least double the size of the block would be needed to accommodate the sloping sides. Moreover, a sophisticated and ongoing monitoring program would probably be imposed by local authorities to ensure that nothing was going wrong. Also, if sulphur markets suddenly improved, it would not be easy to access the sulphur. For these reasons, ASRL suggested a commercial strategy in which sulphur would be covered in a temporary manner affording protection

and inexpensive recovery when market conditions allowed its sale. Also, it was suggested that conventional blocks would be built and only covered after 25 vears when and if it became clear that the sulphur could not be moved into the market. The results of this field trial are discussed in the following section.

#### Storage in covered blocks

The key aspect of sulphur storage in blocks is to prevent access of microorganisms to the surface and limit damage due to freeze-thaw and heating-cooling cycles. Choice of a suitable cover is not quite as simple as it might first appear as it must be relatively cheap and be able to withstand environmental influences. Imagine covering a large block with a water impermeable sheet of plastic and what would happen if 5 cm of rain was received in a 1-2 hour period. The amount of water cascading from such a block would require

a drainage and water collection system as least as sophisticated as any urban setting. Of course, it would be quite easy to apply a plastic cover, and drainage systems are just a matter of investment. One advantage of an uncovered block is that it absorbs water like a sponge during moderate rainfall, releasing it over hours and days after the rain has stopped. The amount of water impinging on the block is the same as for the plastic covered block but the rate at which it cascades from the block is reduced. thus simplifying its management. Hence cover materials which still allow absorption of water into the sulphur during heavy rain may be advantageous.

ASRL, in collaboration with Shell Canada and other ASRI members selected potential covers and constructed four 100 tonne blocks at the Shell Burnt Timber gas plant. Limestone gravel, plastic, and stucco concrete were studied in comparison to a control block (Figure 7). Plastic without additional cover was chosen for study because it was thought to be cheap to implement on a commercial scale, despite the potentially high cost drainage system that would be needed for commercial implementation. Burnt Timber turned out not to be the best of

too cool in the summer for rapid bacterial growth. due to its altitude, and also because the advent of the plentiful shale gas resulted in the premature closure of that facility shortening the period of the project. It is much easier and cheaper to drill and fracture shale reservoirs compared to running a sulphur plant and dealing with the sulphur!

vered block

Fig 9: Vertical side stucco concrete

W

covered block-deterioration of the cover

locations as it was a little

In summary, the plastic cover was not suitable in the Alberta climate as it was destroyed in a particularly vicious hail storm (Figure 8). Most likely, a plastic cover would be adequate if covered with ca. 30 cm of a gravel-like material but then the economics for this option would be less favourable. Another cover that was tested was

a thin layer (ca. 5 cm) of stucco concrete that was sprayed on the top and side surfaces. This option also had limited effectiveness as it deteriorated significantly over the 3 years of the project as a result of weathering (freeze-thaw) effects. In particularly, loss of stucco from the vertical sides (Figure 9) was significant and accelerated with time. The potential chemical effect of stucco was thought to be important as the high pH generated by water penetration of the alkaline stucco creates a condition which inhibits bacterial growth at the sulphur surface. Specifically, neutralisation of any sulphuric acid generated at the surface results in calcium sulphate which should prevent bacterial growth (Figure 10). However, cracking and loss of stucco integrity would probably necessitate ongoing repair to maintain its effectiveness.

The third cover, limestone chips, was perhaps the most effective as no change in sulphur quality was observed and no deterioration of the limestone occurred. Since limestone is alkaline in nature, any sulphuric acid that did develop at the surface would be neutralised, again producing calcium sulphate (Figure 10). Thus, in theory, water run-off from the block would require no treat-

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ment before discharge. In practice, runoff from the limestone block was neutral. However, it is not clear if acid had been generated as even on the control block the cold conditions at Burnt Timber meant that only small quantities of acid was found. In addition, it proved quite difficult to collect water samples from the limestone covered block as even during heavy rain the porous limestone absorbed water which evaporated to the atmosphere after the rain had stopped. One important aspect of the limestone layer was that it was thick enough (ca. 30 cm) to prevent heating of the sulphur surface during summer days. Thus, only small temperature swings were observed at the sulphur surface (13-17°C) compared to the change seen at the control block surface (4-37°C).

## Commercial strategy for long term sulphur storage

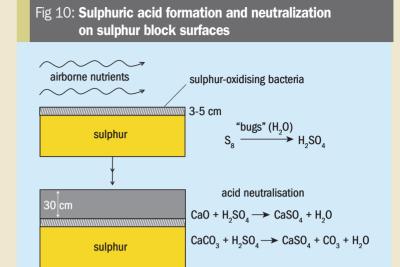
Although the ASRL studies cannot be defined as exhaustive, we conclude that the limestone chip cover would be the most useful. Thus, after a commercial scale block had been in place for some time and it was realized that this sulphur could not be sold in the nearterm, limestone chips could be placed on the horizontal surfaces (Figure 11). Most probably, there would be no need to protect the vertical step sides as any sulphuric acid that did develop on these regions would be neutralized as it washed onto the lower horizontal shelf. Moreover, sulphuric acid that had developed on the sulphur surfaces before application of limestone chips would be neutralized so no special treatment of the sulphur would be needed before placement of the limestone cover. A drainage trough around the base of the block containing limestone with some added calcium oxide would serve to neutralize acid run-off in the period during which the sulphur was uncovered.

Given the vagaries of the sulphur market, the limestone cover would give the desired flexibility needed to meet new demand, should it occur, as it could be removed from sections of the block as needed.

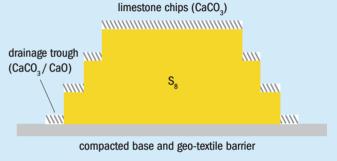
Also, a limestone chip cover would be expected to be durable over many decades and require no special environmental permits for its use.

#### **Acknowledgements**

AMOCO Canada Petroleum Company, BG Technology, Canadian Natural Resources Ltd., Enersul Operations, ENI SpA (ENI Technologie), Hazco Environmental and Decommissioning Services, Shell Canada Limited, Statoil ASA, Suncor Energy Inc., Syncrude Canada Ltd., Prism Sulphur Corporation, Total SA.







- limestone mitigates temperature swings, holds up rainfall, neutralises H<sub>2</sub>SO<sub>4</sub>
- in-situ neutralisation of any sulphuric acid
- sulphur may be recovered as needed (end to end to retain step structure)

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PureChem Services-Canwell, ConocoPhillips Company	Husky Energy Inc.	Porocel Industries LLC	The Petroleum Institute/Abu Dhabi
Enviro-Industries Ltd.	IPAC Chemicals Limited	Prosemat	National Oil Company (ADNOC)
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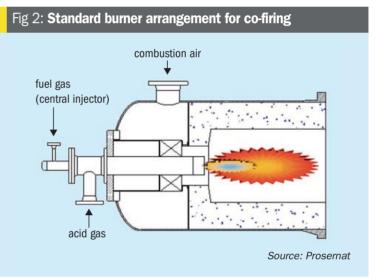
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# **SRE targets continue to rise**

Around the world sulphur recovery efficiency (SRE) targets have been increasing. Over the following pages we report on the technologies being used in sulphur projects around the globe to reduce  $SO_2$  emissions and meet more stringent environmental regulations.

# **SRU design challenges in Russia**





n 2013 Prosernat was awarded the contract for the complete delivery of a sulphur recovery unit for Russia. The customer at that time intended to invest in the revamp of a unit for desulphurisation in connection with an increase in capacity.

Within the framework of this project, Prosernat has designed and supplied the sulphur recovery unit as a complete modular unit. The SRU configuration is a Claus unit with one thermal stage and three catalytic stages including a special burner used in co-firing mode.

#### **Emission standards requirements**

The unit is designed for 10.5 t/d of recovered elemental liquid sulphur.

The guaranteed sulphur recovery shall be no less than 96% of the sulphur processed in the amine acid gas feed. Sulphur produced in the SRU shall meet the requirements for grade 9998 in accordance with GOST 127.1-93.

#### Acid feed gas quality

One specific input for the design of the SRU is the very low  $H_2S$  content in the acid gas. The design value of the  $H_2S$  content in the acid gas is 28 vol-% but this figure varies between 25 to 30 vol-% and represents the main challenge for the design of the SRU. Another constraint is the possible presence of unsaturated hydrocarbons in the feedstock which could have an impact on the operation and performance of the plant depending on the plant configuration.

Operation with low  $H_2S$  content acid gas leads to unstable flame operation in the Claus burner due to the low heat input of the lean gas to be burnt in substoichiometry following the Claus reaction. It is generally accepted that the minimum furnace temperature required to maintain a stable flame is in the 850 to 950°C range.

Various options are available to maintain the flame temperature in this range:

- acid gas enrichment;
- oxygen enrichment;
- acid gas/air preheating;
- by-pass of one part of the acid gas (split-flow);
- fuel gas co-firing (spiking);
- a mix of the last four options.

#### **Technology Selection**

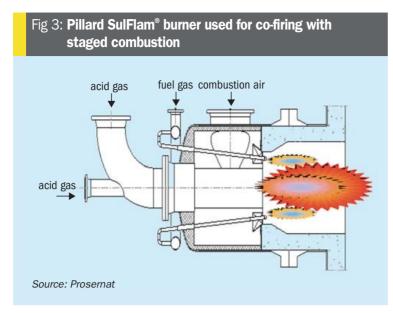
The minimum temperature to be maintained into the reaction furnace has been set at 980°C to ensure the complete destruction of the hydrocarbons contained in the acid gas.

Even if acid gas enrichment can be used to increase the  $H_2S$  concentration in the acid gas, this option appears to be

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expensive both in terms of investment and operating costs.

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The oxygen enrichment option has been excluded due to the operating cost of pure oxygen. It is to be noted that for very lean  $H_2S$  acid gas, oxygen enrichment at 100%  $O_2$  is required to reach the minimum temperature, leading to a more complex operation and higher safety risks associated with pure oxygen operation.

The split-flow configuration (by-pass of one part of the acid gas to the catalytic section) is not possible as the presence of some unsaturated hydrocarbons species on the catalyst leads to the formation of Carsul (polymeric carbon-sulphur compounds) which deactivates the catalyst.

Finally the co-firing option with the addition of air/acid gas preheating was selected to give the best capex and opex solution while providing better flexibility for the operation.

#### **Specific Challenges**

The main challenge for this SRU is to be able to treat a very lean acid gas while reaching the performance and ensuring reliable operation.

Another challenge is the local ambient conditions. The temperature of the coldest five-day period is -35°C. The low ambient temperature exposes the unit to potentially high heat losses. Due to geometric considerations, small capacity SRUs are more exposed to heat losses than high capacity SRUs.

The entire unit has been designed with a proper winterisation system to avoid operating upsets (condensate freezing, sulphur induced corrosion due to cold points, reaction furnace heat losses, line choking...).

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#### Unique design features Main burner

The main concern with co-firing operation is to select an adequate burner in order to avoid problems related to the fuel gas combustion.

With standard burners, the additional fuel gas is often supplied in the centre of the burner and injected in the acid gas (Fig. 2). With such a configuration, the fuel gas combustion is carried out under substoichiometric conditions causing unburnt hydrocarbons, soot formation and COS/  $CS_2$  to increase.

A specific burner is mandatory like the Pillard SulFlam<sup>®</sup> selected, provided by Fives. With this burner additional fuel gas is supplied peripherally and injected in the air where it is burnt with excess air. The remaining air is then available for the Claus reaction. Through this staged combustion, the issues encountered with a standard burner are no longer a concern.

The quantity of fuel gas has been minimised to avoid dilution of the process gas and to limit the part of air dedicated to the fuel gas combustion. A dilution of the process gas thermodynamically affects the sulphur recovery, while too much air affects the control accuracy required to maintain the Claus  $H_2S/SO_2$  ratio at 2.

To minimise the quantity of fuel gas, the acid gas is preheated at  $120^{\circ}$ C and the air at  $320^{\circ}$ C.

#### **Claus catalyst**

While the  $COS/CS_2$  formation is minimised by the implementation of the staged combustion burner, these species still account for a non-negligible amount of sulphur feeding the catalytic stages. Maximum conversion of these species is therefore required to meet the expected sulphur recovery yield. For this reason, it has been decided to load the three catalytic stages with only  $TiO_2$  catalyst (CRS-31, manufactured by Axens), which offers the best solution for this case.

CRS-31 titania catalyst offers some advantages compared to Claus alumina catalyst: high  $COS/CS_2$  hydrolysis performance allowing colder operation (which results into higher sulphur recovery thanks to the more favourable thermodynamics of the exothermic Claus reaction), lower residence time to reach the equilibrium, longer catalyst service life and robustness.

#### **Current status**

Final assembly of the modules at the site took place in December 2015 and commissioning activities were started in January 2016. At the same time, training at the client facility was organised by Prosernat for the client operating team.

Despite difficulties due to the cold weather, the unit was started-up in February 2016 in collaboration with the client operating team and the Prosernat team.

After the start-up, the Prosernat team left the site but the client team and Prosernat experts keep in touch analysing trends from DCS data on a regular basis.

#### Initial operation results

From the start-up, the unit has been stable and performs as specified with a sulphur recovery above 96%, producing a sulphur quality that is bright yellow and shows no sign of carbon contamination.

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#### AMEC FOSTER WHEELER USA

## **State-of-the-art sulphur recovery in Latin America**

S Kafesjian, N Watts and Q Kotter

his case study highlights the emission standards, key design features,

and early start-up operations of a state-of-the-art, very low emission sulphur recovery unit in a rapidly developing nation in Latin America.

Rapid population and economic growth have fuelled a sharp increase in the country's vehicle fleet (48% increase between 2007 and 2012), raising concerns about air quality. The government has prioritised modernisation and upgrade of the country's refineries, with funding provided from a combination of public investment through bonds, loans from international funding agencies, and investment banks, and the refinery owners in the case of nongovernment owned refineries.

Emission standards for vehicles as well as fuel quality requirements have been implemented. As a result, sulphur in diesel fuel will be limited to 50 ppm starting in 2016. These limits are implemented to bring the sulphur content of transportation fuels in line with Euro IV regulations.

To meet new regulatory limits, a major refinery in the country recently completed installation of a middle distillate hydroprocessing unit. The sulphur removed from the fuels is converted to  $H_2S$  that will be separated using amine treating. Some  $H_2S$  will also be present in sour water effluent from the hydroprocessing unit. A new amine regeneration unit and sour water stripper separate and capture the  $H_2S$ , from which elemental sulphur will be recovered in a sulphur recovery unit (SRU). Design basis SRU feed streams are Table 1: Design basis feeds to SRU

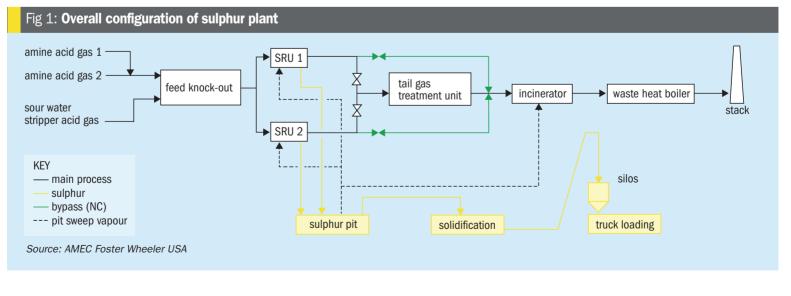
	Amine	SWS acid gas	
Component, mole %	Source 1	Source 2	Source 1
H <sub>2</sub> S	72.4	90.0	23.6
H <sub>2</sub> O	13.3	9.5	42.3
HC	2.1	0.5	0
NH <sub>3</sub>	0	0	34.1
C0 <sub>2</sub>	12.2	0	0
Total	100	100	100
Source: AMEC Foster Wheeler USA			

shown in Table 1. The Claus unit is followed by a hydrogenation/amine tail gas treating unit.

Atmospheric emissions of  $SO_2$  from the SRU must meet the standards of the International Finance Corporation (World Bank), the maximum being 150 mg/Nm<sup>3</sup> (at 3%  $O_2$  dry). As a result of this project, residents will benefit from greatly reduced refinery and mobile source  $SO_2$ emissions. Currently, refinery acid gas containing H<sub>2</sub>S is disposed of by combustion in a refinery heater with no emission controls.

Amec Foster Wheeler's proprietary sulphur recovery technology was selected for the SRU and tail gas treating unit (TGTU). A process design package was supplied by the sulphur technology group located in Salt Lake City, Utah, USA. Engineering, procurement and construction was awarded to a consortium of companies by competitive bidding. The SRU section consists of two identical parallel trains including common feed stream KO drums, separate thermal and catalytic stages, heat recovery and sulphur condensers. A common TGTU, consisting of a hydrogenation/hydrolysis reactor, direct contact cooling, MDEA treating and regeneration, treats SRU tail gas. TGTU off-gas (or SRU tail gas) goes to an incinerator with waste heat recovery then to the atmosphere. Liquid sulphur product is collected in a below grade concrete pit, and pumped to solidification and bulk storage (Fig. 1).

Very low allowed  $SO_2$  atmospheric emission was the principal challenge in this design. The PDP contract required several process guarantees, including atmospheric  $SO_2$  emission level. Overall sulphur recovery in excess of 99.96% would be required to meet the emission standard. A further challenge was imposed when the client stipulated the use of standard (nonformulated) MDEA in the TGTU. Although



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liquid sulphur degassing was not required, the amount of  $H_2S$  outgassing from the sulphur product is significant and could potentially result in excessive  $SO_2$  emission if routed to the incinerator in the conventional manner.

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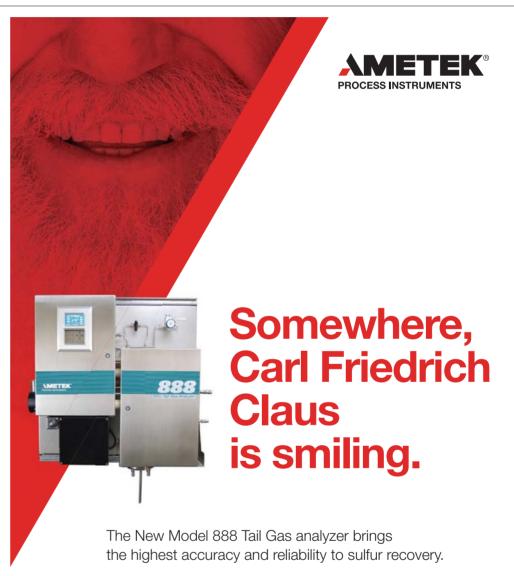
Overcoming the difficult task of meeting restrictive  $SO_2$  emissions was achieved by applying several design practices known to result in very high overall sulphur recovery.

A partial load of titania catalyst was included in the first Claus reactor in each SRU to ensure high conversion of COS and  $CS_2$  by hydrolysis. Although the formation of these compounds in the thermal stage was predicted to be fairly low due to the low  $CO_2$  and hydrocarbon level in the feeds, these compounds can break through the TGTU and result in increased  $SO_2$  emissions. Minimising the COS and  $CS_2$  leaving the Claus units is a key factor in achieving low  $SO_2$  emissions and long TGTU catalyst run time.

Since formulated MDEA was not allowed by the client, special design considerations were required for the amine section of the TGTU. To maximise H<sub>2</sub>S absorption, key process parameters that were addressed are lean MDEA temperature, lean MDEA H<sub>2</sub>S loading, and absorber design. A positive in this respect was the availability of cooling water at maximum 29°C due to a relatively mild climate without extreme high temperature. Design for lean amine cooling to 35°C or lower was accomplished by a combination of air cooling and trim water cooling. Relatively high reboiler steam rates were specified, so that lean loading of less than 0.004 moles  $H_2S$  per mole of MDEA could be achieved. Absorber design to achieve lean-end pinch (a condition where the treated gas leaving the absorber is at or close to equilibrium with the lean amine entering the column) was desired.

Sulphur pit vent handling was another area addressed because of its potential impact on stack  $SO_2$  emissions. The design included provision to route the vent stream to either the thermal reactor or the tail gas incinerator. The vent stream primarily consists of air drawn into the pit vapor space by an ejector and ejector motive fluid, with lesser but non-negligible amounts of sulphur compounds (H<sub>2</sub>S, elemental sulphur vapour, and SO<sub>2</sub>). When the vent is routed to the incinerator, steam is used as the motive fluid – this is the conventional practice. However, this approach leaves little or no margin of safety below the  $SO_2$  emission limit, so the vent can be routed alternatively to the thermal reactor. In this mode of operation, heated plant instrument air is used as the ejector motive fluid, so additional inert gas (steam) is not added to the process. All air that will be introduced to the thermal reactor must be accounted for to properly control the combustion stoichiometry. Introduction of the vent stream to the thermal reactor can affect burner performance and flame pattern, so these factors must be considered in the design. At the time of submission of this article, unit inspection, commissioning, and initial start-up operations have concluded. Unit inspection by Amec Foster Wheeler personnel proved highly valuable, as several potentially serious issues due to deviation from basic design documents were identified and remedied.

Refractory dryout, waste heat boiler and condenser boil-out, and post-dryout inspection have taken place at the time of writing. The unit is on schedule for acid gas introduction, contingent on successful concurrent start-up of the distillate hydrotreater.



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## SHELL CANSOLV SO<sub>2</sub> emissions control in China

L F Wang and M Lebel

n recent years, China's air pollution has attracted the world's attention for the images of its main cities shrouded in haze and heavy smog. Large reforms on the modernisation of environmental protection institutions, the standards to control pollutants, and the work on legal framework, among others, have expressed the will of the central government to advance in the prevention and control of air pollution. As part of China's 12th 5-year plan, Chinese refineries were subject to strict environmental emission regulations particularly with respect to sulphur dioxide (SO<sub>2</sub>) emissions.

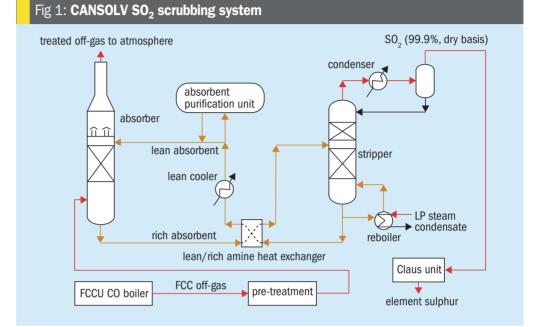
The following case study focuses on the application of a CANSOLV SO<sub>2</sub> scrubbing system in a Chinese refiner's FCC unit, discussing FCC off-gas conditions, technology selection, challenges, process line-up information, performance and operation status.

#### The CANSOLV process

The CANSOLV  $SO_2$  scrubbing system has been used for almost 15 years as a regenerable solution to manage sulphur emissions in flue gases/tail gases from fluid catalytic cracking units (FCCUs), delayed coker units (DCUs), sulphur recovery units (SRUs), spent acid regeneration units (SARUs) and utility boilers/furnaces. Traditional methods to remove  $SO_2$  from these off-gases use non-regenerable caustic solvents which inevitably produce large volumes of liquid waste requiring on-site management.

Moreover, these non-regenerable solutions fail to capitalise on the value of the sulphur which ultimately becomes another form of waste. In contrast, the CANSOLV  $SO_2$  scrubbing system is a regenerable process which can capture  $SO_2$  from the off-gas

Parameter	FCCU conditions
Gas flow rate,	
Nm³/h	150,000-170,000
Gas SO <sub>2</sub> concer	ntration,
mg/Nm³	1,800-2,500
Gas dust conce	ntration,
mg/Nm <sup>3</sup>	100-500
Turn-around tim	e every 3 years



of those different emitters and recycle it to the front-end of the refineries' existing SRU without major modifications. The CANSOLV technology therefore allows waste  $SO_2$  to be converted into valuable sulphur, which is in line with China's vision of a recycle economy.

# Technology selection and challenges

An in-land refinery in China operated an FCCU, emitting dust and sulphur dioxide  $(SO_2)$  directly to the atmosphere. The FCCU off-gas conditions are shown in Table 1.

With the new regulations coming into effect in 2015, the refinery was looking to select a flue gas desulphurisation technology which could achieve the new emission targets (200 mg/Nm<sup>3</sup> for 2015 and <100 mg/Nm<sup>3</sup> for the future), minimise the liquid effluent generation and be economic in both capex and opex. Detailed technical and economical comparisons were made between CANSOLV SO<sub>2</sub> scrubbing system and caustic scrubbing processes. By optimising the construction of materials and the line-up of the CANSOLV unit, it turned out that the capex of the two technologies were equivalent. The CANSOLV SO<sub>2</sub> scrubbing system enabled the waste SO<sub>2</sub> from the refinery to be converted into valuable sulphur in the refinery's existing SRU. The value of this sulphur byproduct offset part of the operating cost of the CANSOLV

 $SO_2$  scrubbing system. Besides that, the option to use caustic scrubbing technology was rejected as it would consume expensive caustic reagent and produce a large amount of liquid effluent containing mostly sodium sulphate and sulphite that would require further in-depth treatment before it would be allowed to be discharged.

#### CANSOLV process description and line-up

The CANSOLV SO<sub>2</sub> scrubbing system is a typical regenerative amine line-up as shown in the flowsheet diagram in Fig 1. Prior to the CANSOLV SO<sub>2</sub> scrubbing system, the FCCU off-gas is directed into a pre-treatment unit, where it is quenched to its adiabatic saturation temperature, and where the dust and acid mist in the gas are lowered to tolerable levels. The off-gas then flows into the CANSOLV absorber where it is contacted with the lean absorbent. The  $SO_2$  in the gas is scrubbed by the absorbent, leaving residual amounts of SO<sub>2</sub> at the absorber stack. The pre-treatment unit and CANSOLV unit were designed to achieve SO<sub>2</sub> emissions <200 mg/Nm<sup>3</sup> (<100 mg/Nm<sup>3</sup> for the future), acid mist emissions <10 ppmv, and dust emissions <20 mg/Nm<sup>3</sup> for this particular project.

The rich absorbent from the absorber is then pumped to a stripper, where it is regenerated by indirect steam stripping. The

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reboiler operates at a temperature below 120°C, and low pressure steam (3.5 barg) is used as heat source for this project.

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The overhead vapour of the stripping tower is cooled in a condenser, usually to a temperature of around 50°C. The SO<sub>2</sub> gas is then separated from the condensed reflux, which is pumped back to the stripper. The product SO<sub>2</sub> is directed to the refinery's existing SRU where it is recovered as an additional 1,000–1,600 t/a of sulphur product, which increases the production capacity of the existing SRU by 5-8%. Since the SRU operates by first converting H<sub>2</sub>S into SO<sub>2</sub>, the external SO<sub>2</sub> provided by the CANSOLV process does not require any modifications to the existing refinery SRU.

Following regeneration, the absorbent is returned to the absorber via a lean/rich exchanger that recovers heat to pre-heat the rich absorbent and a lean cooler to adjust the lean absorbent to an appropriate temperature.

#### Performance and operation status of CANSOLV unit

With the strong support and services from the Shell Cansolv team during each phase of the project, in close collaboration with the technical team of the refinery, the project was executed smoothly and on schedule. The CANSOLV unit was successfully started up in December 2014 and the December 2015 warranty test run was a success.

Since the initial start-up, The CANSOLV unit has required essentially no maintenance. There has been no plant shutdown due to unavailability of the CANSOLV unit.

Some operating data has been reported from the refinery. Due to the source of the crude oil, the inlet  $SO_2$  concentrations were lower than the design value most of the time for the past two years. While, the FCCU off-gas flow rate fluctuated between 30,000–235,000 Nm<sup>3</sup>/h. As shown in the graphs in Figs 2a, 2b and 2c, despite fluctuations in the  $SO_2$  concentration in the inlet gas, the unit has successfully met the design and environmental  $SO_2$  emissions targets and the  $SO_2$  emissions was constantly below 200 mg/Nm<sup>3</sup>.

The captured  $SO_2$  from the CANSOLV unit was injected back to the front end of the existing SRU. There have been no reported problems caused by the  $SO_2$ injection. The CANSOLV unit can meet future more stringent  $SO_2$  emissions

In the very beginning of the project, the refiner expected that more stringent  $\mathrm{SO}_2$ 

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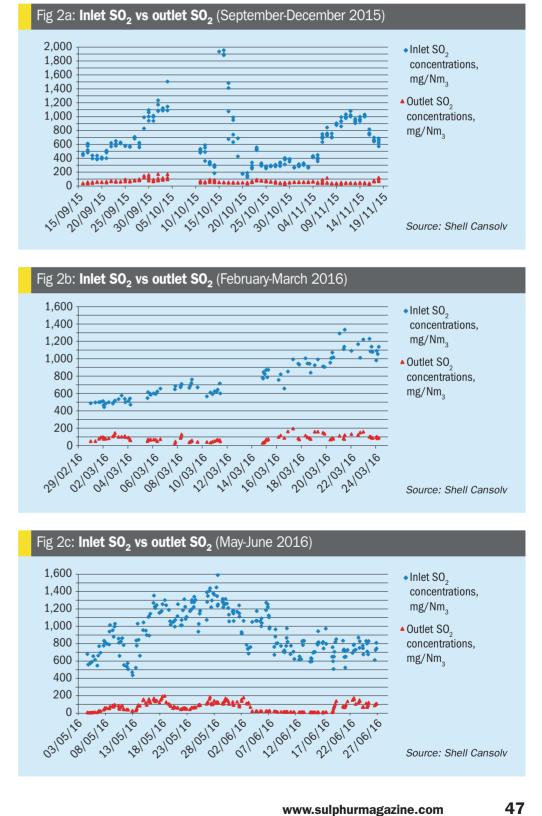
emission (< 100 mg/Nm<sup>3</sup>) would be coming in the near future. There were three options considered in the design phase to ensure future emission compliance:

- cooling the gas down to a lower temperature in pre-treatment unit;
- a balance between steam consumption increase and flue gas temperature reduction;
- adding a caustic polishing on top of the CANSOLV absorber.

The refinery decided to go with the third option, therefore space was reserved for caustic polishing on top of the CANSOLV absorber during the engineering phase. Small quantities of caustic will be needed to potentially reduce the  $SO_2$  emissions from 200 mg/Nm<sup>3</sup> to 100 mg/Nm<sup>3</sup>, or even lower. The refinery will not need a major retrofit in the future.

The CANSOLV  $SO_2$  scrubbing system is a simple, effective, proven and economical way to manage  $SO_2$  emissions from refinery units. More and more refineries in China are now considering using the CANSOLV process to treat off-gases from their SRUs and other units. Regardless of the gas conditions, the CANSOLV process can reach even the most stringent emission regulations.

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#### **JACOBS COMPRIMO® SULFUR SOLUTIONS**

# **Higher sulphur recovery targets in the Middle East**

M van Son and R van Grinsven

acobs recently completed the design and successful start-up of a new tail gas treatment unit at the refinery of a confidential client in the Middle East. The client had been running two three-stage 220 t/d sulphur recovery units achieving a sulphur recovery of up to 98%. Both SRUs were designed to process both amine and sour water acid gas. A third 220 t/d SRU had recently been added, processing amine acid gas only. This unit had been designed to achieve a sulphur recovery efficiency of 97%.

Due to new regulatory requirements, the overall sulphur recovery of the SRUs had to be increased to a minimum of 99.3% at end of run (EOR) conditions. In order to achieve this sulphur recovery requirement, the client selected the Jacobs Comprimo<sup>®</sup> Sulfur solutions EUROCLAUS<sup>®</sup> process.

The EUROCLAUS<sup>®</sup> process is based on the selective reduction of SO<sub>2</sub> present in the Claus process gas to elemental sulphur and H<sub>2</sub>S in a selective reduction stage (EUROCLAUS<sup>®</sup> stage). This stage is operated by H<sub>2</sub>S control instead of traditional H<sub>2</sub>S to SO<sub>2</sub> ratio control. The selective reduction stage is followed by a selective oxidation stage where H<sub>2</sub>S present in the Claus process gas is selectively oxidised to elemental sulphur (TGCU stage) by passing the H<sub>2</sub>S containing gas over a special selective oxidation catalyst.

In order to achieve the higher sulphur recovery targets, all three existing SRUs were converted to EUROCLAUS<sup>®</sup> operation and required the following modifications:

- installation of a common new TGCU selective oxidation stage;
- installation of Jacobs' Advanced Burner Control System (ABC) in all three existing SRUs;
- replacement of the majority of the alumina catalyst in the first stage Claus reactors in each SRU with titania catalyst;
- addition of a layer of titania catalyst in the second stage Claus reactor in each SRU;
- installation of a layer of EUROCLAUS<sup>®</sup> selective hydrogenation catalyst and a layer of titania catalyst in the third stage Claus reactor of each SRU;
- TGCU stage bypass line with triple offset butterfly valve for each SRU.

One of the main components in the successful operation of the Jacobs EUROCLAUS® technology is the proper control of the  $H_2S$  concentration from the third reactor stage in the SRU. As in this particular design there were three SRUs feeding into a common TGCU stage, the control of the H<sub>2</sub>S concentration from each SRU required the installation of a tail gas analyser on each train. The Jacobs Advanced Burner Control (ABC) system was installed in all three SRUs to maintain tight control of the H<sub>2</sub>S concentration in the tail gas from each unit to the TGCU. In addition, a common tail gas analyser was installed at the inlet of the TGCU to allow proper control of the oxidation air required for the selective oxidation reaction with high accuracy as well as to verify the operation of the upstream individual analyzers. In order to be able to have a continuous calculation of the performance of the TGCU, the client elected to install a tail gas analyser at the outlet of the common TGCU stage, which analysed for  $SO_2$  and  $H_2S$ . This analyser, which is not commonly installed due to cost savings, will give the operator insight into the operation and a tool to make adjustments, when needed.

The overall sulphur recovery efficiency is continuously calculated and displayed using the following inputs:

- the feed gas flows to each SRU;
- the calculated tail gas flows from each SRU (part of the ABC control);
- the calculated tail gas flow to the TGCU;
- the measured oxidation air flow;
- H<sub>2</sub>S and SO<sub>2</sub> losses in the TGCU off gas;
   COS and CS<sub>2</sub> losses in the TGCU off gas (initially assumed values and updated after the performance test run):
- Calculated sulphur losses in the TGCU off gas, based on the outlet temperature.

After completing the modifications required for the conversion of the three SRUs to EUROCLAUS<sup>®</sup> and installing the new common TGCU, the overall performance of the sulphur recovery units was tested. During the performance test, the unit was optimised using the available SRU and TGCU tail gas information and the calculated overall sulphur recovery efficiencies were determined to range between 99.61% and 99.76%. These values were confirmed between the TGCU outlet gas analyser and the external testing company's analysis and are the highest recoveries to date for the Jacobs EUROCLAUS® technology.

The following parameters are believed to have contributed to the record high recovery with this technology:

- titania catalyst in the first and second converter resulted in extremely low COS and CS<sub>2</sub> concentrations in the tail gas to the TGCU;
- high sulphur recovery with the 3+1 arrangement upstream of the TGCU resulted in the ability to maintain low H<sub>2</sub>S concentrations to the reactor;
- availability of multiple analysers downstream of the SRUs and at the inlet of the TGCU allow for better control of the unit;
- proper ammonia destruction in the reaction furnaces of the SRUs allowed for minimisation of the temperature from the final condenser;
- installation of the EUROCLAUS<sup>®</sup> hydrogenation catalyst in the third reactors of each SRU minimised the SO<sub>2</sub> going to the TGCU thereby resulting in a very low SO<sub>2</sub> content from the final stage;
- continued development of the selective oxidation catalyst has resulted in higher sulphur yields from the TGCU stage.

In order to have consistent high sulphur recovery efficiencies from SRUs, it is essential to have reliable analysers and stable acid gas flow and composition to the SRUs. Further optimisation of the continuous operation may still be possible by installing acid gas feed analysers and connecting the output from these analysers to the Jacobs ABC+ system to have on-stream correction for compositional changes. In addition, as the excess oxygen levels from the EUROCLAUS® selective oxidation reactor need to be kept to a minimum level to prevent further oxidation of sulphur to SO<sub>2</sub>, the installation of an on-stream oxygen analyser may be considered again as new technology has become available that is reliable in SRU environments.

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## RATE Upgrading sulphur facilities in the USA

M Rameshni and S Santo

Ithough sulphur degassing is still not mandatory in many countries, including the USA, more facilities are targeting  $H_2S$  levels of less than 10 ppmw in their liquid sulphur.

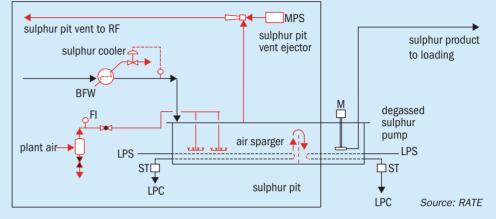
Traditionally, refineries and gas plants in the USA have sold their sulphur as a liquid to local buyers without conducting any sulphur degassing. Because the liquid sulphur was not transported far, the degree of agitation was not great and the amount of evolved H<sub>2</sub>S was limited. In fact, most sulphur producers in the USA have been selling sulphur without having any degassing system or sweeping system in their sulphur pits to remove the evolved  $H_2S$ . The liquid sulphur in the sulphur pit is simply pumped to the storage tank and then sold. At best, undegassed Claus sulphur results in nuisance odours, adversely impacts sulphur grinding and increases the friability of formed solids. At worst, it results in fatalities and explosions.

RATE was recently involved in a project to upgrade a sulphur plant and tail gas treating unit producing 230 t/d at a refinery in the USA. To comply with regulations, the plant was required to reduce the evolved  $H_2S$  by degassing the liquid sulphur and the pit vent gas had to be routed in such a way that it would not have an impact on the emissions from the incinerator. In this refinery liquid sulphur is transferred to trucks and railcars. The vapour space  $H_2S$  levels measured during the loading of undegassed sulphur were invariably above the lower explosive limit (LEL) at the delivery point.

RATE upgraded the sulphur plant, tail gas treating unit and sulphur pit in several steps:

**Step 1:** New sulphur pit eductors/blowers were added to sweep the  $H_2S$  which is evolved from the liquid sulphur. The LEL ranges from 3.5 %-vol in air at 150°C to 4.3 %-vol at 20°C, with a relatively low auto-ignition temperature achievable. It is very important that all piping is designed with steam jacketing to prevent any plugging. The pit sweep air rate (which may include degasser stripping air) is normally based on 0.5 to 2 vol-%  $H_2S$  in the effluent assuming evolution of 300 ppmw  $H_2S$ .





**Step 2:** RATE designed degassing spargers using plant air to degas the liquid sulphur in the pit. The sulphur pit had ample storage residence time, which was reduced to incorporate the sulphur degassing section. The degassing section comprises two compartments. Sulphur is degassed in the first compartment and then overflows to a second compartment, from where the sulphur is pumped out. As a result, the liquid sulphur contains less than 10 ppmw  $H_2S$  in accordance with the performance guarantees provided by RATE.

**Step 3:** RATE also designed a new sulphur cooler to cool the sulphur before entering the sulphur pit. While pre-cooling the sulphur to 130-140°C slightly increases the solubility of free  $H_2S$ , the greater benefit is increased  $O_2$  (or  $SO_2$ ) solubility, since the oxidant must first dissolve in the sulphur in order to be available for reaction with  $H_2S$  the degassing efficiency is much higher.

**Step 4:** RATE designed the vent gases to be routed to the reaction furnace in the sulphur recovery unit. There are several key considerations when routing the vent to the reaction furnace. Solid sulphur accumulates in the air plenum (which can be melted out by temporarily minimising main air), and increased backpressure on the vent gas blowers increases the blower operating temperature from compression heat, thus increasing blower maintenance. The vent gas was injected into the air plenum as close to the burner as possible,

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and offset consistent with the direction of air swirl. The pit vent piping was designed to have steam jacketing.

Step 5: In order to reduce the tail gas emission to the incinerator, the tail gas unit had to be upgraded. The existing tail gas unit was originally designed using generic MDEA and typically achieved around 150 ppmv of  $H_2S$  in the tail gas absorber overhead. The absorber overhead flows to the incinerator where the refinery was managing to keep the SO<sub>2</sub> emission under 250 ppmv. The sulphur was not degassed. RATE evaluated the tail gas unit, and concluded that the MDEA solvent should be changed to a more selective solvent like HS-103 from DOW. or TG-10 from INEOS or similar solvent in the market. These solvents require a larger reboiler duty, basically more steam per volume of solvent. Sometimes the TGU reboilers are overdesigned by a high margin. In this project there was some margin but not enough to achieve 10 ppmv of H<sub>2</sub>S. Since the existing equipment had to be used and not replaced, RATE concluded that a level of 20-25 ppmy H<sub>a</sub>S could be achieved in the absorber overhead. In some cases, switching to a selective solvent may require extra trays in the absorber, but in this project the number of trays was adequate. By changing the solvent, it was possible to reduce the  $H_2S$  from the tail gas unit to the incinerator.

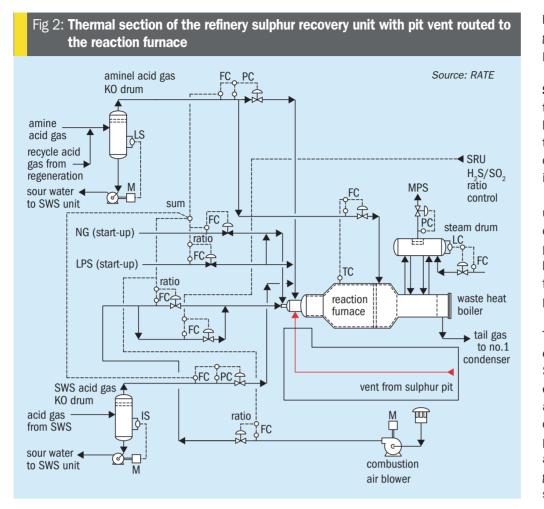
**Step 6:** RATE completed and upgraded the SRU/TGU based on the new pit vent stream to the SRU and generated a new material

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balance based on the new solvent in the tail gas unit. The new equipment for the sulphur pit have been designed and installed.

Step 7: In the first stage of the Claus unit, titanium catalyst was added to improve the hydrolysis of COS and  $CS_2$  and to increase the SRU recovery so that less sulphur compounds from the tail gas flow to the incinerator.

The upgraded SRU/TGU was started up in the second quarter of 2016. The degassed sulphur meets less than 10 ppmw of  $H_2S$  and the  $SO_2$  stack emission has been reduced to less than 50 ppmv from an original design of less than 250 ppmv of SO<sub>2</sub>.

In summary, the operation of the SRU/ TGU has been optimised and the refinery emission is now less than 50 ppmv of SO<sub>2</sub> from the tail gas incinerator. If lower emissions (e.g. less than 10 ppmv of SO<sub>2</sub>) are required in future, a caustic scrubber can be added after the incineration. All performance tests have been completed and RATE met the required performance guarantees for the sulphur degassing and stack emissions.



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#### **KT – KINETICS TECHNOLOGY S.p.A**

## **Tougher environmental regulations in Asia**

M Colozzi

T – Kinetics Technology S.p.A as licensor, technology provider and specialised EPC contractor in sulphur recovery facilities has completed more than 65 projects in six continents in the last ten years. Over time the performance specifications requested by clients and imposed by the market have been steadily increasing. Sulphur recovery efficiencies have increased from 99.5%, to 99.8% to 99.9% and SO<sub>2</sub> levels at the incinerator stack have decreased from 400 mg/Nm<sup>3</sup> to 250 mg/Nm<sup>3</sup> to 200 mg/ Nm<sup>3</sup> to 150 mg/Nm<sup>3</sup> (World Bank standard for refinery application) to 100 mg/  $Nm^3$  of  $SO_2$ .

The SO<sub>2</sub> emission standard requirement in nearly all KT projects over the last five years has been 150 mg/Nm<sup>3</sup> of SO<sub>2</sub> in the flue gas from the stack in North Africa, Asia, Europe and South America, as requested by the World Bank standard; however, KT has already designed plants in Asia with 100 mg/Nm<sup>3</sup> of SO<sub>2</sub> for a petroleum refinery and as low as 50 mg/  $Nm^3$  of  $SO_2$  for a gas field.

In petroleum refinery applications, the feedstocks treated by KT in recent projects for single train plant capacities of up to 1,450 t/d are:

- Amine acid gas (H<sub>2</sub>S: 40-90 vol-%; HC: 10 vol-%;  $H_2O$  saturation,  $CO_2 + N_2$  balance)
- Single sour water stripper acid gas (NH<sub>2</sub>: 20-50 vol-%)
- Double stage sour water stripper acid gases (H<sub>2</sub>S rich sour gas and NH<sub>3</sub> rich sour gas)
- Off gases and vent gases (containing: HC, H<sub>2</sub>S, COS, NH<sub>3</sub>, etc.)

In the majority of cases the plant configuration adopted by KT consists of the following:

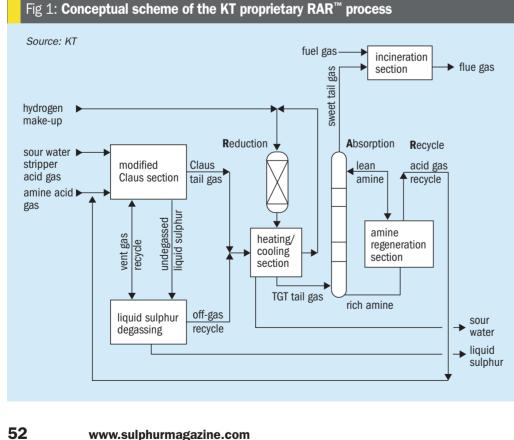
- KT modified Claus section
- KT RAR<sup>™</sup> section (KT proprietary technology)
- KT liquid sulphur degassing section
- KT incineration section

#### **KT process flow scheme**

The modified Claus section, liquid sulphur degassing section and incineration section are integrated with the KT RAR<sup>™</sup> section, which is a reductive amine based tail gas treatment capable of achieving the maximum sulphur recovery efficiency currently available in the market (SRE >99.9+%).

The goal of the process is the reduction/hydrolysis of sulphur compounds

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 $(SO_2, Sx, COS, CS_2)$  into  $H_2S$  and the selective absorption of H<sub>2</sub>S with standard MDEA, formulated amine solution or other absorption liquors based on the specific requirements of the project.

The H<sub>2</sub>S released during the regeneration of the selective solution is recycled to the modified Claus section with the purpose to boost the sulphur recovery efficiency. In addition, the H<sub>2</sub>S released by the liquid sulphur degassing section is fully recycled inside the SRU avoiding any release to the incinerator section: this is one of the unique design features adopted by KT to minimise the  $SO_2$  emissions.

Fig. 1 shows a conceptual scheme of the KT proprietary RAR<sup>™</sup> process.

SO<sub>2</sub> emissions from the stack originate from the combustion of  $H_2S$ , COS and  $CS_2$ .

COS and CS<sub>2</sub> are produced in the thermal reactor depending on the content of hydrocarbons and CO<sub>2</sub> in the Claus feedstock.

In the Claus catalytic reactors, COS and CS<sub>2</sub> are not completely hydrolysed by the following reactions:

$$COS + H_2 O \rightleftharpoons CO_2 + H_2 S$$
$$CS_2 + 2 H_2 O \rightleftharpoons CO_2 + 2 H_2 S$$

The residual amount of COS and CS<sub>2</sub> in the tail gas to the incinerator depends on the conversion of the hydrolysis reactions which take place on the catalyst in the hydrogenation reactor.

With a target of 150 mg/Nm<sup>3</sup> of  $SO_2$  in the flue gas from stack, a special formulated amine solution has to be utilised. In this way H<sub>2</sub>S can be removed completely leaving only a few ppm of H<sub>2</sub>S in the tail gas to the incinerator; the same is not possible for COS and CS $_2$ , since the absorption liquor can only eliminate a few percent of these compounds.

Therefore, to meet the required SO<sub>2</sub> emission, the content of COS, CS<sub>2</sub> and H<sub>2</sub>S in the tail gas to the incinerator have to be minimised. This is only possible with selection of the proper flow scheme, the use of optimised process parameters as well as the use of proper catalysts and absorption liquor.

The hydrolysis of COS and CS<sub>2</sub> in the Claus reactors and/or in the hydrogenation reactor can be improved by utilising the following strategies:

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• Use of TiO<sub>2</sub> catalyst in the first Claus reactor: Compared with an alumina catalyst, the TiO<sub>2</sub> catalyst improves the COS and CS<sub>2</sub> hydrolysis such that the conversion of COS and CS<sub>2</sub> in the hydrogenation reactor is adequate to reach the required SO<sub>2</sub> specification.

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- Reduction of reaction temperature in hydrogenation reactor: The hydrolysis of COS is an exothermic reaction and is limited by the equilibrium condition; for this reason the temperature reduction can improve the conversion, but the reaction velocity is also reduced and consequently the catalyst quantity has to be increased.
- Addition of steam to Claus tail gas: Increasing the steam content in the tail gas, increases the hydrolysis reaction in the hydrogenation reactor; also in this case the quantity of catalyst has to be increased because the total process gas flow rate has been increased.
- Reduction of the space velocity on the catalyst of the hydrogenation reactor (increase of the residence time) improves the conversion of CS<sub>2</sub>, which is practically not limited by the equilibrium, in this way it is also possible to reduce the equilibrium approach for the COS.

The  $H_2S$  at the outlet of the TGT absorber can be reduced increasing the  $H_2S$  driving through a reduction of lean amine temperature and improving the lean amine regeneration.

Two different ways to improve the lean amine regeneration level are:

- increase the steam to amine regenerator reboiler;
- use a formulated amine solution.

The use of a formulated amine solution allows a tail gas with a few ppm of  $H_2S$  to be achieved instead of a few hundred ppm of  $H_2S$  when a plain amine solution is utilised.

A formulated amine solution for selective service is an amine solution with the addition of acidic compounds, which shift the equilibrium of the  $H_2S$  reducing its amine loading.

The driving force at the bottom of the absorber can be increased, reducing the amine loading by increasing the absorption liquor circulation.

Two plants have recently been designed by KT in Asia following the requirements of World Bank: 150 mg/Nm<sup>3</sup> of SO<sub>2</sub> in the flue gas from the incinerator.

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During the EPC phase, the environmental regulations were changed and the client requested KT to achieve the new target value of 100 mg/Nm<sup>3</sup> of SO<sub>2</sub>. The feed-stock of the plants is a typical petroleum refinery feedstock: an amine acid gas with a limited content of  $CO_2$  and with a moderate quantity of sour water stripper acid gas. The challenge was to achieve the new target for SO<sub>2</sub> emissions while minimising the impact on the current design. With the appropriate use of the strategies outlined above it was possible to achieve the goal with full satisfaction of the client. Some

clients in Europe and the Middle East are also considering the possibility of achieving 150 mg/Nm<sup>3</sup> SO<sub>2</sub> in plants designed for much lower sulphur recovery efficiency and are looking to implement the necessary modifications to achieve the new target.

It is of paramount importance that clients investing in new sulphur recovery units select the most appropriate technology and plant configuration to comply with the most stringent environmental regulations and to allow safe and smooth operation in all possible operating scenarios.

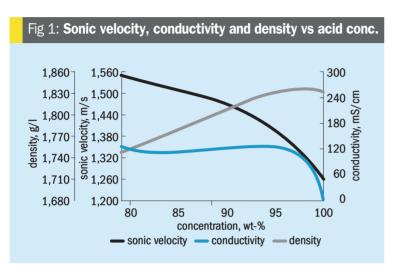


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# Monitoring sulphuric acid concentration





dvanced ultrasonic sensing technology provider SensoTech has been focused on the development of inline analysis systems for process liquids for more than 25 years. In sulphuric acid applications, the monitoring of sulphuric acid and oleum concentration (wt-%) online and in real time enhances the safety and efficiency of the plants. Manual sampling is time-consuming and may involve safety hazards. Laboratory analyses can only provide delayed data, making timely intervention in the process impossible. By contrast, methods using in-line measurements allow sulphuric acid concentration to be monitored directly in the process and in real time, enabling continuous measurements and providing on-line data.

Due to the physical properties of sulphuric acid, the most suitable method for determining the acid concentration is sonic velocity measurement. Fig. 1 shows the dependence of sonic velocity, conductivity and density on acid concentration (wt-%). As shown in the graph, conductivity probes do not provide a clear signal between 80 wt-% and 95 wt-% and density meters do not provide a clear signal between 95 wt-% and 100 wt-%, whereas sonic velocity provides a clear signal across both ranges.

In the chemical, petrochemical and mining industries, the relevant acid concentrations in production processes are typically in the range 70 wt-% to 100 wt-% sulphuric acid and 20 wt-% to 35 wt-% or 50 wt-% to 60 wt-% oleum. SensoTech's LiquiSonic<sup>®</sup> analyser (Fig. 2) is based on sonic velocity measurement and provides clear and high-precision data on the acid concentration in these ranges using only one single sensor.

In pickling and etching baths in the metallurgical and chemical sector, acid concentrations typically range between 0 wt-% and 30 wt-%. The LiquiSonic<sup>®</sup> sensor can also be used to provide reliable measurements of acid concentration in this range. For acid bath monitoring, sonic velocity is combined with a second physical value to determine the salt concentration as well.

On-line monitoring can also be used to improve process efficiency and reduce sulphuric acid consumption. For example, in refinery alkylation units sonic velocity meters reduce the amount of the spent acid and provide efficient control of the rate of fresh acid addition.

The LiquiSonic<sup>®</sup> analyser is successfully employed in plants worldwide to determine the sulphuric acid and oleum concentration. The sensor is installed directly in the existing pipe or vessel and provides provides stable measurements updated every second with an accuracy of up to 0.03 wt-%. For process automation, the real-time data can be transferred to process control systems via 4-20 mA signal, digital outputs, serial interface, fieldbus or Ethernet.

Made of Hastelloy C-2000, the sensor is fully corrosion resistant. The robust construction requires neither gaskets nor moving parts, so the sensor is maintenance-free with long-term stability. The LiquiSonic<sup>®</sup> measuring method is based on a travel time measurement, sending a sonic signal from one side to the other of the sensor. Because the distance between the transmitter and receiver is known and constant, the sonic velocity can be determined using the data of path and time. The acid concentration and sonic velocity in the acid form a clear, functional relationship. Since sonic velocity also depends on the temperature, the LiquiSonic® sensor includes a high-precision temperature measurement. From the sonic velocity and temperature data, temperature-compensated and repeatable calculations of the acid concentration is possible.

The LiquiSonic® controller displays the measured values and in the event of deviations from reference values, a signal is sent to the control system. The measured values are stored in the controller and the clear trend view provides a quick overview of the process course. Through secure remote access options via the network and web server, the user can operate the controller from the PC at the workplace or via a tablet. The analyser is delivered as a plug and play system to guarantee simple and fast commissioning. Up to four sensors can be connected to one controller, which reduces the investment costs for several measuring points.

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# KT is the way to Sulphur

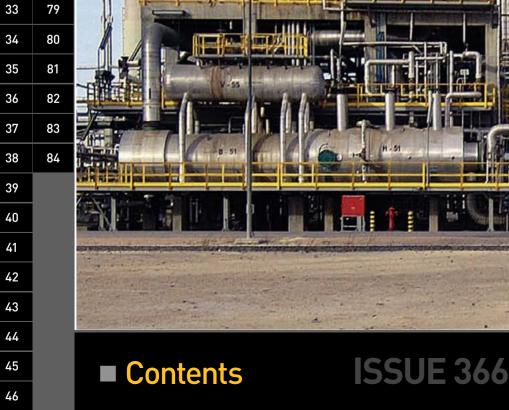
**KT - Kinetics Technology**, process engineering excellence part of Maire Tecnimont Group, counts on more than 40 years' experience in licensing, designing, constructing and operating Sulphur Recovery Facilities. KT is the leader in delivering **"end-to-end" tailor-made turnkey solutions**, with the highest quality standard and with unrivalled competence and competitiveness. We leverage on our core values: Commitment and Passion to serve our Clients, Pursue of Continuous Innovation and Flexibility, unconditioned respect of our Human Capital and Environment.



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# Sulphuric acid catalysts guidelines

Guidelines and rules of thumb can be important tools for making first assessments of anything from catalyst choices to what operational parameter settings to choose. General guidelines can also be very useful for optimising daily operation and finding potential issues in the plant. In this article **M Granroth** of Haldor Topsoe discusses different guidelines involving the catalyst or converter in sulphuric acid plants.

eneral recommendations can be very useful for making first assessments on everything from catalyst replacement needs to what gas conditions to operate with and design for. Guidelines will also allow for fast evaluation of plant performance and for the operator to optimise operation of the catalyst without the need for advanced software, equipment or specialty knowledge.

#### **Designing the catalyst loading**

#### **Catalyst types and volumes**

Although it is often advisable to simulate the specific case before deciding which, and how big, a catalyst loading should be loaded in order to reach the requirement of the acid plant, using a rule of thumb can be useful to have a general idea of how much catalyst will be needed and if caesium or other special catalyst is recommended. Fig. 1 shows roughly what emission levels can be achieved with different catalyst loadings for a sulphur burning 3+1 double absorption plant.

The graph shows that a 3+1 double absorption plant would normally be able to achieve 99.9% conversion, or around 140 ppm, operating on 11% SO<sub>2</sub> with standard potassium-promoted catalyst as long as there is reasonable room in the converter. If a higher conversion is required or if there are constraints on available volume, a caesium-promoted catalyst or even more advanced catalyst is needed. A 3+2 double absorption plant will be able to achieve an even higher conversion, while a 2+2plant will be limited to a lower conversion.

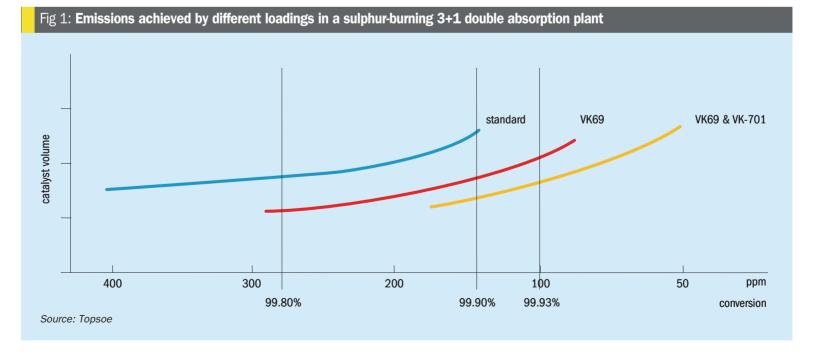
The lower the feed  $SO_2$  concentration, the more the curves in Fig. 1 will be pushed to the right, and very high conversion,

99.95+%, has been reported even with standard catalyst when operating on gases with  $SO_2$  well below 10%.

#### Choosing size and shape Shape

In most cases, a shape-optimised catalyst pellet, such as a Daisy, will be preferable to older rings or cylinders. In modern converters, the pressure drop over the catalyst beds is rarely so low that it will result in significant flow distribution issues on its own. In borderline cases, it is often better to add more shape-optimised catalyst than to switch to older shapes, as this provide more activity with the higher pressure drop, and the higher void of the shape-optimised shapes will reduce the pressure drop buildup rate.

Despite all the advantages of using shape-optimised catalyst, there are still



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Table 1: Approx relative pressure dropsfor different size and shape catalysts				
Catalyst s	size and	Relative pressure drop		
6-mm cyli	nders	200		

200
100
75
100
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cases where using rings or even cylinders will be advantageous. A good rule of thumb is to consider using rings or cylinders if the pressure drop of a bed with shape-optimised catalyst drops significantly below 50 mm WC, or 5 mbar.

#### Size

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The size of pellets used is a compromise between pressure drop and dust capacity on the one hand and activity on the other. In most beds and conditions, a 12-mm pellet is the most optimal compromise for shape-optimised catalyst. There are, however, some special cases where pellets of other sizes are a better solution, most notably larger pellets for dust protection layers or smaller pellets for highly active catalyst operating in low SOx environment. In a dust protection application, high activity is not crucial and the larger pellet size increases the penetration depth of the dust, resulting in higher dust capacity. When employing a highly active catalyst in a gas with low SOx concentration, the internal mass transport plays a more important part, and together with little or no dust capacity requirements in these environments, a smaller pellet is more optimal.

#### **Pressure drop estimation**

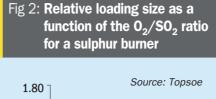
The pressure drop per metre of bed height is a function of the catalyst particle equivalent diameter, d<sub>e</sub>, and the bed void fraction,  $\epsilon$  (the fraction of the total bed volume that is open for passage of the gas stream flowing through the bed). d<sub>e</sub> is the diameter of a sphere with the same volume-to-surface ratio as the particle in question.

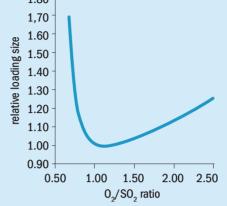
The pressure drop per unit bed depth is inversely proportional to  $d_e$  and increases strongly with decreasing  $\epsilon$ :

$$\Delta p = k x \frac{1}{d_e} x \frac{1 - \varepsilon}{\varepsilon^3}$$

 $\epsilon$  is 0.35-0.40 in beds of cylinders or spheres, 0.48-0.52 for ring-shaped

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catalysts, and 0.54-0.56 for Topsoe's 12 mm Daisy-shaped catalysts. Table 1 gives approximate relative pressure drops for a selection of the currently available shapes and sizes.

#### Choosing the right $0_2/S0_2$ ratio

Many different factors need to be considered when choosing which feed gas composition to operate with. Overall, there will be process constraints, decided by the source of SO<sub>2</sub>. Within those constraints, one will need to find the best compromise between energy usage, steam generation, conversion and catalyst requirements. Optimising the feed gas composition and taking all different factors into account can be complex. However, understating how the catalyst volume required to reach a certain conversion changes with changing  $O_2/SO_2$  ratio, will help when comparing different scenarios. As already mentioned, the optimum  $O_2/SO_2$ ratio depends on many parameters, however, the general trend is the same. Fig. 2 shows an example of a sulphur burner.

The trend seen in Fig. 2 is a good guideline for how the necessary catalyst volume depends on the feed gas composition. There will be a relative flat optimum where, although the distribution between the different beds might change, the total volume required to reach the stipulated conversion will be similar. At ratios below the optimum, the relative loading size will increase exponentially as the ratio decreases. A consequence of the exponentially increasing loading sizes required below the optimum ratio, is that it is rarely economical to go to ratios that are significantly lower than the optimum.

Above the optimal ratio, the relative loading size increases more linearly with increasing ratio. The reason for this behaviour is that the more favourable gas composition in the later beds does not compensate for the larger gas volume and lower temperatures in the earlier beds. The effect of the linear increase with higher ratio is that in case higher ratio is necessary in order to achieve a better conversion, this can be achieved with only a moderate increased catalyst loading.

#### **Operation**

#### **Optimising inlet temperature**

Each set of operating conditions (i.e. inlet flow and  $SO_2$  strength) will require different pass inlet temperatures in order to optimise the operation. Temperatures should therefore be optimised whenever the operating conditions have changed significantly.

Owing to the temperature dependence of the equilibrium, the lower the inlet temperature to a catalyst bed is, the higher the equilibrium conversion will be. On the other hand, the lower the catalyst temperature is, the lower the rate of reaction will be. For each catalyst bed, there will therefore exist an inlet temperature at which the conversion (and correspondingly the temperature rise across the bed:  $T_{out} - T_{in}$ ) is maximum for each set of operating conditions.

In Fig. 3, operation at an inlet temperature of  $T_{in}$  will correspond to an optimum outlet temperature of  $T_{out}$  which is close to equilibrium. Decreasing the inlet temperature would lead to more favourable equilibrium conditions, but the reaction rate is not sufficiently high to reach equilibrium and hence, conversion will be reduced. On the other hand, increasing the temperature would lead to a higher reaction rate but the equilibrium conversion reached will be lower than at optimum inlet temperature.

Optimisation of the converter inlet temperature is therefore a trial-and-error search for the inlet temperature at which  $T_{out}-T_{in}$  and thereby, conversion will be maximised.

- 1) For the optimisation, it is presumed that the converter is operating at stable load and stable inlet conditions in terms of flow and  $SO_2$  strength.
- 2) The inlet temperature to the first pass is decreased by 5-10°C and the converter is allowed to stabilise at the new condition for 6-12 hours. If the changed inlet temperature causes ∆T across the pass to increase, the inlet temperature

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should be decreased further. However, if the lower inlet temperature has resulted in lower  $\Delta T$  across the pass, the steps should be in the opposite direction.

- The inlet temperature is changed in steps as per (2) until the optimum value has been determined within 2-3°C.
- While the inlet temperature to the first pass is maintained at the optimum value, the optimum value of the inlet temperature to the second pass is determined as per (2) and (3) above.
- 5) Finally, the inlet temperature to the third bed is optimised while keeping inlet temperatures to the first and second passes constant at their optimum value. Since  $\Delta T$  may be small, it is suggested also to observe the stack gas SO<sub>2</sub> level. However, it should be noted that this level may change due to possible changes in the fourth bed inlet temperature caused by adjustments of the third bed inlet temperature.
- 6) For optimisation of the fourth pass, the  $\Delta T$  across the catalyst bed is normally quite small and the effect of changing of the inlet temperature may not be easily detectable. It is therefore recommended to optimise the fourth pass inlet temperature by monitoring of the SO<sub>2</sub> emission level.
- 7) When the first to fourth pass inlet temperatures have been successively optimised as described above, the conversion will be maximised and the stack SO<sub>2</sub> emission will be minimised.

#### **Check temperature increase**

A crucial part of finding issues in the plant is to be able to check if the recorded temperatures match the total expected temperature rise over the beds for that feed  $SO_2$ level. Since the reaction is exothermic, the temperature will rise with approximately 28°C per mole % of  $SO_2$  converted across the catalyst bed, i.e. the total theoretical temperature rise across the converter can easily be calculated from:

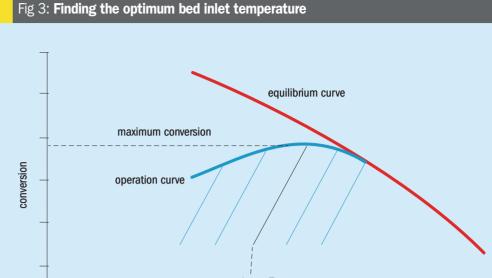
 $\Delta T_{\text{total, theoretical}} = \% \text{ SO}_2, \text{ inlet } \text{ x } 28^{\circ}\text{C}$ 

The actual temperature rise across the converter can be calculated from the temperature rise across each catalyst bed:

$$\Delta T_{\text{total, actual}} = \Delta T_{\text{bed 1, actual}} + \Delta T_{\text{bed 2, actual}} + \dots \Delta T_{\text{bed n, actual}}$$

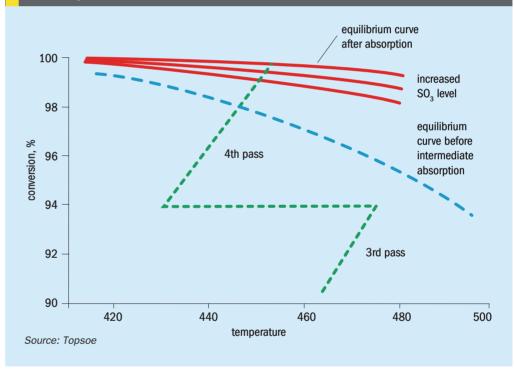
The million dollar question now is: Is the total temperature rise across the catalyst passes in agreement with the  $SO_2$  inlet concentration?

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 $\Delta T_{\text{total, actual}} = \Delta T_{\text{theoretical}} = \% SO_2$ , inlet x 28°C

If the theoretical and actual temperature rises do not match either the temperature or  $SO_2$  measurements must be erroneous, or there must be some kind of issue in the plant. Many different issues may result in a mismatch between the actual and theoretical temperature rises, some of the more common being uneven flow distribution over one or more beds, uneven composition or temperature inlet one or more beds and leaks in heat exchangers or the converter itself.

#### Check SO<sub>3</sub> inlet bed after the IAT

The presence of  $SO_3$  at the inlet of the catalyst pass located after the intermediate absorption tower (IAT) can originate from either poor performance of the IAT or from leaking reheat-exchangers. In many double absorption plants, the cold gas from the IAT is reheated with the exit gas from the third pass before entering the final catalyst pass(es). This means that  $SO_2$  gas containing no  $SO_3$  is reheated with the partly converted  $SO_2$  gas containing high amounts of  $SO_3$ . The amount of  $SO_2$  on an  $SO_3$ -free basis is the same in the two gas streams

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#### rth bed inlet

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# This is more than an SRU.

"It's the culmination of more than 60 years of sulphur leadership. It represents knowledge from technical experts around the world, and opportunities to learn from them.

And it's my contribution in safely delivering clean fuels to my hometown."

Oscar D., WorleyParsons
 Mechanical Engineer, USA



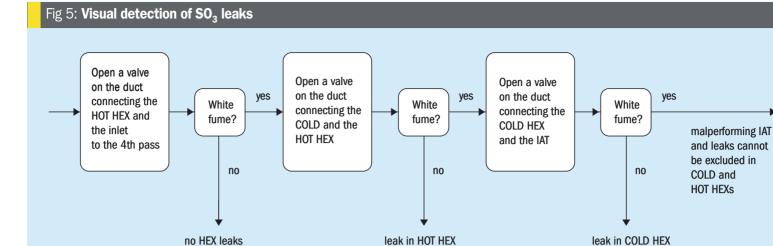
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and the leak thus cannot be detected by measuring the  $SO_2$  concentration. The gas coming from the IAT may contain acid carryover, and the result is corrosion and leaks in the hot and/or cold reheat-exchangers. Consequently, an  $SO_3$  increase will be experienced at the inlet of the final catalyst pass(es). This has a negative effect on the equilibrium, and the equilibrium curve is pushed downwards as illustrated in Fig. 4. The final result is a lower conversion in the catalyst passes after the IAT and consequently increasing  $SO_2$  emissions.

Source: Topsoe

and the IAT is

performing properly

When a gas containing SO<sub>3</sub> mixes with humid air, white acid fume is formed immediately. This phenomenon can be used in detecting the presence and origin of SO<sub>3</sub> downstream the IAT. The gas leaving the IAT should be clear. If this gas is visible, too much SO<sub>3</sub> is slipping through the IAT. If the gas leaving the IAT is clear, but the gas entering the last pass(es) is visible, there is a heat exchanger leak. If there is more than one heat exchanger between the IAT and the converter, the leaking exchanger can be determined by checking the gas inlet and outlet of each heat exchanger. The heat exchanger with clear gas at the inlet and visible gas at the outlet is the leaking heat exchanger (Fig. 5).

#### Detecting uneven gas distribution

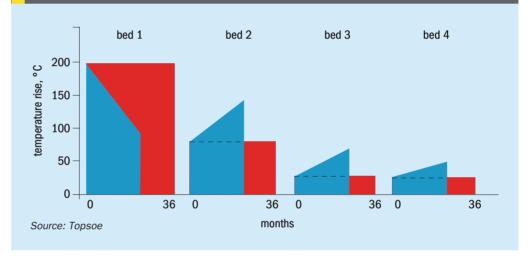
Uneven gas flow distribution through the catalyst bed or channelling may be caused by: a collapsed grid causing a hole in the catalyst bed; high gas velocities inlet the converter causing catalyst movements and possible "holes" in the catalyst bed; or dust build-up in the top of the catalyst bed, thus reducing the "available" catalyst area. Channelling will cause non-uniform

temperature and concentration profiles

Fig 6: Effect of channelling in bed 1 on temperature rises. Red: No channelling. Blue: Channelling due to dust deposition

and leak in HOT HEX

cannot be excluded



at the exit of the bed. A drop in the outlet temperature will only be detected if the thermocouple(s) are located right below the "channelling" area(s). Sometimes the temperature rise is apparently as expected, and sometimes an average temperature rise is seen corresponding to a mixture of converted and partly unconverted gas. The average conversion taking place in the bed will be lower than expected i.e. a higher concentration of SO<sub>2</sub> will enter the following bed and give a temperature rise in the following beds which is higher than expected.

Fig. 6 illustrates the effect on temperature rise in a four-bed converter with and without channelling. The red colour illustrates the temperature rise across each bed during a three-year period in case of no channelling. A slightly decrease in the temperature rise across each bed is caused by the normal catalyst deactivation. The blue colour illustrates the temperature rise across each catalyst bed during a two-year period in case of channelling caused by dust build-up in the top of the first bed. The figure clearly shows that as the dust deposition develops in bed 1 and the degree of channelling increases, the missing conversion in the first bed (shown as a drop in the temperature rise) will show up as increasing temperature rises in the lower beds. As mentioned above, the location of the thermocouple at the outlet of bed 1 may result in the drop in average outlet temperature as shown in Fig. 6 not being recorded. As a result, looking for changes in the remaining beds can often be crucial to spot the channelling.

To distinguish between the different channelling reasons, it is important to study the speed of the change in temperature rise: Is it developing over time or is it a sudden change taking place overnight? In addition, pressure drop measurements may support such investigations: Is the pressure drop increasing due to dust deposition, or does it decrease due to a "hole" in the catalyst bed or a dropped grid?

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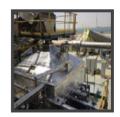
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# Managing emissions in transient conditions

During start-up, shutdown, feed change, and process upsets, unfavourable operating conditions of the sulphuric acid plant typically lead to increased emissions. These emissions are attracting more attention from regulatory authorities and proactive plant owners, and some plants have regulatory emission limit requirements during the start-up period. The general challenge for plant operators is to shut down and start up as fast as possible with a minimum fuel consumption and with minimum  $SO_2$  and acid mist emissions.

ulphur dioxide (SO<sub>2</sub>) discharged from the stack is one of the main airborne emissions from a sulphuric acid plant. Since the 1970s SO<sub>2</sub> emissions from sulphuric acid plants have been steadily decreasing due to advancements in plant and catalyst technology. Although most of the advancements have focused on emissions during steady state operation, the reduction of transient emissions during situations such as cold start-up, plant upsets, changing smelter operation, or various emergency scenarios etc., is increasingly becoming the focal point of reducing overall SO<sub>2</sub> emissions during the entire operating campaign of any acid plant.

In the contact process for sulphuric acid production, sulphur dioxide is reacted with oxygen in the process gas to produce sulphur trioxide via a series of catalytic converter beds. The catalyst employed using a vanadium pentoxide melt phase is required to be above a certain temperature (known as the ignition or activation temperature) to become chemically active and allow SO<sub>2</sub> conversion to take place. If the temperature of the catalyst is below or close to the activation temperature then reaction rates will be insufficient to achieve the desired SO<sub>2</sub> conversion leading to high stack emissions.

The minimum  $SO_2$  emission is determined primarily by the catalytic converter, and it is affected by the equilibrium of the  $SO_2$  oxidation reaction, bed inlet temperatures, gas distribution, and amounts and activities of the catalysts in the converter beds.

The emission of  $H_2SO_4$  is primarily governed by the efficiency of the downstream

absorption of SO<sub>3</sub> and acid and mist elimination equipment. Both  $H_2SO_4$  and unabsorbed SO<sub>3</sub> are emitted as micron or submicronsized sulphuric acid mist because SO<sub>3</sub> reacts rapidly with water vapour present in the ambient air or in the process gas.

Modern sulphuric acid plants can achieve very low emissions of  $SO_2$  and  $H_2SO_4$  during stable operation if properly designed and maintained, but transient states present challenges that even experienced operators and robust catalyst systems may struggle to manage.

For example, during plant start-up, the catalyst in the catalytic converter is in a transition state from colder temperatures towards regular optimum operating conditions. When  $SO_2$  is first passed over the catalyst, the SO<sub>2</sub> emissions may spike to above 1000 ppm for several minutes (or longer) until regular temperature profiles are established. Also during start-up, as the sulphuric acid in the absorption towers heats up to normal optimum operating temperatures, the sulphur trioxide  $(SO_3)$ absorption efficiency is lower and a persistent acid plume may be seen from the plant stack until the acid temperature is sufficiently high. Blue smoke is also sometimes visible from start-up stacks during catalyst preheating.

Different strategies to reduce the  $SO_2$ and  $H_2SO_4$  emissions during start-up include: catalyst selection, catalyst purging and preheating, simultaneous preheating of catalyst beds, sulphuric acid preheating (using acid cross-flow or acid heaters), acid aerosol removal (using wet electrostatic precipitation, Brownian diffusion mist eliminators or fluidised bed scrubbing), and  $SO_2$  scrubbing.

Often the solution to maintaining low emissions during transient states is a holistic view of the plant, including design, operation, and training.

#### Design

In the design phase of a sulphuric acid plant, the owner specifies the raw materials and utilities that are available to the designer. It is then the responsibility of the designer to take this information and to choose the appropriate steady state and auto-thermal  $SO_2$  concentration to the converter. Setting the  $SO_2$  gas strength is the most important decision a designer must make because it affects emissions, energy and capital.

Stack design should include a reducer tip to increase gas velocity exiting the plant stack. This will improve  $SO_2$  dispersion from the stack. Almost all new plant designs will include some kind of environmental emissions dispersion modelling to ensure the ground level  $SO_2$  emissions are below statutory requirements.

For many years, conventional vanadium based catalysts were the workhorse of the industry, able to provide 99.7+% conversion efficiency for most sulphuric acid plant designs.

For example, the optimum gas strength for sulphur burning plants is ~11.5 vol-%. The resultant 0.8  $O_2/SO_2$  ratio readily allows for 99.7% conversion with reasonable conventional vanadium catalyst loadings and good energy efficiency.

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For spent acid recovery (SAR) and metallurgical units the gas strength can vary significantly, depending on the diluting effect of the fuel used in the decomposition furnace or by ingress air around the hoods. In both cases, moderate gas strengths (8 vol-% to 11 vol-%) and  $O_2/SO_2$  ratios between 0.75 and 1.0 result. Conversion of 99.7% is readily achievable with reasonable catalyst loading.

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However, over time, the game has changed. Environmental regulations have become more stringent, requiring 99.9+% conversion and minimal emissions during start-up and shutdown. In addition, metallurgical acid plants have migrated towards flash smelting technologies, which produces SO<sub>2</sub> concentrations of 14 vol-% to 20 vol-% with  $O_2/SO_2$  ratios from 0.75 to 1.0. With these smelting improvements came challenges of controlling the exothermic heat of reaction in the first pass and achieving high overall conversions.

This is where caesium-promoted catalysts have made a positive impact on the design of sulphuric acid plants. Caesium catalysts have good light off at temperatures in the 380°C to 390°C range. This "low bite" capability allows feeds to be introduced at a lower temperature during start-up, to provide a wider operating range for higher gas strengths and to favourably shift equilibrium in order to increase the overall conversion.

With caesium catalyst, sulphur burning plants with a gas strength of 11.5 vol-%  $SO_2$  are able to achieve 99.89% conversion (150 ppm) or 99.93% conversion (100 ppm) with 11 vol-%  $SO_2$ . This can be accomplished with the help of caesium catalyst in passes 1 and 4 or 5.

In metallurgical acid plants, less than 100 ppm can be achieved with 14 vol-% SO<sub>2</sub> and 14 vol-% O<sub>2</sub>. Caesium catalyst in the first pass controls the outlet temperature to just below 650°C. Other metallurgical acid plants, using a pre-converter, have

successfully operated as high as 18 vol-%, on an unconverted basis to pass 1.

As catalyst continues to improve, the bounds of conventional sulphuric acid plant design will continue to grow. Gas strength will increase, conversion will improve and plants will become more energy efficient. However, it is not reasonable to expect that catalyst design can account for all potential operating scenarios and remain cost effective. The challenges of maintaining the desired conversion during changing conditions will still require operator intervention.

#### Operation

#### Sulphur furnace operation

Plant operations should ensure the sulphur furnace is operating and maintained as per vendor's recommended procedures. It is good practice to exchange the sulphur guns with new units that have been pressure tested every time the plant is shutdown. This will ensure the sulphur gun nozzles are not compromised (Fig. 1) which will lead to poor atomisation or in the worst case, nozzle failure, which will leads to liquid sulphur pooling on the furnace floor, resulting in high  $SO_2$  emissions during subsequent plant restart.

#### Cold sulphuric acid plant start-up

Many things happen during the startup of an acid plant, and every plant will have unique procedures. The following is a generalised description of a cold plant start-up focusing on the elements with importance to the emissions of  $SO_2$  and  $H_2SO_4$  during start-up.

Preheating of the acid plant is necessary in order to "ignite" the  $SO_2$  oxidation catalyst before  $SO_2$  is introduced to the converter. Vanadium pentoxide catalyst is a "supported liquid phase" catalyst. The active phase is a liquid salt mixture filling the pores of a porous support. The "ignition" of the catalyst is the temperature at which the solid salt mixture melts to allow the dissolution and diffusion of the gases (SO<sub>2</sub>, O<sub>2</sub> and SO<sub>3</sub>) in the liquid, and where precipitated, catalytically inactive vanadium(IV) compounds dissolve into the melt as active vanadium(V) compounds. The "ignition" temperature is in the range 310-360°C depending on the type of catalyst. Furthermore, the preheating of the plant ensures that the gas equipment including converter and heat exchangers are dry and above the dew point of the sulphuric gas.

Gaseous  $H_2SO_4$  emissions are made up of three sources:

- H<sub>2</sub>SO<sub>4</sub> vapour from the strong sulphuric acid in the final absorption tower where the gas is saturated with acid;
- non-absorbed SO<sub>3</sub> gas;
- acid aerosols and acid mist generated in the final absorption tower and not removed by the mist eliminators.

#### Sulphur furnace preheating

Sulphur burning plants will typically preheat the sulphur furnace by combustion of hydrocarbons. Starting with a cold plant, the resulting wet combustion gas will be vented through a start-up stack/vent, downstream of a boiler before entering the converter. This operation is necessary since the catalyst cannot be exposed to water vapour until it is above 100-150°C; the recommended temperature varies between vendors), or it may be destroyed by the moisture.

The vented combustion gases may have a strong odour, but no significant  $SO_2/H_2SO_4$  emissions occur during this stage, unless the furnace has a frozen pool of sulphur inside of it, or if the start-up fuel has high sulphur content.

#### **Dry blows**

Once the sulphur furnace is hot e.g. 800-1,000°C heat is transferred from the furnace to the catalyst by dry blows. During dry blows, dry air from the sulphuric acid drying tower is blown through the preheated furnace where it picks up heat from the hot refractory and transfers it to the cold catalyst. The temperature of the furnace will decrease and the catalyst temperatures increase. Once the furnace temperature drops to about 200°C the converter is isolated, and the sulphur furnace preheating resumed. This dry blow procedure is continued until all the catalyst in the converter is above the minimum temperature 100-150°C to avoid damage from moisture. The number of dry blows

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required depends on the plant design.

The vented combustion gases, again, may be smelly, but no significant  $SO_2/H_2SO_4$  emissions occur during this stage.

#### **Burn through**

Once all the catalyst has reached the minimum temperature during dry blows, the catalyst can be heated directly with the wet combustion gases until the desired ignition temperatures are reached. During this phase, the wet combustion gases are normally exhausted through start-up vents upstream of the sulphuric acid absorption towers so as to avoid unnecessary dilution of the strong acid inventory and to avoid equipment corrosion problems.

As a minimum the catalyst in the first pass has to be heated to the ignition temperature to be able to convert SO<sub>2</sub> and produce sulphuric acid. However, due to emission concerns it is customary to heat most or all catalyst beds at least to the ignition temperature and perhaps even higher, 400-475°C is not uncommon. When the ignition temperature is reached and the catalytic salt melts, any "trapped" SO<sub>2</sub>/SO<sub>3</sub> gas will diffuse out of the catalyst, pass through heat exchangers and generate a "blue smoke" from the start-up vents. This "blue smoke" consists of sub-micron sulphuric acid aerosols formed by the reaction of  $SO_3$  and  $H_2O$  and condensation of the resulting H<sub>2</sub>SO<sub>4</sub> gas. This form of emission is a concern to some producers.

#### **Firing sulphur**

Once the catalyst has been heated to the required temperatures, the hydrocarbon fuel burner is stopped and the sulphur burners installed, start-up vents are closed and damper and blind positions are changed to configure the plant for normal process gas flow and exhausting only through the plant stack. Sulphuric acid will also have to be circulating over all towers before introducing sulphur.

When sulphur is combusted in air to produce  $SO_2$  and the  $SO_2$  gas passes through the converter it will be oxidised to  $SO_3$ . However, the preheated catalyst is not yet at the optimum temperatures, and it is normal that not all the  $SO_2$  will be converted to  $SO_3$ , which results in "high"  $SO_2$  emissions for a period of time during the initial firing of sulphur. Initially, sulphur is usually fired at low rates producing  $SO_2$ gas of lower concentration as compared to design conditions, which improves the conversion of  $SO_2$  to  $SO_3$ , due to higher excess amounts of catalyst and improved chemical equilibrium conditions.

The catalytically generated  $SO_3$  passes through the acid absorption tower(s) to be absorbed into the acid. However, during initial sulphur firing the circulating acid is often cold and may not be at the optimum concentration for  $SO_3$  absorption. It is thought that the high viscosity of the cold acid results in a liquid boundary layer of oleum due to low counter diffusion rates of H<sub>2</sub>O to the surface. Non-absorbed  $SO_3$ gas leads to sulphuric acid emissions from the stack, resulting in a "bluish-white" persistent plume from the stack. This plume will have a high fraction of sub-micron acid aerosols, which are difficult to remove.

If the ratio of sulphur to air is not controlled properly, sulphur may not be burned completely in the furnace. Sulphur pooling may occur in the furnace, or sulphur vapours may be carried over to downstream equipment. These sulphur vapours may condense or sublime on cold surfaces and become a fire hazard. Such sulphur fires have been observed in several plants causing major damage to the equipment. Carry over sulphur will often reach demisters and cause plugging and equipment damage. Unburned sulphur from the furnace can also have important effects on the SO<sub>2</sub> emissions from the plant. If unburned sulphur leaves the furnace there may also be little or no oxygen left to oxidise  $SO_2$  to  $SO_3$  in the converter, which can result in the SO<sub>2</sub> concentration in the stack reaching dangerous levels. This latter scenario is known to have caused hospitalisation of people exposed to the start-up SO<sub>2</sub> emissions. Although this sulphur-to-air ratio control issue could happen at any time, it is more likely to happen during start-up.

## Preheating systems for metallurgical and SAR plants

All sulphuric acid plants have to preheat the catalyst in dry gas to above the dew point, and to above the ignition temperature in dry/wet gas. Metallurgical and sulphuric acid regeneration plants do not have a sulphur furnace to allow a dry blow procedure. Instead, it is customary to have a hydrocarbon-fired preheating system consisting of a preheat furnace with a preheater gas-gas heat exchanger. The dry side of the sulphuric acid plant is heated indirectly by transferring heat from this preheat furnace to the dried process air. Depending on the design of the system this can be a faster and easier way to heat up the plant than with dry blows in sulphur burning plants.

Especially for some metallurgical acid plants, it can be difficult to achieve a high enough  $SO_2$  concentration initially to run autothermally, which can result in loss of catalyst ignition and  $SO_2$  emissions. In these cases, the start-up preheating system can be utilised to recover to normal operation.

# Strategies for reducing start-up emissions of SO<sub>2</sub>

As with all problems or disease, you can choose to attack the causes or treat the symptoms. In the case of start-up emissions of  $SO_2$ , the causes are related to the catalyst and the preferred strategy may be to manage the source of the problem. An alternative solution is tail gas scrubbing, which treats the symptom.

#### **Catalyst preheating**

The catalyst needs to be preheated to above the ignition temperature to be able to oxidise  $SO_2$  to  $SO_3$ . The higher the temperature, the faster the kinetics of the reaction. However, since the oxidation reaction is an equilibrium reaction, too high a temperature will slow down the kinetics and limit the extent of the reaction. Therefore, the temperature profiles of the catalyst beds are of paramount importance in reducing the start-up emissions of unconverted  $SO_2$  through the stack.

To predict the ideal catalyst bed temperature profiles for start-up is very complex because the catalyst, as well as the plant itself, is in a transient state. In addition to temperature, the catalyst activity is affected by pressure, gas concentrations, and the state of the catalyst before introduction of  $SO_2$ . The latter depends on the shut-down procedures, and is important because the catalyst may absorb considerable amounts of  $SO_2$  or  $SO_3$ , up to 10% of the catalyst mass. If for example the  $\mathrm{SO}_{\mathrm{3}}$  content in the catalyst is low when process gas is introduced, the bed can become quite hot (due to the heat of sulfatisation) and conversion can be limited by equilibrium.

In former times, when start-up  $SO_2$ emissions were not scrutinised, sulphur would be fired as soon as the first catalyst bed was heated to somewhat above the ignition temperature. The downstream beds would be below the ignition temperature, preheated with whatever heat was left in the gas having passed through the

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# Quality Service

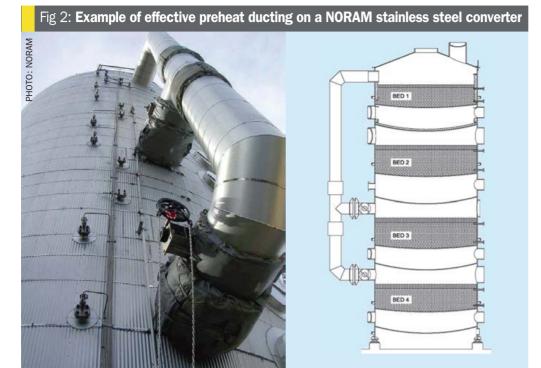
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upstream beds. Once the hot  $SO_2$  gas is passed through the first catalyst bed a lot of heat is released from the oxidation reaction and this extra heat results in a much faster heat up of the remaining catalyst and equipment than achievable in the previous "burn through" stage with wet combustion gas. Today, this method is only acceptable in sulphuric acid plants with a  $SO_2$  tail gas scrubber, which can effectively remove the otherwise high emissions of  $SO_2$ .

Most plants today have to preheat all catalyst beds to above the ignition temperature to limit the  $SO_2$  emissions. Heating all converter passes and all of the ancillary equipment is challenging. At the peak of preheating, there is about a 55°C temperature drop across each pass. Therefore, with 510°C gas entering the first pass, the preheated gas entering the second pass will only be about 455°C. After two passes, the preheated gas is below the strike point of conventional vanadium catalyst.

To alleviate this problem in double absorption plants, provisions are normally made to separately heat passes 4/5, allowing the plant to be started up in the 2+1 mode. Process heat can then be used to heat up pass 3. Some owners and operators install caesium catalyst in pass 3 to improve start-up conversion. However, starting up in 2+1 mode must be done with care, as SO<sub>2</sub> concentrations in excess of about 8 vol-% will exceed the capability of the catalyst to oxidise SO<sub>2</sub> and cause high SO<sub>2</sub> emissions. In addition, a conscious effort must also be made to operate pass 2 inlet above the normal operating temperature in order to simultaneously bring the temperature of pass 3 up while keeping pass 4 above the minimum operating temperature. This is not a simple undertaking and will require some skill on the part of the operator.

With increasingly more stringent environmental regulations and pressures to return to production as soon as possible, preheating becomes even more important.

In many plants, the preheated gas temperature is limited to 510°C because of carbon steel ducting and equipment. To overcome this limitation, the preheating strategy changes slightly. In order to get pass 3 up to operating temperature, a preheating duct is routed to that pass as well. After passes 1 and 2 are up to temperature, some of the 510°C gas can be diverted to pass 3 to allow for final preheating of that pass. Some owners and operators have opted for preheat ducts to all passes for more flexibility during heat up.

Fig. 2 shows NORAM's preheating ducts to beds 3 and 4 in a 3+1 double absorption sulphuric acid plant. Another important variable in the heat up process is the preheated gas volume. The typical preheated gas volume is about 40% of the design gas volume. This typically means that it takes anywhere from 36 to 48 hours to preheat the plant once the catalyst is above the dew point. As the preheated gas volume increases, the heat up time decreases. At 100% of the rated volume, the preheat time is reduced to 12-24 hours.

With all of the passes at or near normal operating temperatures, when feed is introduced, all beds will be converting  $SO_2$ , minimising emissions. Still, some care needs to be taken. For example, in a sulphur burning plant, the steaming equipment after pass 1 must be bypassed until pass 1 outlet comes up to normal operating temperature. This practice provides the hot interpass heat exchanger with enough heat to preserve pass 4 inlet temperatures. Operators must learn these dynamics in order to know how to react.

This preheating operation is time consuming, and the fuel required to heat the catalyst is expensive. It's no wonder that operators are anxious to reach an acceptable preheat level and to start producing acid. But, minimising the time to heat the plant to an acceptable level and starting the plant up while juggling gas strength and changing heat loads with minimal emissions, requires a big picture understanding of the process.

To put this all into perspective, DCS trends from an actual hot start-up, utilising MECS<sup>®</sup> XCs-120 and XLP-110 catalysts at Asarco's Hayden smelter are shown in Figs 3-5. Asarco set out to lighten their impact on the environment by identifying and focusing on key operating parameters that affect converter temperatures and SO<sub>2</sub> emissions following maintenance shutdowns.

This site has a 3+1 converter with heat up ducts to passes 1 and 4. The preheater is a typical 40% of design capacity, but due to its age, the preheated gas temperature was limited to 445°C.

Fig. 3 is a graph of pass 1 inlet and outlet temperature, along with  $SO_2$  concentration to pass 1 plotted against time. This particular startup followed an 8-hour hot shutdown. The goal was to float the preheater and control the gas strength to < 10 vol-%, which would give enough external and process heat to get all of the converter passes hot, without exceeding temperature and emission limits.

Although pass 1 inlet temperature hovered around 345°C, which is below the recommended minimum operating temperature of 390°C, after about 15 minutes of operation, pass 1 outlet began to rise, indicating that the caesium catalyst was active and converting. Note that it was several hours before the catalyst mass came up to the preheated gas temperature.

On this occasion, the dilution air could not keep up with concentrate feed rate at the smelter and the concentration of the gas exceeded the target. Even with caesium catalyst, pass 1 outlet temperature and emissions trended upward, causing

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#### SULPHURIC ACID PLANT EMISSIONS

the operator to make a big dilution air adjustment. The dilution air had the desired cooling effect on pass 1 outlet, but also dropped the gas strength to about 7 vol-%, which carried heat away with it. It took about an hour for the ensuing cold wave to make its way through the converter and 4-6 hours to get all of the converter beds up to operating temperature.

While this startup did result in the plant coming on-line, valuable time was lost getting the converter beds up to operating temperature and the smelter back to full rates. The lesson learned is that even caesium catalyst cannot compensate for the loss of concentration control.

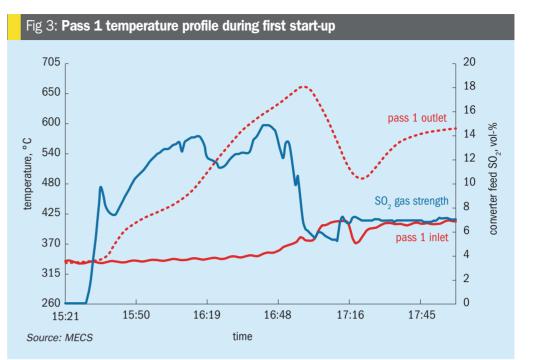
Fig. 4 is another hot startup at the same smelter, but with the benefit of experience. As the trend shows, the concentration control was much tighter and the pass 1 outlet temperature remained under control. It is also important to note that the emissions remained under the limit during the entire startup. This particular startup is very impressive; emissions requirements and gas strength are controlled well and result in a fast on stream time and a low environmental impact.

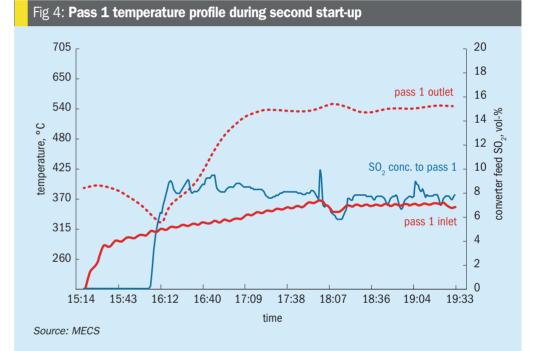
Fig. 5 is the same data as Fig. 4, but with additional converter temperature trends over a longer period of time. This trend shows that all converter beds were up to operating temperature and near steady state conditions in a little over three hours, which allowed the smelter to quickly reach full capacity.

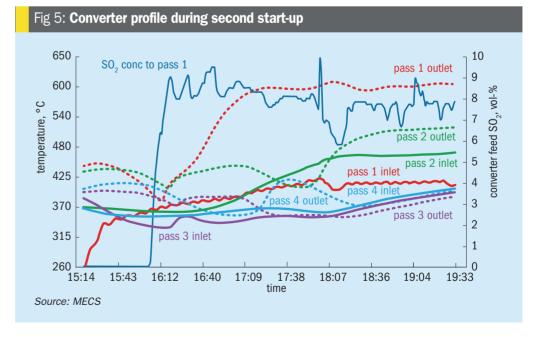
In Chemetics designed acid plants the following preheat approaches have been successfully adopted:

- **Direct preheat duct to bed 4:** In a typical DCDA plant, after the third catalyst bed the process gas will be cooled in the inter tower. During start up the gas entering bed 4 will be too cold thus a direct preheat duct to bed 4 is required. This allows the warm air from the preheat furnace system to enter bed 4 directly without any cooling. When the preheating is complete a blind is inserted into this duct to prevent SO<sub>2</sub> bypassing between beds 1 and bed 4.
- Modern preheat system: A modern preheat system should be able to handle fast transient conditions in upstream smelter operations. If the preheat system is not able to fire up fast enough to maintain the contact plant above the autothermal point during changes to the smelter operations (e.g. change from strong SO<sub>2</sub> gas in smelting step to weak SO<sub>2</sub> gas in









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# **BCInsight**



the converting step), the catalyst temperature will drop which will result in high  $SO_2$  emissions. Chemetics preheat furnace system is designed to heat up from ambient to >700°C in less than 15 minutes. This is achieved through specialised furnace refractory design and use of Chemetics patented radial tube stainless gas-gas heat exchangers (Fig. 6)

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Steam assisted preheating: This novel approach whereby the boiler acts as a temporary condenser is an alternative approach to the traditional "heat and blow" method to heat up the catalyst in sulphur burning sulphuric acid plants. Utilise the boiler supplied as part of the contact section design, acid circulation is started in the towers and the blower is set to deliver approximately 30% of the design plant flow rate. Medium pressure steam is then delivered to the boiler from battery limits thereby heating the dry air prior to the converter beds. This approach reduces the number of times necessary to swing blinds during catalyst preheating, which results in more time spent on heating up the catalyst. In addition, since the heat up air is recycled and stays dry, the overall amount of start-up acid required is reduced.

#### **Catalyst types**

It is well-known that start-up procedures and type of catalyst have considerable influence on how fast plants start up and the associated emissions. Caesium-promoted catalysts are considerably more active than conventional potassium promoted catalysts and have a lower ignition temperature, providing plants with the possibility of reducing start-up emissions while starting up faster (Fig. 7). A layer of caesium catalyst on the top of catalyst beds can be very helpful during start-up to reduce emissions, especially if it is difficult to get the beds up to the higher ignition temperature required by conventional catalyst. Once the catalyst is above the ignition temperature the heat of reaction of the  $SO_2$  oxidation will help to reach steady state quicker, and all the catalyst in the bed is then used for converting  $SO_2$  which reduces  $SO_2$  emissions.

The effect of partly or fully substituting conventional catalyst (VK38) in the fourth bed in a 3+1 double absorption (DA) plant with caesium catalyst (VK69) is shown in Fig. 8 after a hot standby where the temperatures in all beds have dropped  $60^{\circ}$ C.

The  $\mathrm{SO}_2$  emission during start-up can be reduced 50% by replacing one-third of

bed 4 with VK69 and by 75% for this specific plant when using a full bed of VK69. Caesium catalysts offer additional benefits when the  $SO_2$  emission limit is not an issue as their low temperature activity enables plant to maintain the emissions during prolonged hot standbys. Fig. 9 shows the relative time a 3+1 DA plant can be allowed to cool down with different catalyst configurations.

The graphs shows that substitution of one-third of bed 4 with VK38 with VK69 can compensate for 10% longer cooldown and full substitution can compensate for 25% longer cooldown with no increase in emission. This improvement in startup performance of the plant is an added benefit to the improvement in steady state conversion, which in most cases is the main reason for adding a caesium layer in the final bed. The positive effects of hot purging during shutdown does not nullify the effect of installing caesium catalyst in the final pass as the two effects can be combined for even greater SO<sub>2</sub> emission reduction during start-up.

A new catalyst from Clariant, SulfoMax<sup>®</sup> EV, features a much lower ignition temperature (<300°C) than previously possible and can start operating, on a continuous basis, from 360°C onwards. By installing EV type catalyst in the final pass of the sulphuric acid converter, the heat up time required to bring the catalyst beds to sufficient temperature for first SO<sub>2</sub> conversion can be significantly shortened. Multiple benefits achieved using SulfoMax EV in the final bed include:

- managed SO<sub>2</sub> emissions during transient conditions;
- faster plant start-ups (by reducing heat up time);
- lower energy (fuel/electricity) spent in heating up the catalyst bed to >380°C;

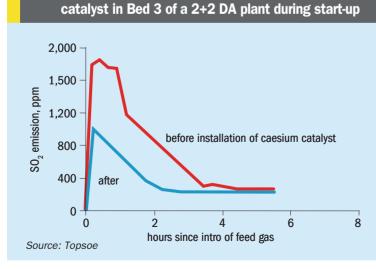
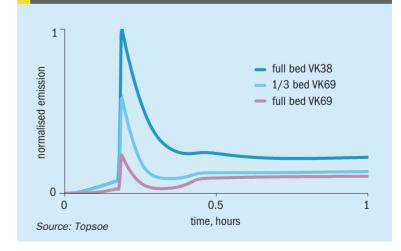


Fig 7: Industrial data showing the effect of using caesium

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Fig 8: The effect on the start-up SO<sub>2</sub> emission of using caesium catalyst (VK69) in bed 4 in a 3+1 plant.

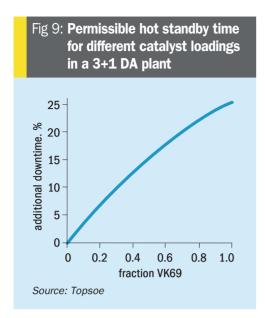


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 with an operating temperature of 360°C, SulfoMax EV can ensure lower emissions on a long term sustained basis.

#### SO<sub>2</sub> scrubbing

If none of the catalyst related strategies result in the required reduction of  $SO_2$ emissions during start-up, then a tail gas SO<sub>2</sub> scrubber may have to be installed after the final absorption tower. Alkaline scrubbers use caustic, soda ash or limestone to remove SO<sub>2</sub> from the process gas. Emissions of less than 10 ppmv  $SO_2$  can be achieved. These scrubbers have relatively low capital costs but the downside of these scrubbers is that a liquid effluent is generated which needs to be disposed of. Alkaline scrubbers can be designed using a two stage approach with separate pH control on both stages which allows saleable sodium meta-bi-sulphite (SBS) to be produced as a by-product (Fig. 10).

Alternative scrubbing medium such as ammonia can be used to generate ammonium sulphate which can be used for fertilizer production. While, the addition of a scrubber to an existing acid plant or in the design of a new plant with tail gas scrubbing may add to the chemicals handled on site, it also adds a number of process and operational benefits.

Firstly, with a scrubber, start-up duration can be considerably shortened since, only the first catalyst bed needs to reach the ignition temperature. The scrubber will handle the otherwise too high  $SO_2$ emission. Secondly, it adds flexibility in plant operations and a layer of protection in terms of avoiding emissions during a plant upset.

When considering scrubbing, the first distinction to be made is between start-up

Fig 10: Sulphuric acid plant with tail gas caustic scrubber



and continuous operation. Is the scrubber going to be used only at start-up or also during normal operation? At start-up the gas flow rate is usually only about half that of normal operation and the air blower will most likely have excess pressure discharge capacity. Therefore, a dedicated start-up scrubber can be designed to be much smaller than a scrubber for continuous operation.

For start-up scrubbers, which are only used for short periods, hydrogen peroxide offers a compelling choice as the reaction of  $SO_2$  with hydrogen peroxide produces more sulphuric acid. This weak acid can be temporarily stored and added as contact plant dilution water once the plant is running stable, thus eliminating the production of any new effluents.

If the scrubber is selected to do both start-up and normal operation duties, then a fluidised bed scrubber is an interesting option due to its flexibility. During normal operation the scrubbing efficiency can be tuned on-line to find an optimum between scrubbing efficiency and pressure drop. During start-up operation it can be operated at higher liquid circulation rates and gas pressure drop to reduce emissions of  $SO_2$  and acid aerosols (i.e. start-up stack plume or "blue smoke") efficiently and simultaneously.

The biggest obstacles for the plant operator with a tail gas scrubber are the scrubbing chemicals cost and handling as well as the waste product handling. For some operators it may be attractive to use an inexpensive scrubbing chemical like slaked lime or a limestone suspension, especially if the gypsum waste product  $(CaSO_4/CaSO_3)$  can be disposed of properly in existing gypsum piles or mining tailings. However, standard fixed, packed beds cannot handle slurries without fouling and plugging, and spray towers are large and not very efficient. A proven, compact, and non-fouling, fluidised bed scrubber system, NORAM's TurboScrubber<sup>®</sup>, has been proposed as a good candidate for use in such lime slurry applications for the sulphuric acid industry.

Another potential issue is the loss of sulphuric acid production resulting from increased pressure drop of a continuous add-on scrubber. Again, fluidised bed scrubbing technology has been proposed to add a "pressure drop neutral" tail gas  $SO_2$  scrubber. This can be achieved by replacing upstream high pressure drop mist elimination candles with a mesh pad and utilise the "freed up" pressure drop towards the add-on fluidised bed scrubber, which can remove  $SO_2$  and acid aerosols simultaneously.

Regenerative  $SO_2$  scrubbing has received renewed attention lately due to new market players with improved solvents. In regenerative  $SO_2$  scrubbing,  $SO_2$ in the tail gas is absorbed into a lean, cold solvent. The resulting rich, solvent leaving the scrubber is then regenerated in a smaller stripping tower using steam to heat the rich solvent and strip the dissolved  $SO_2$ .

The stripped SO<sub>2</sub> gas is saturated with water and can be returned to the front end of the acid plant for conversion to acid. The idea and use of regenerative SO<sub>2</sub> scrubbing has been around for a long time, using a variety of solvents. Regenerative SO<sub>2</sub> absorption systems (e.g. CANSOLV) have been implemented successfully in a limited number of sulphuric acid plants, mainly to reduce emissions during normal operation. However, as regenerative SO<sub>2</sub> scrubbing technologies are capital intensive compared to simple chemisorption scrubbing (caustic, peroxide, ammonia, lime etc.) they are not warranted for startup  $SO_2$  scrubbing only.

# Strategies for reducing start-up emissions of H<sub>2</sub>SO<sub>4</sub>

The cause of the majority of the emissions of  $H_2SO_4$  during start-up is really the emission of  $SO_3$  gas from the plant forming acid aerosols when reacting with  $H_2O$  in the gas or from the atmosphere and when cooled. Different strategies attacking the cause or the symptoms of these emissions are discussed in the following.

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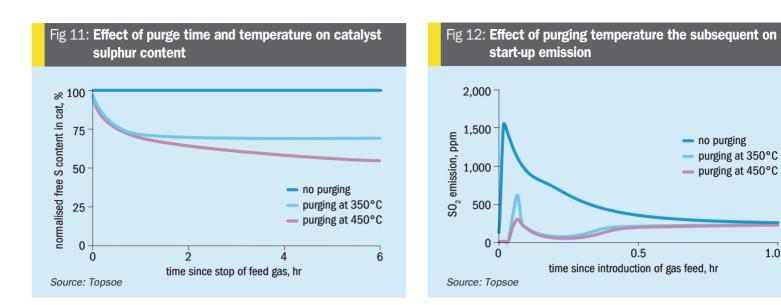
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#### **Catalyst purging**

Reducing  $SO_2$  and acid emissions during start-up has to be considered during plant shutdown. The way the catalyst is purged during shutdown will have a profound effect on  $SO_2$  and  $SO_3$  emission when the plant is started back up. Fig. 11 shows the effect of different temperatures and purging time on the catalyst sulphur content, while Fig. 12 shows how that different purge temperatures affect the emission during the subsequent start-up.

From Figs 11 and 12, it is apparent that there is much to gain in terms of reduced start-up emissions by spending some more time and money on a longer or warmer purge of the catalyst when shutting down. What is achievable in practice is of course plant specific, but even a small improvement may be what it takes to get the emission peak below the limit.

It is generally good practice to do a "hot blow" to purge the catalyst bed for a few minutes before any planned shutdown. This requirement is because  $SO_2$  and  $SO_3$ gas is dissolved in the catalyst molten salt phase and needs time to be stripped out. Once the catalyst temperature drops below about 400°C  $SO_2/SO_3$  will be trapped in the catalyst. When the plant is heated back up during start-up and the catalyst reaches 350-370°C, or even lower temperatures with caesium catalyst, "blue smoke" will be seen in the stack or start-up vents. Though some SO<sub>2</sub> is stripped, the majority of the sulphuric species will be SO<sub>3</sub> since the catalyst is still active. It is the SO<sub>3</sub> with water that forms "blue smoke".

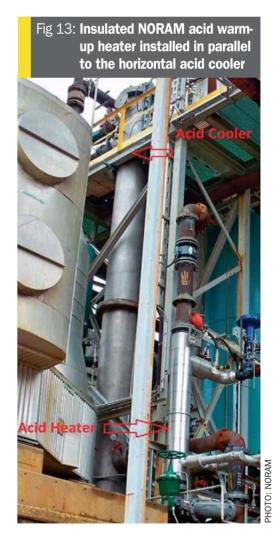
To minimise this problem, the catalyst must be purged with dried (hot) air while the catalyst is still warm. The catalyst temperatures should be kept above 400°C while purging by using by-passes around boilers, superheaters, gas-gas heat exchangers etc. Purging must continue until no  $SO_2/SO_3$  – no "white smoke" is present in the gas from the sample lines after the final catalyst pass.

The reason  $SO_2$  and  $SO_3$  are trapped in the catalyst during shutdown is that the sulphur furnace and other equipment cool down rather quickly, so that it is difficult to obtain a good purge before the catalyst melt freezes. Plants with a preheat system, should consider using this to keep the catalyst hot during shut-down until the catalyst has been satisfactorily purged. Sulphur burning plants without a preheat system should consider reducing the dry air flow rate through the furnace and converter as much as possible. This would increase the duration of purging time above 400°C, and improve the stripping of  $SO_2/SO_3$ , which is primarily limited by internal mass transfer and largely unaffected by a lower gas flow rate.

These strategies attack the cause of the problem, but may not be effective enough to completely alleviate the problem.

#### **Acid preheating**

It is known that acid plant stacks can have a highly visible acid plume during initial introduction of  $SO_2$  to the converter. It is also known that this plume disappears or at least is significantly reduced as soon as the circulating acid in the absorbing towers reach a temperature of about 80°C at the bottom of the towers. As the cause of this problem is well known, the simple solution is to preheat the acid. On a site that have several acid plants this can be achieved by cross-flowing hot, 98% acid from a neighbouring acid plant in operation to the plant preheating for start-up. For single plant sites, this is not an option. Instead, acid warm-up heaters can be installed to preheat the circulating acid before firing sulphur. This strategy has been proven as a successful technology in removing the start-up stack plume completely. A photo of a NORAM acid warm-up heater is shown next to the acid cooler used for normal operation in Fig. 13.



#### Acid aerosol removal

If catalyst purging and acid preheating are not acceptable to the operator, or do not achieve the desired result, then the following methods can be considered to

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remove the acid aerosols resulting from the emission of  $\mathrm{SO}_3$  gas.

#### WESP

Wet electrostatic precipitators (WESP) are one of the most efficient technologies available to remove sub-micron sulphuric acid aerosols. The incoming gas containing the  $SO_3$  is prequenched with water/ weak acid to cool and saturate the gas with water. In this prequench stage the  $SO_3$  gas reacts with H<sub>2</sub>O to form sulphuric acid aerosols, which are easily removed by the WESP by >99% efficiency. However, WESPs are fairly expensive and are not likely to be an economic solution for solving a start-up problem that last in the order of hours per year. Furthermore, WESP will not have any additional benefits in the removal of SO<sub>2</sub>.

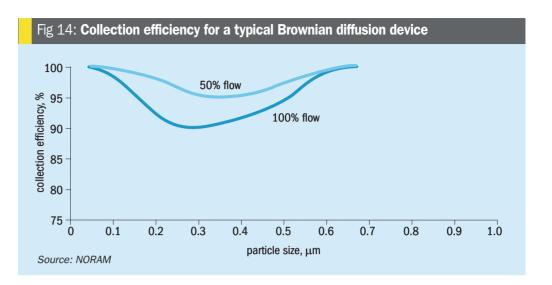
#### **Brownian diffusion mist eliminators**

Brownian diffusion mist eliminators are high efficiency sub-micron aerosol separation filters. As such they may be employed to efficiently abate the acid mist start-up plume from the main stack or from the start-up vents during preheating. As seen in Fig. 14, Brownian diffusion filters can remove more than 90% of sub-micron aerosols in the range 0.2-0.4 micron, and more than 98% of a typical, total distribution of acid aerosols and mist.

For plants that are lucky enough to already have Brownian diffusion candles (BD candles) in the final absorption tower, small modifications to the equipment should suffice to make them work as "start-up plume eliminators".

As discussed in the section on firing sulphur, the cold acid irrigating the absorption towers during start-up may become surface saturated with  $SO_3$  during start-up allowing  $SO_3$  slippage until the acid heats up. In addition, increased acid/oleum aerosols formation can be expected due to shock cooling of the hot gas while the acid is cold and if the acid concentration is not optimal, e.g. lower than 98 wt-% H<sub>2</sub>SO<sub>4</sub>. Hence, during start-up there will probably be increased rates of both non-absorbed  $SO_3$  gas and sub-micron aerosols.

BD candles will remove the majority of the sub-micron aerosols formed in the tower irrespectively of whether they are irrigated or not. If not irrigated, the BD candles will also become saturated with  $SO_3$  and slip  $SO_3$  gas, due to the cold acid temperature and because they catch the oleum aerosols generated at the inlet to the cold tower.





However, if the BD candles can be continuously wetted with 98% acid, they will become efficient SO<sub>3</sub> scrubbing devices, due to the high wetted surface area and intimate contact with the flowing gas through the candles compared to the lower surface area and gas contact of the packing in the tower. The key to removing SO<sub>3</sub> at start-up with candles is to make sure the BD candles are saturated with acid, and preferably warm, 98.5 wt-% acid. This candle irrigation can be implemented either with spray nozzles located at the tubesheet inlet to standing candles or with spray nozzles located above from the top of hanging candles. There are also more robust pre-wetting systems available as shown in Fig. 15. In this proven candle prewetting system, the acid flow should be started prior to the introduction of  $SO_2$  to the converter, to make sure all candles are saturated with flowing acid.

#### Fluidised bed scrubbing system

The use of fluidised bed technology to perform start-up  $SO_2$  absorption has already been mentioned. This technology also has merits in the abatement of particulate matter and aerosol removal, which can be achieved simultaneously with  $SO_2$  absorption in the same unit.

#### Training

Clearly, the experience and capabilities of owners and operators is a key component in keeping  $SO_2$  emissions low during startup. However, experience can take years, even decades to accumulate. Thankfully, modern tools exist for accelerating the rate at which operators build experience.

Operator training simulators (OTS) have recently begun to gain popularity in complex operational environments, especially where there are great rewards to be realized from well-trained operators and great penalties associated with mis-operation. Start-ups and shutdowns for sulphuric acid plants are certainly examples of such "high stakes" operations. Thus, it is no surprise that simulators are now being used to accelerate operator training, especially for startups, shutdowns, and other nonroutine and dynamic events.

In the case of sulphuric acid plant startups, specifically, an OTS can be configured to accurately simulate the startup behaviour of a real plant, but in a virtual environment. Operators can then practice their startup skills in a consequence-free environment so that they are well prepared to skillfully execute real life startups. Advanced OTS systems can even be programmed with scoring features that enable instructors to effectively grade operators on their startup capabilities by allocating points to key startup performance indicators like emission levels, fuel gas usage, and startup speed.

In order to be effective, operator training simulators need:

- robust dynamic simulation capabilities so students can interact with the OTS in real time;
- customisability so that the OTS can be configured to match the student's actual plant;

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#### high fidelity so that the OTS accurately mimics real life plant behavior.

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An effective OTS is built upon a dynamic simulation platform. Dynamic simulation programs, such as proprietary software like DuPont<sup>™</sup> TMODS, are different from steady state simulation in that dynamic simulators allow for changes to occur in real time (or in the case of advanced simulation packages, faster or slower than real time). Whereas steady state simulation takes inputs, runs algorithms, then produces outputs, dynamic simulation is a continuous dialogue between the student and the simulator. The dynamic simulation capabilities of an OTS allow the student to interact with a "virtual plant" via a user interface. In essence, the OTS is like a flight simulator that allows students to pilot a "virtual airplane."

In order to serve as an effective training tool, the flow scheme associated with the "virtual plant" clearly must match the flow scheme of the actual plant that is being simulated. This necessitates that an effective OTS must offer customisable flow schemes, but effective customisation does not stop with the flow scheme. What about graphics, interlocks, alarm points and control loops? To accurately model a real plant in a virtual environment, it is not sufficient to accurately mimic the flow sheet. The operator interface, graphics, and DCS control logic must also be integrated into the OTS so that the training environment looks and feels like the real thing.

In order for an OTS to truly achieve a real "look and feel," high fidelity is a must. This is perhaps the greatest challenge that simulators must overcome in order to be useful training tools for owners and operators. Simulators that lack high fidelity represent a highly academic and theoretical collection of complex equations that do not accurately portray the way plants behave in real life. To achieve high fidelity, an OTS should be developed and tested by experts who are intimately familiar with the real life behavior of the process that is being modeled. When done properly, an OTS that is based on calculations and theory can then be "tweaked" by a team of process experts to more accurately reflect real life behaviour.

Though effective dynamic simulation of a sulphuric acid plant is difficult, robust OTS systems are increasingly being used to accelerate operator training and to maximise the gains associated with proper plant and equipment design. When executed properly, an effective OTS program can be the missing link between a plant's current and desired start-up performance. Operators can practice keeping SO<sub>2</sub> emissions low during start-up so that when the time comes, they are ready.

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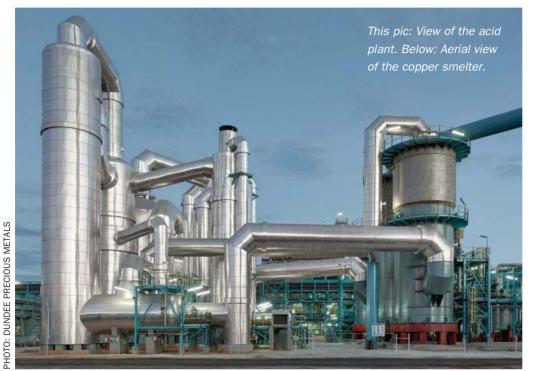


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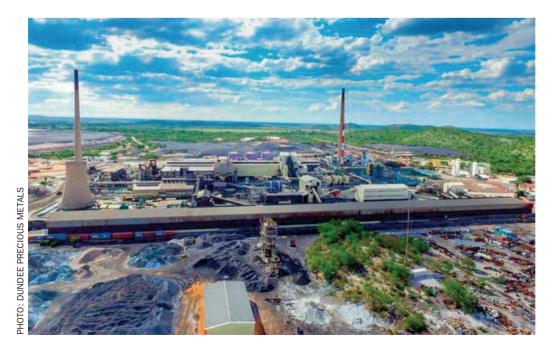
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## **Dundee's world-class** sulphuric acid plant



In April of this year, Dundee Precious Metals officially opened its new sulphuric acid plant in Tsumeb, Namibia. This project demonstrates the latest in sustainable technology and a commitment to social responsibility beyond project implementation.





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undee Precious Metals, a Canadian mining company, is located in Tsumeb, Namibia approximately 430 km north of the capital, Windhoek. Tsumeb is the closest town to the Etosha National Park and has a population of 14,000 people.

The Tsumeb smelter was constructed in the early 1960s to process concentrate from the Tsumeb copper mine and is one of only five commercial-scale smelters in Africa. It is linked by rail to the Atlantic port of Walvis Bay in Namibia. The primary smelter is a refurbished Ausmelt furnace and the facility employs close to 600 people, including contractors.

The smelter is one of only a few in the world which that is able to treat arsenicbearing copper concentrates and is therefore able to conclude long term favourable contracts to treat such concentrates. From the concentrates, the smelter produces blister copper, arsenic trioxide (As<sub>2</sub>O<sub>3</sub>) and sulphuric acid. The blister copper is delivered to refineries for final processing and the  $As_2O_3$  and acid is sold to third party customers.

Currently, half of the smelter's business comes from Dundee's Chelopech mine in Bulgaria. Additional business is solicited from a variety of sources globally, primarily South America.

#### Project background

In 2012, Dundee entered into a contract with Outotec, a global leader in minerals and metals processing technology, for the design and delivery of Peirce Smith (PS) converters, a gas cleaning system, sulphuric acid plant and related technologies downstream of the existing copper smelter (left). This was later converted into a full EPC contract. The key design data of the project are listed in Table 1.

Outotec's scope of delivery included the basic and detail engineering, procurement, supply, erection and commissioning of PS converters, a gas cleaning system and sulphuric acid plant, an effluent treatment plant

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#### Fig 1: Block diagram of the overall plant

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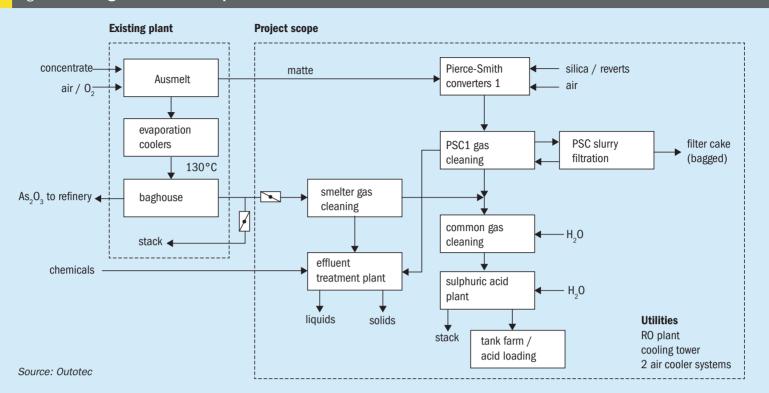


Table 1: Project key design data	
PSC matte per batch, t	160
Gas cleaning plant capacity, Nm <sup>3</sup> /h (dry)	110,000
Acid production (nominal, 100 wt% $H_2SO_4$ ), t/d	1,540
Acid plant SO <sub>2</sub> emissions, ppmv	< 300
Effluent treatment capacity, m³/h	30
Slurry filtration capacity, m <sup>3</sup> /h	4

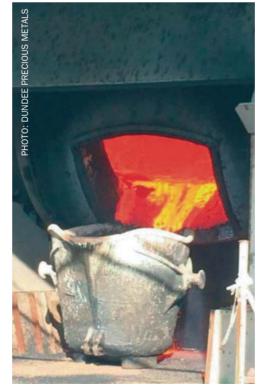
as well as a sulphuric acid tank farm based on proprietary Outotec<sup>®</sup> technologies.

Outotec supplied the entire chain of Outotec technologies and services to complement the existing Ausmelt smelter, which since 2010 also belongs to Outotec's technology portfolio. With its integrated solutions, Dundee Precious Metals now has a world-class process plant that is designed to meet international  $SO_2$  emission standards.

Built at a cost of almost NAD\$2.6 billion, the plant created over 1,400 contract jobs during construction and currently provides 50 full time positions. Sulphuric acid is a critical component in the mining industry which is produced in this instance by taking a byproduct from copper production and turning it into something of value for Namibia's mining economy, while at the same time ensuring a positive environmental outcome.

The entire project was delivered with no serious injuries, a commendable achievement given the brownfield nature of the work.

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Charging of the new Peirce-Smith converter.

## Focus on environmental sustainability

Environmental sustainability was achieved by the treatment of smelter and converter gases. The gases, which are high in sulphur dioxide, are now being treated and converted into sulphuric acid, which is sold as a product.

The new converter hoods provide much improved gas capture of the fumes generated in the copper converter process. This off-gas is cleaned from impurities in the gas cleaning plant and finally the  $SO_2$  is removed in the sulphuric acid plant, where it is converted to sulphuric acid.

The new PS converters provide not only a much more environmentally friendly solution, but are also larger in capacity and allow for the production of larger quantities of blister copper. PS converter dust is recovered in a converter dust slurry neutralisation and filtration process, maximising metal recovery.

As water is a limited resource in Namibia, the newly installed effluent treatment plant treats the process water required for the gas cleaning process. The water is neutralised and impurities including arsenic are removed.

A big effort was made to minimise the plant cooling water make up requirements by using air cooled cooling water systems for most of the cooling tasks, and the selection of a tailor made high yield

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Dundee Precious Metals' new sulphuric acid plant in Tsumeb.

Peirce Smith converter gas cleaning.

reverse osmosis plant for cooling water which is co make-up treatment. The con

Lastly, a tank farm, truck and train loading facilities allow the safe handling of this product.

#### **Peirce Smith converters**

The two new PS converter produce blister copper with a copper content of 98-99% from matte. For oxidation to take place, air is blown directly into the molten matte through tuyeres at the back of the converter.

One important design aspect is that the primary converter hood is tailor-made and has a tight fit against the PS converter to minimise false intake of air.

#### Gas cleaning technology

A gas cleaning and sulphuric acid plant has been installed downstream of the existing Ausmelt and the new Peirce Smith converters. The gas cleaning plant comprises three separate streams for cleaning the Ausmelt off-gas and the off-gas from the two Peirce Smith converters, which operate alternately, followed by a common gas cleaning section where the combined off-gas from the streams is cleaned.

Each stream consists of a high efficiency scrubber with an integrated quench section on top followed by a droplet separator and an ID-Fan. By selecting this technology no evaporation cooler or hot ESPs are required for the PS converter off-gas.

The high efficiency scrubbers cool the gas by water evaporation and remove the main fraction of the dust in the scrubbing zone by turbulent mixing of scrubbing liquid and dust loaded gas. This turbulent mixing requires a pressure drop in the scrubber which is compensated by ID-fans.

The common gas cleaning section consists of a gas cooling tower and four wet electrostatic precipitators arranged in two stages.

The gas cooling tower, which consists of a tower filled with an irrigated random packing, cools the gas to adjust the humidity of the gas according to the requirements of the downstream sulphuric acid plant. Final removal of dust and acid mist particles takes place in the wet electrostatic precipitators.

All remaining small particles are removed in an electrostatic field. The scrubbing acid, which contains all impurities scrubbed out of the gas, is transferred for cleaning via the  $SO_2$  stripper, where  $SO_2$  is stripped from the weak acid, to the effluent treatment plant.

A major portion of the dust removed in the converter gas cleaning streams is collected in settling tanks and pumped to a slurry filtration and bagging unit.

#### Acid plant process

The clean off-gas from the gas cleaning plant is treated in a 2+1 double absorption acid plant. The unusual 2+1 acid plant is a tailor made approach to the gas conditions. Ceasium-promoted catalyst is used in the last converter bed to achieve a high overall conversion.

The acid plant is designed for a wide range of process conditions. A key feature is flexible heat management which is achieved by parallel gas coolers in the gas route to the intermediate and final absorption tower.

The re-heat exchanger for the gas downstream of the intermediate absorption is of Outotec's typical CORD<sup>™</sup> design with a horizontal stainless steel part operating under corrosion optimised conditions. This results in a long lifetime for both the horizontal and the vertical carbon steel part, even under fluctuating process conditions. The benefit of this sustainable approach is that it has no sacrificial parts that require frequent replacement.

A feature of the absorption section is the closed loop cooling system for the drying tower and absorption tower acid which uses air coolers to save water. This leads to the choice of Outotec Edmeston SX<sup>®</sup> stainless steel as material of construction for the acid coolers of the closed loop cooling water systems. Outotec Edmeston SX<sup>®</sup> sustains much higher wall temperatures than conventional acid coolers, so much higher cooling water temperatures are favourable regarding the air cooler size and power consumption.

The product acid is stored in three acid storage tanks. Further scope of the project was an acid loading station for filling road tankers and tank wagons.

#### **Cooling water systems**

An open cooling water tower as well as two air cooler systems with closed loop cooling water systems have been delivered for cooling the cooling water required by the gas cleaning and the sulphuric acid plant.

The two air cooler systems have been installed to minimise the consumption of the cooling water make-up. They operate at two different temperature levels to minimise air cooler size and electrical power consumption: The hotter one cools the strong sulphuric acid, while the colder

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system cools the first stage of the weak acid cooling in the gas cleaning plants.

The evaporative cooling water tower is used to achieve the necessary low temperatures for the second stage cooling in the gas cleaning plant and is used for product acid cooling.

A reverse osmosis plant was chosen to remove the high impurities from the available water, to allow for a maximum number of cooling water concentration cycles in the evaporative cooling tower. This reverse osmosis plant is equipped with an independent second stage to maximise the water vield. The reverse osmosis water is also used for dilution water in the acid plant.

#### **Effluent treatment plant**

Outotec's effluent treatment process is designed to treat weak acid effluent from the gas cleaning plant with a sulphuric acid concentration of 12.5 g/l and an arsenic concentration of 5 g/l.

The weak acid is collected in an effluent collection basin. From the effluent collection basin effluent is pumped to the effluent treatment plant where it is purified in a precipitation process. In the precipitation process, acid is neutralised and arsenic as well as other soluble impurities are precipitated by adjusting the pH by adding lime milk.

From the Outotec precipitation reactors the slurry produced flows by gravity to the Outotec clarifier for solid-liquid separation. Clarifier underflow slurry is pumped through a filter feed tank to the Outotec PF filter. Filtrate and wash waters from the



feed of clarifier and dried filter cake is discharged through a cake conveyors to the bagging station where cake is bagged for solid disposal purposes.

The moisture content of the filtrated solids is less than 40 wt-%. Clarifier overflow flows by gravity to a pump tank and is reused in overall plant processes. The effluent treatment process yields water containing less than 100 mg/l of arsenic and suspended solids.

#### **Converter slurry filtration process**

The Outotec converter slurry filtration process is designed to neutralise and filter the dust slurry from the gas cleaning plant's settling tanks to recover valuable metals

The design capacity of the converter dust neutralisation and filtration plant is designed for converter dust slurry with a sulphuric acid concentration of 30 g/l and dust solid concentration of 110 g/l.

Converter dust slurry filtration plant.



solution. This neutralised slurry is then filtered in an Outotec PF filter for filtrating the solids Dried filter cake is discharged to a bag-

ging station where the cake is bagged.

#### **Outotec's commitment to** community investment

Outotec (together with Dundee Precious Metals) also initiated a community project to build a new dining hall at Ondudu Primary School. This dining hall will allow young students to rest and prepare themselves for learning lessons. The project consists of more than just monetary support, and required the great enthusiasm, passion and commitment of the project teams.

The dining hall was inaugurated on November 25, 2015, by the honourable Ester Anna Nghipondoka, deputy Minister of Education, Arts and Culture, in Tsumeb. During the inauguration Dundee and Outotec representatives expressed the importance of the social project and the commitment of both companies for social sustainability.

Rick Howes (President and CEO of DPM) said: "The acid plant was the largest project ever undertaken at the Tsumeb smelter and one of the largest private sector investments in Namibia This investment represented our commitment to improve the quality of life for our employees and the local community and reduce the impact the smelter has to the natural environment. It was the culmination of the efforts of many to bring this project to completion."

Outotec would like to acknowledge Dundee Precious Metals in the production of this article and thank them for their input and use of photographs.

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**Technical Editor:** LISA CONNOCK lisa.connock@bcinsight.com

Contributor: MEENA CHAUHAN meena.chauhan@integer-research.com

Publishing Director: TINA FIRMAN tina.firman@bcinsight.com

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#### Subscriptions Manager / enquiries: MARIETTA BESCHORNER

Tel: +44 (0)20 7793 2569 Fax: +44 (0)20 7793 2577 marietta.beschorner@bcinsight.com Cheques payable to BCInsight Ltd

#### Advertising enquiries:

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Published by: BCInsight Ltd Southbank House, Black Prince Road London SE1 7SJ, England Tel: +44 (0)20 7793 2567 Fax: +44 (0)20 7793 2577 Web: www.bcinsight.com www.bcinsightsearch.com

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