

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

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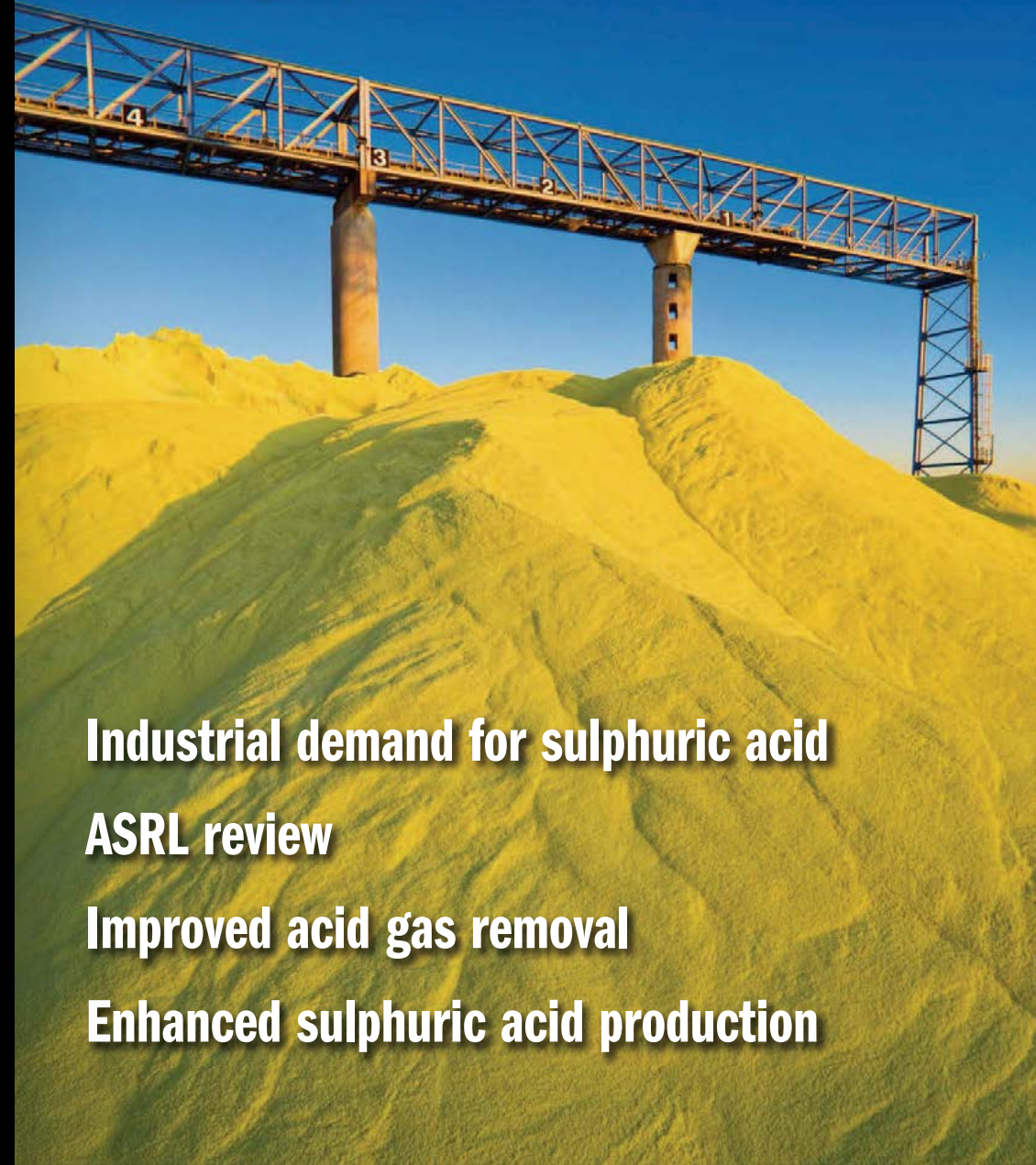
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Number 364

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SULPHUR

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Industrial demand for sulphuric acid

ASRL review

Improved acid gas removal

Enhanced sulphuric acid production

CONTENTS

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

Improved acid gas removal

COVER FEATURE 4

Enhanced sulphuric acid production

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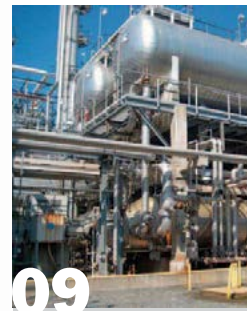
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09
Industrial acid consumption
Mixed fortunes for chemical and industrial uses.



26
CO₂ emissions
Trade-offs with sulphur recovery.

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SULPHUR

www.sulphurmagazine.com

NUMBER 364

MAY | JUNE 2016

CONTENTS

- 9 Industrial uses of sulphuric acid**
Although phosphates and sulphur fertilizers represent the majority of sulphuric acid demand, its use in a wide variety of industrial applications has been a major growth area in recent years.
- 11 Working in concert – sulphur and sulphuric acid**
Harold Weber, Vice President, Regulatory Affairs and Special Projects and Craig Jorgenson, Vice President, Transportation and Regulatory Affairs for The Sulphur Institute discuss the organisation's work on sulphur and sulphuric acid regulatory affairs.
- 12 SOGAT 2016**
A report on the Sour Oil and Gas Advanced Technologies Conference, held in Abu Dhabi in March.
- 13 Acid gas reinjection**
With increasing volumes of sulphur from sour oil and gas projects now beginning to reach the market, will companies have to more seriously consider reinjection of acid gas?
- 14 TSI 2016**
A report on The Sulphur Institute's 2016 Sulphur World Symposium was held from April 12th-14th, in Vancouver, British Columbia.
- 15 Sulphur forming listing**
Sulphur's annual listing of new sulphur forming projects around the world.
- 15 ASRL Review**
The chemistry and technology of sulphur degassing.
- 18 Improved acid gas removal**
Acid gas removal has been improved over the years with the development of new solvents and novel process line-ups, tailored to specific project requirements.
- 20 Combining technologies for enhanced acid production**
New sulphuric acid plant designs are being proposed that combine innovative technologies in new process line-ups to optimise the economics of sulphuric acid production and reduce emissions.
- 24 Sulphur recovery from waste metallurgical gases**
O.G. Eremin and A.V. Tarasov discuss laboratory investigations that have been conducted by the Gintsvetmet in Moscow, Russia, to study the process of catalytic reduction of SO₂ using carbon monoxide.
- 26 Sulphur recovery, energy efficiency and carbon management**
UniverSUL Consulting explores the relationship between SO₂ and CO₂ emissions in sulphur recovery facilities and investigates whether there is a point at which further increases in sulphur recovery efficiency results in diminishing returns, in terms of energy consumption and associated CO₂ footprint.

REGULARS

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

CONTENTS

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

Improved acid gas removal

COVER FEATURE 4

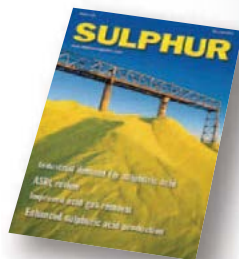
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The world's biggest company?



Saudi Arabia sent shockwaves through the global oil industry in April when it announced that it was "reviewing" the possibility of an IPO of Saudi Aramco. Aramco is far and away the world's largest holder of oil reserves, at 260 billion barrels, ten times those of the nearest private oil company, ExxonMobil. With production of over 10 million barrels per day, it out-produces the entire United States of America. A stock exchange listing would in effect create the world's largest publicly traded company.

However, before anyone gets too carried away, Crown Prince Muhammad bin Salman, who is in charge of the 'Vision 2030' plan to diversify the Saudi economy, has suggested that Saudi Arabia only wishes to sell an initial 5% tranche of the company by 2017-18, as part of a bid to kick start a \$2 trillion sovereign wealth fund for the Kingdom which would then, like Norway's similar but smaller \$850 billion fund, invest internationally on behalf of the public. Other components of the fund could come from \$600 billion of fiscal assets and sale of state land and industrial areas, and the privatisation of state hospitals and some distribution segments. As part of this, the value of the 5% Aramco share sale has been estimated at \$100-150 billion, based on reserves and output, but in truth no-one really knows how much Aramco is worth – the company is legendarily inscrutable, and the global oil industry is frequently sceptical of its figures. Likewise the oil reserves themselves will not, apparently be up for grabs – the sale will reportedly focus on a downstream spin-off of part of Aramco, probably including refining and chemical production.

Born in the 1930s as the Arabian American Oil Company (hence Ar-Am-Co), Aramco was nationalised in the 1970s, as part of the wave of 'resource nationalism' that swept the post-war, post-colonial world. But it has long been a plaything of the ruling Saudi elite. It does not report revenues, and in addition to its vast oil, gas and petrochemical assets, runs a fleet of eight airliners and a hospital system that treats 360,000 people. Many hope that a listing would force the company into greater transparency, and possibly to tackle some of its inefficiencies. The risk for investors however is that they instead end up playing second fiddle to Saudi

Arabia's use of Aramco as a cash cow, foreign policy tool and job generator for Saudi citizens, in a similar way that Russia has occasionally used state gas producer Gazprom.

Nevertheless, Saudi Arabia's need to give itself a greater hedge against low oil prices has been made apparent by the current crash – albeit one in which Arabia itself has colluded, in order to "maintain market share" – generally regarded as code for bankrupting US shale oil producers and keeping rivals Russia and Iran on a tight leash. The Kingdom counts on oil revenues for 70% of state income, with which it funds one of the world's most generous public provisions of services and welfare, along with low tax burdens on its 28 million citizens. As a result, Saudi Arabia has required an oil price of over \$100/bbl to break even, and at the current \$40/bbl it is hemorrhaging its banked reserves, with a budget shortfall of \$87 billion projected for 2016. The government has been forced to raise retail fuel prices by up to 80% and cut subsidies on electricity, water and other services, but it also frets about social unrest. The recent push to develop the Kingdom's phosphate reserves via Ma'aden has also been another step along its journey to try to become more than just a petro-state.

Saudi Aramco is also of course one of the world's largest sulphur producers and exporters, although its top spot in the Middle East is currently yielding to Abu Dhabi following the start up of Shah and the latest phase of Habshan. It could be that sulphur is one of the areas which Aramco considers to be peripheral to its core, oil-based activities, and which forms part of a de-merged entity. It will be interesting to see where this story goes.

Richard Hands, Editor



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CONTENTS

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

Improved acid gas removal

COVER FEATURE 4

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Price trends



MARKET INSIGHT

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

SULPHUR

Uncertain outlook

The global sulphur market outlook remains uncertain, as prices have remained weak through April, although there are signs the market may have reached a floor. The downstream phosphates market remained under pressure, with limited uptick in trade adding to the uncertainty in the sulphur market on how the second half of the year is likely to unfold.

Major Middle East sulphur producers have continued to hold prices relatively stable in monthly price postings. In Qatar, Tasweeq dropped its price for April by \$9/tonne to \$78/tonne f.o.b. Ras Laffan. The May price was subsequently increased by \$1/tonne – signalling the producer's expectation of a more stable outlook for the weeks ahead. Meanwhile, in the UAE, Adnoc decreased its April price by just \$3/tonne to \$85/tonne f.o.b. Ruwais for shipments to the Indian market. Despite the new supply stream from the UAE with Al Hosn's 3-million t/a Shah project heard to be running at full capacity, availability for spot cargoes from Ruwais have not been seen in the spot market. Significant volumes are understood to have been committed under contract to buyers including Morocco. Aramco Trading in Saudi Arabia

has had limited spot availability in recent weeks, and is understood to be sold out through April and May on the back of a maintenance turnaround. The lack of availability from the Middle East may add some stability in the short term outlook, particularly during a period of slow demand. However, additional supply in Qatar from the new Barzan project was expected online during Q2 2016, and is due to add significant volumes to the market. Sources have indicated the project has yet to start up and has not been reflected in any additional export availability. The official ramp up date for the project is unclear. Phase 2 of the project is also scheduled to come online in 2016. Any delays to projects adding new supply could lead to increased stability in the 2H of 2016.

Over in China, import statistics released for Q1 2016 show a 21% rise year-on-year at over 3 million t/a. Supply from the UAE, South Korea and Canada have all shown significant increases while trade from Kazakhstan and Iran dropped. Sulphur inventory levels at the nine major ports in China have been on the rise through 2016, reaching a peak of around 1.6 million tonnes and dropping slightly to 1.5 million tonnes in April. Some speculative traders are thought to have entered the market, with a portion of the stocks in the hands of traders rather than end users. Local

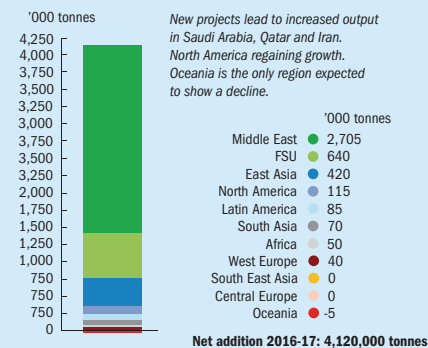
producers have been dropping prices, a reflection of the hand-to-mouth strategy adopted by end users and weaker market sentiment.

Spot prices in India have also eased down to the mid/high-\$90s/tonne c.f.r in recent deals. Both FACT and Coromandel entered the market for spot volumes. FACT held a tender closing 18 April for 25,000 tonnes for arrival 18-22 May at Cochin. Coromandel purchased a similar sized cargo for May arrival. IFFCO remained out of the market in April, preferring instead to purchase direct sulphuric acid, due to its competitive pricing at \$10-15/tonne c.f.r. Surplus sulphuric acid in Asia has put downward pressure on the market, beyond the lower sulphur prices.

Vancouver spot prices have also ticked down, following the downward global trend. Sulphur exports to China increased however in Q1 2016, from less than 100,000 t/a earlier to over 250,000 t/a. The start up of the Mosaic melter meanwhile has yet to show any significant impact on trade from Canada to the US market, with exports of molten sulphur stable at around 140,000 tonnes in January 2016, on a par with monthly exports through 2015. US sulphur production in 2016 is expected to see some recovery, following the overall decline in 2015 from the oil refining sector as some refineries took to processing lighter crudes. US refineries are reported to be running at over 90% of capacity rates in Q2 2016.

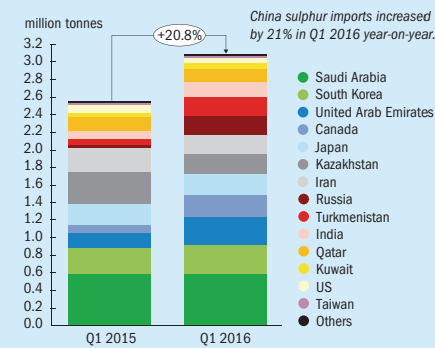
In Latin America, Brazilian sulphur demand has been stagnant, with contract shipments the main focus. Q2 contracts

Fig 1: New sulphur capacity 2016-17



Source: Integer/GTIS

Fig 2: Chinese sulphur imports in Q1 2016



Source: Integer/GTIS

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CONTENTS

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

Improved acid gas removal

COVER FEATURE 4

Enhanced sulphuric acid production

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were set at \$75-81/tonne c.f. AFT/Fertinal in Mexico booked a cargo to arrive in early/mid May from California. The buyer's next enquiry is likely to be at the end of May/early June, expected to be sourced from Vancouver. In Argentina, Meranol is in the market for 20,000 tonnes for arrival in late July and anticipating low price offers.

Contracts have also been the focus in North Africa, with prices settling at a decrease for Q2 of over 30% to the mid/high-\$70s/tonne c.f. Demand from Morocco continues to rise, with shipments from the UAE remaining strong as OCP expands its processed phosphates capacity. Any improvements in the phosphates market will be important for a recovery in sulphur pricing in the outlook as phosphates prices have added downward pressure to the market. While DAP stocks are reported to be healthy in India, the forecast for a good monsoon could help prop up the market in the second half of the year. DAP operating rates in China have been easing however, dropping down to 60% in April, due to the lack of interest for export volumes and low price expectations.

SULPHURIC ACID

Weak sentiment

Sulphuric acid prices have remained under pressure in recent weeks. There has been some stability in Northwest Europe however, with the price range holding at \$0-5/tonne f.o.b. through April. The European market

has been balanced despite the weaker trend in other key markets. Contract prices for Q2 have been agreed at a rollover, a reflection of the stable local market, despite the drop in liquid sulphur prices.

Trade to Morocco has remained healthy through 2016 so far, with expectations that OCP will continue to import acid through the second quarter as it ramps up its processed phosphates production. Prices also remain attractive for smelter acid from European suppliers.

Significant price drops have been seen in Asia meanwhile, with contracts settlements reflecting decreases. Inventory levels at Japanese smelters have been reported to be high, adding to the downward pressure. Some contract volumes were not booked for Chile, leading to additional length in the market during Q1. The Taganito nickel project in the Philippines also underwent a maintenance turnaround, reducing acid consumption. Shipments from Korea to China were heard settled in the \$10/tonne c.f. range and low pricing has been seen in Indonesia and Malaysia. Japan/Korean export acid prices have dropped into double digit negative netbacks, up to \$-30/tonne c.f. As market prices have remained weak, the China export price reported at \$0-15/tonne f.o.b. for sulphur-based acid has not been tested with any new business. Imports of acid to China have been on the increase meanwhile, with volumes up by 2% in March. South Korea remains the main supplier, representing 68% of total supply. Tonnes were

also shipped from the Philippines and Japan.

Spot prices in India have dropped through April, down to single digit c.f. levels. There has been interest for spot volumes from end users, with some buyers preferring to purchase competitively priced acid cargoes over sulphur.

Demand in Chile remains subdued, with contract shipments reflecting the majority of trade and prices have eased for confirmed deals. BHP was heard agreeing a price in the \$40 c.f. range. The low commodity price trend is still a hindrance to acid demand in the metals leaching sector. Chile sulphuric acid imports dropped 3% in 2015 year on year. We expect to see a softer tone for imports in 2016 as the outlook for copper remains pessimistic in the short term.

Acid demand in Brazil has also been slow, as the downstream fertilizer market has remained lacklustre through 2016 to date. Some acid spot deals were heard concluded at \$40-50/tonne c.f., while others discussed prices in the Petrobras tender in the \$55-60/tonne c.f. range. Imports have dropped significantly, a reflection of the slowdown in the market, down by 60% in January-February compared with a year earlier. Availability from Boleo in Mexico continues to put pressure on the broader market, due to the competitive prices. Any additional tonnage offered from Mexico through the remainder of 2016 will be a bearish factor on the market, particularly if the processed phosphates market does not see a meaningful recovery. ■

Price indications

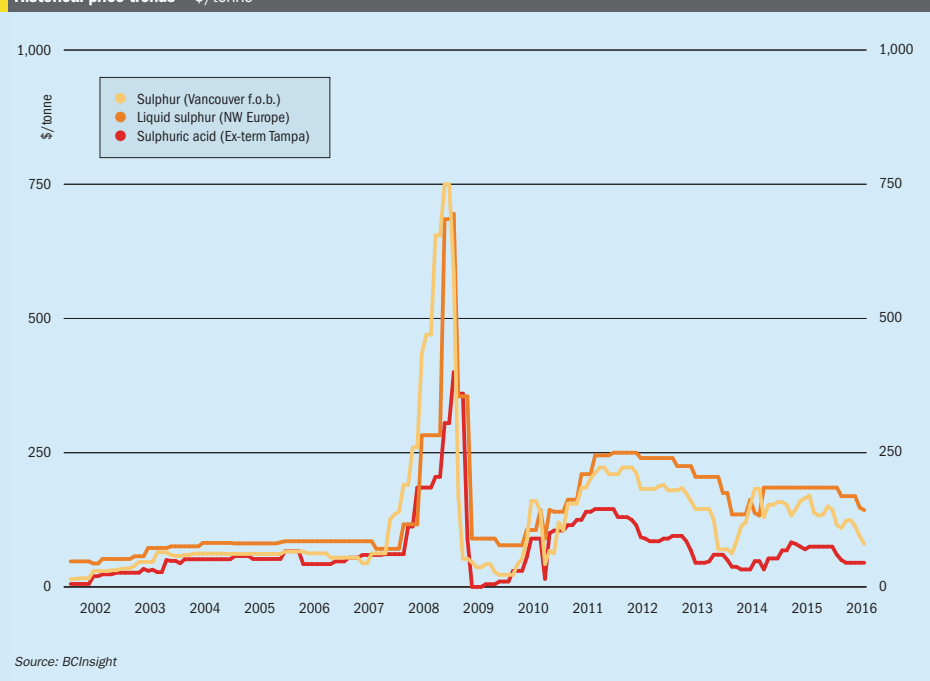
Table 1: Recent sulphur prices, major markets

Cash equivalent	November	December	January	February	March
Sulphur, bulk (\$/t)					
Vancouver f.o.b. spot	120-125	125	113	95	80
Adnoc monthly contract	130	130	122	105	88
China c.f. spot	125-145	125	108	100	86
Liquid sulphur (\$/t)					
Tampa f.o.b. contract	110	110	95	95	95
NW Europe c.f.	153-185	148	148	148	143
Sulphuric acid (\$/t)					
US Gulf spot	40-50	45	45	45	45

Source: CRU

Market outlook

Historical price trends \$/tonne



Source: BCInsight

SULPHUR

- Prices may have reached a floor, but further softening is possible unless demand and interest in spot volumes improves. Any sustained period of tightness in the Middle East could help support prices to stability and then recovery.
- Demand is key question for the coming quarters: can the processed phosphates market see a significant improvement. Activity in India will be a major focus in Q2 and Q3 – as a boost phosphates imports could lead to improved pricing and further aid sulphur prices.
- New supply from the Middle East will be critical in determining the global supply/demand balance and influence pricing in the 2H of 2016. Delays to projects could lead to improvement in short term prices.
- The impact of the Mosaic melter remains to be seen and the level the project is utilised at will influence trade to/from North America this year. Any developments in forming projects in Canada may also set the scene for

increased exports from Vancouver in the outlook.

● Projects planned to add new sulphur supply in China will influence the country's import requirement in the longer term outlook. While imports remain healthy to date in 2016, as new oil and gas projects in the pipeline come online may impact the historical levels of import demand, leading to increased availability for other markets.

● **Outlook:** The short term supply dynamics will be a key focus for pricing, as well as developments in end user markets. Prices are expected to remain in a lower price range overall for 2016, with potential to see smaller price movements, as uncertainty continues to lead buyers to continue purchasing on a hand-to-mouth basis.

SULPHURIC ACID

- Mexico continues to export surplus acid, a key bearish factor for the market and potentially for the outlook. Any slowdown in exports could help stimu-

late the spot market in Brazil, leading to a potential price recovery.

- Demand is also key for sulphuric acid, with the broader commodity slowdown influencing the market. The remainder of 2016 is expected to be under pressure, as metals and phosphates prices continue to weigh on demand.
- Imports of acid to Chile are expected to remain on a downward trend through 2016. The slowdown in Brazil may see improvement, should the processed phosphates market see improvement in the 2H of 2016.
- Toros has started its sulphur burner in Turkey and has reduced its sulphuric acid imports. As nickel prices remain under pressure, the leaching projects in the country are likely to see a slower than expected ramp up.
- **Outlook:** Acid prices are expected to remain relatively stable in Europe in the upcoming quarters. The upcoming change in 2017 from acid to sulphur in Cuba at Sherrit's Moa project poses questions as to where the acid will be diverted to. ■

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

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COVER FEATURE 4

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MIDDLE EAST

Collaboration on heavy fuel oil upgrading project

Canadian-based clean technology engineering company Genoil Inc says that it has signed a Letter of Intent with the Beijing Petrochemical Engineering Co Ltd (BPEC) for a \$5 billion desulphurisation and upgrading project which the companies will jointly develop "in the Middle East". The project will see the use of Genoil's proprietary technology to produce 500,000 bbl/d of low sulphur crude oil. Loans have been agreed via one of China's largest banks, and the companies are aiming to partner with "a major party" in the Middle Eastern region. The LoI goes on to discuss the possibility of ultimately developing 3.5 million bbl/d of desulphurisation capacity at a total cost of \$35-50 billion.

The bold move is aimed at supplying the shipping market with low sulphur fuel; steadily tightening International Maritime Organization (IMO) regulations are moving towards a 0.5% global cap on sulphur in marine fuels, and as low as 0.1% in specified Emissions Control Areas, with the global cap potentially expected by 2020. Genoil says that its technology is able to produce low cost compliant LSFO from refinery residue without the need for

blending, and which can be priced much more competitively than marine gasoil (MGO).

Commenting on the development, Bruce Abbott, President and Chief Operating Officer, Genoil commented: "with Genoil's GHU technology we can take refinery residue and turn it into LSFO meeting 2020 legislation. With financial and engineering support from around the world, we are committed to developing sustainable sources that will help solve some of the energy challenges that we face today. The shipping industry is experiencing increased environmental regulation, and seismic change within the fuel supply chain. Genoil's ability to provide the industry with compliant products in time to meet 2020 regulations will go a long way to alleviating the pressure on refiners, charterers, ship owners, as well as fuel suppliers in having access to adequate, cost effective products."

Another project looking to produce 1 million bbl/d is also said to be currently under consideration by a second national oil company. ■

GERMANY

Shell and UFT collaborate on sulphur-enhanced urea

Shell and Uhde Fertilizer Technologies (UFT), part of thyssenkrupp Industrial Solutions, have announced a partnership to integrate UFT's fluid bed granulation technology with Shell's sulphur enhanced urea Urea-ES technology. The two companies say that they have completed successful trials using Urea-ES emulsion in UFT's fluid bed granulation pilot plant in Leuna, Germany. Urea-ES aims to provide vital sulphur nutrient to soils by incorporating elemental sulphur into the world's most commonly used fertiliser, urea, helping to unlock higher crop yields and improved soil health. The new partnership aims to allow the largest urea plants in the world to produce granulated sulphur-containing urea.

"Fertiliser producers had been asking us about incorporating sulphur into their urea for a long time," said Matthias Pothoff, Director of Uhde Fertilizer Technologies. "From the first discussions with Shell Thiogro about a partnership, it was clear this would be a win-win relationship."

Urea-ES technology uses Shell patented technology to emulsify micron-sized particles of elemental sulphur evenly throughout urea, forming a homogeneous emulsion, in contrast to existing elemental sulphur-containing urea technologies, which typically coat urea in a layer of elemental sulphur.

The microscopic size of the sulphur particles, at under 40 micrometres (µm), promotes the oxidation of the sulphur within the crop season. The elemental sulphur liquor is finely dispersed in the urea melt before the solution is fed to the granulator. The flexibility of the UFT granulation process allows the production of Urea-ES without any significant changes; as in the normal urea granulation, the particles grow through the solidification of tiny droplets on the seed material. The result is a very hard granule, which UFT says is superior in quality to granules produced through layering or agglomeration-based processes. This slow accretion process is unique in permitting the water present in the urea solution to be thoroughly stripped on a continuous basis, resulting in the end product having a low moisture content. The bulk of the crystallisation heat released as the Urea-ES solidifies is removed by evaporating the water in the urea solution. This method of heat release reduces the amount of ambient air required for cooling and the evaporation is highly efficient because it takes place directly on the granule surface.

ALGERIA

Contracts awarded for three new refineries

Amec Foster Wheeler says that it has been awarded a front-end engineering design (FEED) contract by Sonatrach for three new refineries, to be located in Biskra, Tiaret and Hassi Messaoud. The three refiner-

ies will each have a processing capacity of 5 million t/a of Algerian crude oil and will also contain facilities for atmospheric distillation, LPG separation, hydrocrackers, desulphurisation units, bitumen production, utilities, blending, effluents treatment, control rooms and laboratories. The Biskra site will also include lubrication oil facilities. Amec Foster Wheeler will also support Sonatrach in the selection of technology licensors for all three refineries.

Roberto Penno, Amec Foster Wheeler's Group President for Asia, Middle East, Africa, and Southern Europe, said: "Sonatrach is a long-term customer of Amec Foster Wheeler and this is a strategically important project for the Algerian Oil & Gas industry. We will apply our significant global refinery expertise to enable maximum efficiency of these three new refineries."

Amec Foster Wheeler's scope of work is scheduled for completion in the third quarter of 2017.

MALAYSIA

Petronas to install DynaWave® scrubbers

MECS DynaWave® technology has been selected by oil and gas services provider Petrofac for the installation of three custom engineered scrubbing systems for sulphur dioxide removal at Petronas. The units will be part of the company's new RAPID Project refinery in Pengerang on Southern Johor, and will be delivered dur-

ing 2Q 2016. RAPID (Refinery and Petrochemicals Integrated Development) is a massive \$16 billion refinery project being undertaken by Petronas, and is expected to be capable of processing 300,000 bbl/d by the time it comes on-stream in 2019. As part of the project three 470 t/d sulphur recovery units will be installed.

"Each of the scrubbers will treat the off-gas of one sulphur recovery unit (SRU) and its dedicated tail gas treatment unit (TGTU)," explained Angus Yip, MECS Sales Manager for South East Asia & Australia - New Zealand. "Petronas requires SO₂ emission levels to be lower than 150mg/Nm³, which we can guarantee under any given set of upstream conditions."

Each scrubber consists of two reverse jet stages located in an inlet barrel, which is connected to a disengagement vessel. They are capable of handling high inlet acid levels, which makes it possible to bypass upstream TGTUs while still meeting and even exceeding regulatory emissions requirements, according to MECS. They can be designed to cope with inlet temperatures of up to 1,200°C, but for Petronas the choice fell on optimising heat recuperation from the incinerator so that the units will take incoming gas at around 300-350°C.

SAUDI ARABIA

Start-up for Hasbah

Saudi Aramco says that it has begun producing gas from its sour offshore Hasbah field. At full production the project will add 39 million m³/day (1.3 billion scf/d) of non-associated sales gas to help supply Saudi Arabia's growing requirements. The field was due to begin production last year, but has been delayed by technical issues. Aramco says that the project has been "one of the most challenging non-associated gas field developments". The gas, which contains 4-8% hydrogen sulphide, is being supplied to the Wasit gas processing plant, but will be switched to the Fadhili plant when the latter is completed in 2019-20.

The higher costs of processing the sour gas make Hasbah gas more expensive, at around \$3.50-5.50/MMBtu, much higher than domestic prices in spite of a 40% hike to \$1.25/MMBtu earlier in the year. Hasbah is part of a trio of sour offshore developments. The Karan gas field began producing in 2013, and the 1.2 billion scf/d Arabiyah field is due to begin production soon.

CANADA

Blackbird to process gas from Elmworth

Blackbird Energy says it has signed a letter of intent with a "third party" for the transportation and processing of sour gas produced from its Elmworth project in Alberta. A gas handling agreement is expected "soon." The terms cover transportation to the sour gas plant and processing of 6 MMcf/d of natural gas and associated liquids from the project. Transportation and sour gas processing is expected to begin on or before 1 January 2017. Blackbird is developing the Montney shale at Elmworth near Grande Prairie, Alberta.

Although it has not specified the processor, the Pembina Pipeline Corp. has also recently agreed to acquire 250 MMcf/d of sour gas processing capacity and associated infrastructure in the Montney shale from Paramount Resources Ltd., and the two companies have also agreed to a 20-year midstream services agreement, in a deal valued at C\$591 million (\$452 million). Pembina will acquire Paramount's newly-constructed Musreau Complex, which includes 250 MMcf/d of gas processing and 22,500 bbl/d of condensate stabilisation; an amine processing train; gathering lines; sales transportation pipelines and future disposal wells.

UNITED STATES

Shell and Aramco agree to split Motiva JV

Saudi Aramco and Royal Dutch Shell have agreed a non-binding Letter of Intent to separate the assets of their Houston-based refining joint venture Motiva Enterprises LLC, which has been 50% owned by the two companies since 2002. The partners have agreed to evaluate options before finalising a definitive agreement to divide and transfer Motiva's assets, liabilities, and employees. Aramco's holding subsidiary Saudi Refining Inc will keep the Motiva name and take 100% ownership of the 600,000 bbl/d refinery at Port Arthur, Texas, as well as 26 distribution terminals, and rights to use the Shell brand for gasoline and diesel sales in Texas and some other parts of the US. Shell keeps the 235,000 bbl/d Norco refinery, where it also operates a separate petrochemical facility, and the 240,000 bbl/d Convent refinery, plus nine distribution terminals, ■

and rights to sell Shell-branded products in Florida, Louisiana and the northeastern states. The companies' 300,000 bbl/d Arabian joint venture refinery Sasref at Jubail will be unaffected by the split.

Refiners face credit crunch

The introduction of 'Tier 3' regulations on sulphur in gasoline could lead to a massive hike in the cost of emissions permits from January 1st 2017, according to industry experts. US fuels are moving from a 30 ppm sulphur standard to a 10 ppm standard, putting them in line with Europe and many other nations. However, the huge capital investment required is leading to many refiners opting to purchase emission credits to extend their compliance period to 2020, according to Reuters. The EPA awards credits to refiners who produce fuels below regulated levels, and they can transfer credits from existing programmes into the Tier 3 programme or buy credits from other refiners. Tier 3 credits are reportedly trading at around \$400 apiece, as compared to around \$25 for Tier 2 credits. This probably explains why, in spite of tighter refining margins, US refinery capital spending is expected to remain robust over the next couple of years, with estimates of about \$9.2 billion worth of active capital projects planned for 2016 and \$9.3 billion in 2017.

New ProTreat version released

Optimised Gas Treating has released version 6.0 of its ProTreat software for sulphur plants. OGT says that version 6.0 includes a complete sulphur plant state-of-the-art simulator which can be fully integrated with upstream AGRUs, AGEs, and SWSs and with downstream quench towers and TGTUs. All current licensors will have access to the new sulphur plant simulator free of charge until 31st December, 2016.

ABU DHABI

Al Hosn looking at Shah expansion

Saif Ahmad Al Ghaffi, the chief executive of Al Hosn Gas, has told local media that production from the Shah sour gas field is set to be increased by 50% by 2021. Shah began operations last year and reached its full capacity of 1 billion cfd in 2Q 2015. Al Ghaffi said that the company is "planning to increase production to 1.5 billion cubic feet per day within five years". Al Hosn Gas is a joint venture between the state owned Abu Dhabi National Oil Company (Adnoc) and US-based Occidental Petroleum. ■

FINLAND

Outotec awarded an acid plant contract from Boliden

Outotec has agreed with the Swedish mining and smelting company Boliden on the main design and delivery of proprietary equipment for a sulphuric acid plant to be built in connection with the Harjavalta nickel and copper smelter in Finland. The order has been booked in Outotec's 2016 first quarter order intake, for an undisclosed sum.

The Boliden Harjavalta plant is one of the largest nickel-copper smelters in Europe. The new gas cleaning and sulphuric acid plant solutions designed by Outotec will process off-gas from the smelters into high grade sulphuric acid. The plant will meet all current and planned European environmental requirements through innovative gas cleaning, production of sulphuric acid and an efficient heat recovery system. In order to recover as much energy as possible, the heat recovery system uses the surplus

heat of the SO₂ converter and turns it into high-pressure steam. The surplus heat from the drying and absorption section of the acid plant is converted into hot water and then supplied to the adjacent power plant for further use.

The first construction phase of the sulphuric acid plant is expected to be operational in May-June 2018.

"We are extremely pleased that our long-term partner Boliden awarded us this order. Outotec's advanced gas cleaning and sulphuric acid plant solution will improve the environmental performance of the Harjavalta smelter and reduce the need for external energy, which will shorten the payback time of the investment," says Robin Lindahl, Head of Outotec's Metals, Energy & Water business unit.

UNITED STATES

Copper SX/EW project posts update

Excelsior Mining has updated its estimates for its Gunnison Copper Project, which it is developing in Cochise County, 65 miles (105km) east of Tucson, Arizona. Excelsior plans to develop the in-situ copper leaching project in three stages, the first generating 25 million lbs/year of copper cathode (11,375 t/a), the second stage three times, that and the third stage full production of 125 million lbs/year (57,000 t/a). The project is expected to have a production life of 27 years, with first production beginning in 2018, according to a revised pre-feasibility study completed in January 2016.

The in-situ leach will involve drilling boreholes and pumping an acidic solution into the injection wells to dissolve the copper ore. The solution moves through the rocks in a controlled manner to the recovery wells, and from there it is pumped to the surface for processing at the adjacent Johnson Camp Mine, which Excelsior bought from Nord Resources in December 2015, using solvent extraction/ electrowinning (SX/EW). The initial 11,375 t/a SX/EW facility will be upgraded to 22,750 t/a in year three.

Acid consumption is expected to be high – Excelsior estimates around 9.3 tonnes of acid will be consumed per tonne of copper produced, implying acid consumption of 106,000 t/a in the first stage, rising to 530,000 t/a in the third stage. A sulphur-burning acid plant is planned to be constructed at the project site in year six, according to Excelsior.

NAMIBIA

Official inauguration of new acid plant

Namibian president Hage Geingob has officially inaugurated Dundee Precious Metal's new sulphuric acid plant at Tsumeb. Construction on the 280,000 t/a acid plant began in 2013 and was completed late last year. It will reduce sulphur dioxide emissions from the smelter at the site by about 95% – SO₂ emissions from the furnace stack, particularly over Tsumeb or the work areas of the smelter, have been a bone of contention with residents for many years.

"The acid produced here will create business opportunities for TransNamib and other companies," president Geingob said during the commissioning ceremony. "These are the types of investments we value, investments that produce positive spillovers into the rest of our economy. Today we can confidently say that Tsumeb Smelter is close to full compliance with Namibian standards, pending the finalisation of the certification process, and I expect this process to be concluded expeditiously." The event was also attended by the Minister of Environment and Tourism Pohamba Shifeta, the Minister of Defence Penda ya Ndakolo and Minister of Mines and Energy Obeth Kandjoze.

KAZAKHSTAN

Copper production ramping up at leach site

Central Asia Metals says that it produced 3,207 tonnes of copper cathode in Q1 2016 from its Kounrad dump leach, sol-

vent extraction and electro-winning (SX-EW) copper recovery plant in Kazakhstan, up from 2,350 tonnes for the same quarter of 2015. The company, which is extracting copper from mine tailings, says that it "remains on track" to meet its production guidance of 13–14,000 t/a of copper in 2016. Central Asia also says that it has started groundwork for the Kounrad Stage 2 expansion, which will enable it to leach copper from larger resources within the Western Dumps, beginning in the first half of 2017. Phase 1 remains on schedule and below budget. Acid consumption is around 5 tonnes of sulphuric acid per tonne of copper recovered, according to CAM, or around 70,000 t/a in 2016.

TUNISIA

Production up, but still at reduced levels

The Gafsa Phosphate Company says that it produced 908,000 tonnes of commercial phosphate in Q1 2016, 40% lower than its production goal of 1.54 million tonnes. However, this was also 40% up on the same quarter for 2015, when the company produced 604,000 tonnes. According to CPG, phosphate produced at Metlaoui, Kef Eddour and Mdhillia (7 units) was estimated at 856,000 tonnes, while production at the Redayef and Umm Larayes units was less than 52,000 tonnes during the same period, set against a target of 340,000 tonnes. Production at Redayef and Umm Larayes was virtually at a standstill during the quarter because of a continuing sit-in by unemployed workers, which is also blocking rail and truck distribution channels at the sites.

CANADA

Acid sales agreement signed

Commerce Resources Corp. (CRC) says that it has signed a Memorandum of Understanding (MOU) with Glencore subsidiary NorFalco. Under the terms of the MoU, NorFalco will be the sole provider of sulphuric acid required for CRC's Ashram project, at what are described as "highly competitive market rates and terms". The agreement is for an initial five year term and may be re-negotiated thereafter.

The Ashram rare earth deposit is located in Nunavik, in the northeastern of the province of Quebec. A preliminary economic assessment of the project is based on a 4,000 t/d open-pit operation with an initial 25-year mine life. NorFalco is one of North America's largest traders of sulphuric acid, responsible for the marketing and distribution of about 2 million t/a, taking sulphuric acid production from four major Glencore North American production facilities and offtake agreements with several other producers.

BRAZIL

Anglo American sells phosphate business to China Molybdenum

Anglo American has reportedly agreed to sell its Brazilian niobium and phosphate businesses to China Molybdenum Corp for \$1.5 billion. Anglo is looking to raise \$3.4 billion from the sale of non-core assets as part of a major restructuring plan in order to reduce the company's \$13 billion of net debt to a more 'manageable' level of around \$10 billion or less. The company sold a further \$2 billion worth of assets last year, and is also discussing sale of its Brazilian nickel operations and coal extraction in Australia. Anglo American shares fell 75% in 2015, but have recovered about half that this year.

The assets that are being sold include 6,000 t/a of niobium production, including an expansion at the Boa Vista mine that would turn the unit into the world's second-largest producer of the metal, and 1 million t/a of phosphate production. The business unit generated revenues of \$544 million and underlying operating profits of \$119 million in 2014, mainly from phosphate fertilizer sales.

Other bidders included US phosphate producer Mosaic, Brazilian mining group Vale, and BHP spin-off South32.

Sulphur 364 | May-June 2016



BHP Billiton's Olympic Dam mine in South Australia.

AUSTRALIA

BHP looking at faster expansion of Olympic Dam

BHP Billiton is considering ways of expanding production at its huge Olympic Dam mine in South Australia faster than originally planned, looking towards a resurgence in the copper market three or so years down the line. Production was 180,000 tonnes of copper in 2015 and is expected to reach 200,000 t/a this year, but the company has plans to bring this up to 255,000 t/a by 2020 and is considering expanding that to 280,000 t/a. While the previous massive \$20 billion expansion plans have been shelved, this allows the company to preferentially target higher grade zones, raising the average ore grade from 2% to 2.2% Cu. The company aims to achieve lower cost expansion via debottlenecking parts of the operation, including its smelter and grinding and extracting facilities. BHP is also examining heap leaching options which could lower costs by a further 10-15%.

VIETNAM

Letter of intent for rare earth leaching project

Australia's Alkane Resources Ltd, via its wholly-owned subsidiary Australian Zirconia Ltd, has signed a letter of intent with Vietnam Rare Earth JSC for the latter to process rare earth concentrate from the \$1 billion Dubbo Zirconia Project in Australia. Alkane recently gained environmental clearance for the project from the New South Wales government, signalling that it can proceed with securing financing. Vietnam Rare Earth is a specialist Vietnamese chemical and advanced materials company which operates a processing plant located near Hanoi, to where the rare earth concentrate will be transported for processing. Low processing costs in Vietnam – comparable with China,

CONTENTS

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

Improved acid gas removal

COVER FEATURE 4

Enhanced sulphuric acid production

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People

Natlata Partners Ltd, a private investment company which is the largest single shareholder in PetroNeft Resources has asked shareholders to vote for its proposals at an EGM held in Dublin. Natlata has proposed that **Dennis Francis, David Sanders, Paul Dowling and David Golder** are removed as directors of the company and that in their place the following are elected: **Anthony Sacca**, a senior financial executive with a previous career as a partner at PwC, and later as the CFO of a major Russian corporation; **David Sturt**, an oil and gas industry professional over nearly 30 years and capital markets experience; and **Maxim Korobov**, to be acting CEO, the beneficial owner of Natlata, a businessman with 20 years' experience in the Russian oil and gas sector. Natlata hopes that existing directors **Thomas Hickey** and **Gerard Fagan** will remain on the board for the purposes of continuity. The new board will, the company argues, therefore have four independent directors and one Natlata nominee. It argues that these changes are necessary "because the last few years have demonstrated beyond all doubt that the current board clearly do not have the right capability and experience to maximise the company's assets".

Summing up his letter to shareholders, Maxim Korobov, said: "I fully understand that many of you will be wary of taking

the risk of changing the management of your company. Some of you believe that the better devil is the one you know, but you know in your hearts all too well what will happen if you again award your trust to the current board: stagnant or declining production, new debt, attempts to blame anybody and anything but not themselves. This management has done little to show that it deserves your support, and much to show the opposite. I currently see potential in PetroNeft and its share price. In order to unlock its value Natlata wishes, with your support, to change the board and put the company back on track. I have confidence that the proposed new board under the leadership of David Sturt and myself, Maxim Korobov, will do just that. I hope that you share this vision."

Royal Dutch Shell has named **Ali Al Janabi** as the new head of its Abu Dhabi operations, as it begins the process of integrating new acquisition BG into its global operations, following closure on that deal in February. Mr Al Janabi takes over from **Andrew Vaughan**, who is retiring.

Mr Al Janabi, who holds dual Iraqi-British nationality, joined Shell in 2001 after working for Halliburton. He has degrees in finance and a master's degree in engineering from Imperial College London. He also worked for financier Goldman Sachs for a period before rejoining Shell in 2009.

Although Shell exited the Bab sour gas project development in January, it retains a 15% share in Gasco. The company's 9.5% of Abu Dhabi's onshore oilfield operating company, Adco expired at the end of 2013.

Andrew Vaughn also had oversight responsibility for Kuwait and Syria, and **Walid Al Nader** will thus become the new head of Shell Kuwait, reporting directly to Shell's head of upstream, Andy Brown.

Baker Botts L.L.P., has announced that **Stuart Jordan** has joined the firm's London office as a partner in the Global Projects Group. "We are delighted that Stuart is joining us as we continue to grow our London office," said Andrew M. Baker, managing partner of Baker Botts. "Adding a lawyer of Stuart's caliber is a natural extension of our strength as a leading global energy firm," added Baker. Stuart Jordan's practice focuses on the oil, gas, power, transport, petrochemical, nuclear and construction industries. His work has also centred on professional appointments, technology licenses, Operations & Maintenance (O&M) and concession agreements. He has extensive experience in the Middle East, Russia and the UK. Mr. Jordan joins the firm from King Wood & Mallesons. He graduated from London's Guildhall University with a Bachelor of Law in 1998.

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Calendar 2016

MAY

22-26

2nd Annual Brimstone Sulphur Symposium, ABU DHABI, UAE

Contact: Brimstone STS Ltd
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Email: mike.anderson@brimstone-sts.com

30 - 1 June

84th IFA Annual Conference 2016, MOSCOW, Russia
Contact: IFA Conference Service
Tel: +33 1 53 93 05 25
Email: conference@fertilizer.org
Web: www.fertilizer.org

JUNE

8-9

European Sulphuric Acid Association (ESA) General Assembly, WARSAW, Poland
Contact: Patricia De Hertogh, Cefic
Tel: +32/2/676 72 53
Fax: +32/2/676 72 41
Email: pdh@cefic.be

10-11

40th AIChE Annual Clearwater Conference 2016, CLEARWATER, Florida, USA
Email: chair@aiche-cf.org
Web: www.aiche-cf.org

27-28

CRU China International Sulphur & Sulphuric Acid Conference 2016, SHANGHAI, China
Contact: CRU Events, Chancery House, 53-64 Chancery Lane, London WC2A 1QS, UK.
Tel: +44 20 7903 2167
Email: conferences@crugroup.com

29

ASRL Chalk Talks, CALGARY, Alberta, Canada
Contact: Patricia Alegre, Alberta Sulphur Research Ltd
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OCTOBER

9-11

3rd Middle East Sulphur Plant Operators Network Forum (MESPON) 2016, ABU DHABI, UAE
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Web: www.universulphur.com/mespon

NOVEMBER

7-10

CRU Sulphur 2016 Conference and Exhibition, LONDON, UK
Contact: CRU Events
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
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CONTENTS

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

Improved acid gas removal

COVER FEATURE 4

Enhanced sulphuric acid production

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Industrial uses of sulphuric acid

Although phosphates and sulphur fertilizers represent the majority of sulphuric acid demand, its use in a wide variety of industrial applications has been a major growth area in recent years.

As is well known, sulphuric acid is the most widely used industrial chemical in the world in terms of consumption, with over 260 million t/a estimated to be used in 2015. The phosphate and fertilizer market continues to represent the majority share of all consumption, at around 55% of all acid demand. However, the remaining 45% is a large slice of demand which is spread between literally hundreds of different end uses. Chemical and industrial end-use markets for sulphuric acid have grown slightly more quickly than fertilizer uses, and chemical uses particularly so. However, the slowdown in global chemical and metal/commodity markets means that this may not necessarily be the case over the next few years.

Metal leaching

Perhaps the largest slice of industrial demand for sulphuric acid comes from its use to extract metals from their ores. Three metals in particular dominate this

use; copper, nickel and uranium – there is also acid used for leaching of precious metals, rare earths and one zinc leach plant in Namibia, but consumption is relatively modest for these uses. Overall demand for acid for metal leaching was around 26 million t/a in 2015, or about 10% of all sulphuric acid demand, and over 20% of all chemical and industrial demand, and this is an area where demand has risen rapidly, from around 10 million t/a of acid in 2000. Much of this extra demand has come from nickel production via a few large high pressure acid leach (HPAL) plants, in Australia, Madagascar, Papua New Guinea, New Caledonia and the Philippines. In just 5 years, acid demand for nickel leaching rose from 2.5 million t/a in 2010 to 8 million t/a in 2015. However, the recent collapse in nickel prices and a switch towards cheaper nickel pig iron and ferronickel processing has scotched new desire for expensive and technically complex HPAL plants, and so fresh demand from this sector looks

unlikely. On the uranium side, the Fukushima accident has had a chilling effect on demand for uranium, which these days is almost all for civil nuclear power plants. The rapid expansion of uranium capacity in Kazakhstan has increased acid demand considerably as many of the extraction plants are in-situ leaches in basic rocks which require a considerable amount of acid, and acid demand for uranium leaching has climbed to just short of 4 million t/a. However, Kazakhstan is now moving towards less acid consumption in its uranium leaches, and uranium demand continues to grow only relatively slowly.

Copper has always consumed the largest slice of metal leaching demand; about 14 million t/a in 2015, according to CRU. Chile has traditionally been the main consumer, with a number of large scale copper solvent extraction/electrowinning (SX/EW) plants. Chilean demand has begun to tail off, however, due to falling ore grades, and in recent years the largest slice of new demand has come from capacity in the Democratic Republic of Congo (DRC). The fall in copper prices as China's economy slows has impacted disproportionately upon SX/EW mines, as several of them are towards the higher end of the copper cost curve. Although there is new copper leaching demand on the horizon, it will be at least in part offset by declines in Chile and plant shut-downs, and so demand may rise only slowly over the next few years.

Overall, the slump in metal markets and slowdown in China's industrialisation has severely affected the prospects for new demand from this sector, which may only represent a couple of million tonnes of extra acid demand to 2020.

Titanium dioxide

Titanium dioxide is a brilliant white pigment used extensively in the paper, pigment and cosmetics industry. Its UV reflectiveness and high refractive index mean that it has excellent opacity and a brighter, bluer and less yellow colour than some other white pigments. Two competing processes each have around half of the market for titanium dioxide production; the chloride process and the sulphate process. The sulphate process, which requires sulphuric acid, is often seen as the 'cheap and dirty' option for acid production, and uses lower grades of titanium ore and is often suitable for less demanding applications. However, the

chloride process is in the hands of only a handful of licensors, mainly concentrated in North America and Europe (plus Cristal in Saudi Arabia), and they have resisted licensing their technology to other companies. For this reason, China's rapid growth in TiO_2 consumption has been based mainly on the sulphate process, and China now produces about 40% of all TiO_2 . The amount of acid consumed in titanium dioxide manufacture depends on the grade of ore and the specific details of the process; governments have steadily clamped down on acidified water waste from the process, leading European producers to pioneer acid recycling technologies. As a result, European producers use only around 1 tonne of acid to make 1 tonne of TiO_2 , whereas in China the figure can be 3 tonnes or more. Even so, as Table 1 shows, titanium dioxide manufacture actually represents a significant slice of European sulphuric acid demand, at around 1.8 million t/a in 2014.

Titanium dioxide demand was 6 million t/a in 2014, and is growing at about 3.5% per year. However, while China's sulphate-based capacity is, like many industries in China, oversupplied, and running at low operating rates, a new factor in the past couple of years has been the development of domestic chloride-route capacity in China, which may begin to displace sulphate route plants. Thus while titanium dioxide demand for sulphuric acid runs at several million t/a, this may actually decrease in the coming years.

Pulp and paper bleaching

Within the pulp and paper industry sulphuric acid is used in large volumes for chlorine dioxide generation (for bleaching), tall oil splitting and for pH adjustments of solutions. The pulp and paper industry was traditionally concentrated in forested countries, particularly the US and Canada, Scandinavia, as well as Japan and China. However, in recent years growth has stagnated in North America and Western Europe, while Asia, Latin America and Eastern Europe have shown substantial growth. Asia now represents 40% of global paper-making fibre consumption, although this has been on the back of global trade in pulp – global wood pulp consumption has been relatively flat since 2000.

The US remains one of the larger producers, with around 15% of paper production and 30% of pulp production. In the US, as Table 2 shows, use of sulphuric acid in

the pulp and paper industry amounted to about 500,000 t/a of acid in 2013.

Water treatment

Sulphuric acid is often used as a pH balancing agent in waste water treatment. It can also be used for some drinking water applications, and also has some uses in pH control of irrigation water for very basic soils that are heavy in carbonates, where it has the advantage that it deposits sulphates in the soil which have beneficial fertilization effects. In drinking water, sulphuric acid added into the softened water just before filtration to maintain a pH level of about 6.5 to allow any un-precipitated materials to be filtered. A further addition of sulphuric acid is applied to the filtered water through a secondary acidification step designed to reduce the bicarbonate content and avoid calcium carbonate precipitation.

However, there are a number of rival acids which can also be used in all of these applications, including acetic and citric acids and hydrochloric acid. Carbon dioxide can also be used to generate carbonic acid. There can be severe corrosion issues in using sulphuric acid, especially in steel pipes, and careful control of concentration is required. This is not a major use of acid, but it represented about 120,000 tonnes of demand in the US in 2013.

Acid manufacture

Sulphuric acid can be used in the manufacture of other acids, particularly hydrofluoric acid (HF). The major use for HF is in the manufacture of fluorocarbon polymers such as polytetrafluoroethylene (PTFE), although it also has uses in the manufacture of aluminium fluoride and fluoroaromatics, as well as in metal pickling, glass polishing and as an alkylation catalyst. Consumption of HF in Europe in 2014 was 290,000 tonnes, requiring about 850,000 t/a of sulphuric acid (100% acid basis in both cases).

Refining – alkylation

The alkylation reaction combines isobutane with light olefins (primarily C4s but also some C3) in the presence of a strong acid catalyst. The resulting highly branched, paraffinic product is a low vapour pressure, high octane blending component. Although alkylation can take place at high temperatures without a catalyst, the only

processes of commercial importance today operate at low to moderate temperatures using either sulphuric or hydrofluoric (HF) acid catalysts. The light olefins and most or all of the isobutane come from the refinery fluid catalytic cracking (FCC) unit, hence alkylation units are found only in refineries having FCC units. As the US has a preponderance of FCC capacity this has also helped with the relative concentration of alkylation capacity in the US.

Increasingly stringent environmental regulations are leading to a boost in demand for alkylation capacity, and safety concerns about the hydrofluoric acid route are also leading to a slight preference for the sulphuric acid process, boosting acid demand in refineries in the US and worldwide, although HF still retains a considerable grip on the market. Of course – extra demand for HF is in effect also increased demand for sulphuric acid, as described above.

Global alkylation capacity continues to rise rapidly, and while it has traditionally been concentrated in the US, there are now a growing number of alkylation plants in refineries around the world, in China, India, Trinidad, Russia, Chile and South Korea. DuPont, a major supplier of the technology, estimated global alkylation capacity at 2 million bbl/d in 2014, around 60% of which was based in the United States. As Table 2 shows, refinery alkylation is actually the major industrial consumer of sulphuric acid in the US, representing almost 4 million t/a of demand, and globally this application consumes around 7-8 million t/a of acid. Increasing conversion capacity and increasing demand for gasoline in many regions of the world has led to the installation of new grassroots capacity, and this use continues to grow at around 5-6% per year.

Car batteries

Sulphuric acid is of course a key component of lead-acid batteries, used predominantly in the automotive sector. While the lead from the batteries is often recycled, the spent acid is less so, and increased use of vehicles around the world and the growing use of electric and hybrid electric vehicles is also helping to boost demand for sulphuric acid for batteries. Nevertheless, in terms of overall acid demand this remains a relatively minor use, consuming 75,000 tonnes of acid in the US in 2014, and a few hundred thousand tonnes globally.

CONTENTS

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

Improved acid gas removal

COVER FEATURE 4

Enhanced sulphuric acid production

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Sulphates

Sulphuric acid is used in the production of metal sulphates, especially copper and aluminium sulphate. Copper sulphate is used primarily (ca 75%) in agriculture, mainly as a plant fungicide. Global consumption is around 200,000 t/a, according to the Copper Development Association. It also has uses in dyeing, fibre manufacture and electroplating. Aluminium sulphate ('alum') is mainly used in water treatment, where it forms aluminium hydroxide which removes colloidal particles and clarifies water. It is also used in paper manufacture, and some small-scale chemical uses. Total sulphuric acid demand for these uses is estimated at a few hundred thousand tonnes per year.

Fibres

Sulphuric acid finds end uses in the fibre industry, via caprolactam, which is the intermediate for production of nylon 6. Sulphuric acid reacts with cyclohexanone oxime via an intermediate step to produce caprolactam and ammonium sulphate. In Europe caprolactam consumption is 750,000 t/a, mainly ending up in resins for plastics and films, as well as fibres, but globally about 60% of caprolactam goes into fibre production.

Caprolactam capacity has risen rapidly in the past few years, driven primarily by new production in China, which now has about 30% of the market, and where caprolactam capacity is approaching 3 million t/a out of a total capacity just short of 7 million t/a. In a story familiar to many other industries, Chinese capacity building has pushed the market into considerable oversupply. Caprolactam consumption is around 4.7 million t/a worldwide, and it requires a comparable amount of sulphuric acid. Demand has grown at 3% per year in recent years.

Sulphuric acid is also used in the production of cellulosic fibres, particularly Rayon. Global capacity for Rayon production stood at 3.5 million t/a in 2010, and had seen a massive trend of production moving to China, which had 60% of global manufacturing capacity at that time. Consumption of acid for Rayon production is almost exactly one tonne per tonne. Table 1 shows that Western European consumption of acid for Rayon production in 2014 was 600,000 t/a, and globally it represents over 3 million t/a.

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Steel - acid pickling

Steels are treated with acid to remove surface impurities, rust, scale and inorganic contaminants. Sulphuric acid was one almost exclusively used for this purpose, but hydrochloric acid has come to be a major competitor. HCl does bring with it disadvantages, being much more difficult to transport than sulphuric acid - it is usually carried as a 30% solution, meaning you ship a lot more water than with H₂SO₄. It has been cheaper than sulphuric acid, but in the US HCl's use in fracking fluids has caused demand to rocket and prices to climb and become more volatile.

Methyl methacrylate

Sulphuric acid is used in the manufacture of a number of important chemicals, one of the chief among which is methyl methacrylate (MMA). Acetone is reacted with cyanide to produce acetone cyanohydrin, and this is then reacted with sulphuric acid to produce first methacrylamide sulphate, and finally methyl methacrylate and ammonium sulphate. MMA is used in the manufacture of acrylic sheeting for signs, displays, lighting fixtures, glazing and other building materials, and molded components in cars, appliances, household goods etc, as well as coatings and other uses. European consumption in 2014 was 545,000 t/a, and the continent consumed almost 1 million tonnes of sulphuric acid to produce it. Global MMA consumption was around 3.4 million t/a in that year, with consumption growing at around 3.4% per year. Large volumes of spent acid are generated by the process, around three tonnes per tonne of MMA, and this is encouraging the recycling of spent acid and the development of other, rival processes.

'Other uses'

The difficulty with putting complete figures on the various segments of sulphuric acid demand is the sheer variety of industrial processes in which it is used, often areas which do not keep reliable consumption figures. It is relatively easy to work out 'apparent consumption' of industrial sulphuric acid by simply subtracting the volumes used in fertilizer production from total production, but tracking sulphuric acid through production of, e.g., pharmaceuticals, pesticides, soaps and detergents, and sundry speciality chemicals etc

Table 1: Sulphuric acid consumption in Western Europe by end use, 2014

Fertilizer manufacture	44%
Titanium dioxide	15%
Methyl methacrylate	8%
Hydrofluoric acid	7%
Caprolactam	6%
Rayon	5%
Hydrochloric acid	4%
Aluminium sulphate	2%
Citric acid	2%
Other industrial uses	8%
Total	12.1 million t/a

Source: IHS

Table 2: Sulphuric acid consumption in the US by end use, 2013

Phosphate fertilizers	66.0%
Nitrogen fertilizers	2.1%
Other agricultural chemicals	0.7%
Petroleum refining	15.9%
Copper and other ore leaching	4.4%
Pulp and paper	2.1%
Paints and pigments	1.3%
Other chemical manufacture	1.3%
Plastics and rubber	0.9%
Water treatment	0.5%
Batteries	0.3%
Explosives	0.1%
Unidentified	3.4%
Total	24.0 million t/a

Source: USGS

etc is a virtually impossible task. For this reason Tables 1 and 2 and all discussions of sulphuric acid in industrial and chemical markets will all have a significant section which is simply labelled 'other uses'.

Industrial consumption

As noted above, industrial consumption of sulphuric acid has been through a period when it has grown faster than fertilizer consumption in percentage terms. Two of the major drivers for this have been the rapid expansion in metal leaching capacity and the growth in Chinese chemical and particularly fibre production, and to a lesser extent the growth in refinery alkylation capacity. However, with growth in metal leaching now slowing and Chinese chemical sectors suffering from over-building of capacity, it looks unlikely that this trend will be continued over the next few years. ■

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CONTENTS

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

Improved acid gas removal

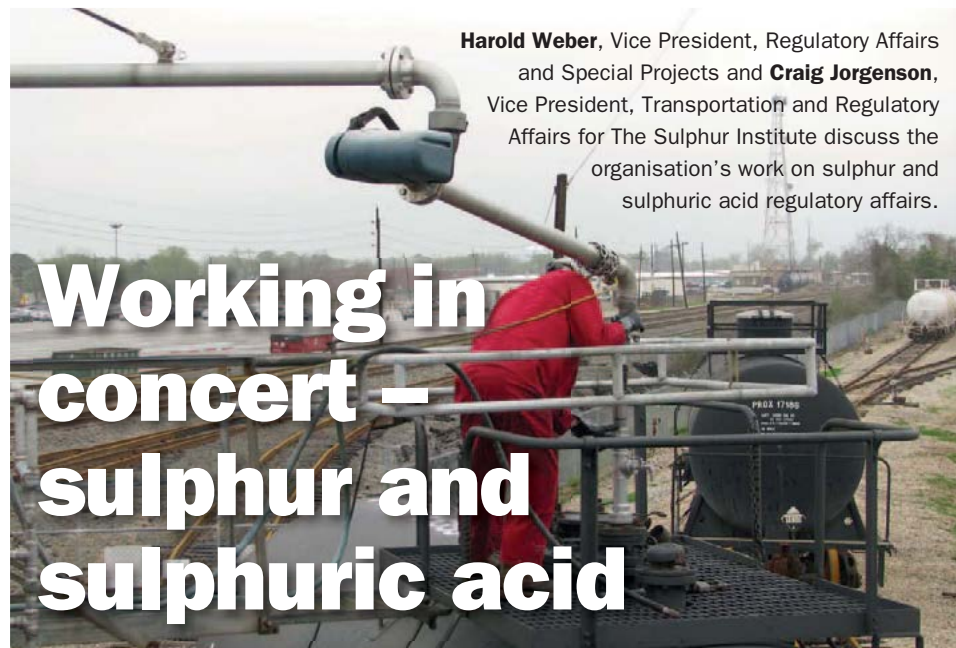
COVER FEATURE 4

Enhanced sulphuric acid production

SULPHUR
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Harold Weber, Vice President, Regulatory Affairs and Special Projects and **Craig Jorgenson**, Vice President, Transportation and Regulatory Affairs for The Sulphur Institute discuss the organisation's work on sulphur and sulphuric acid regulatory affairs.

Working in concert – sulphur and sulphuric acid

The Sulphur Institute (TSI) is an international, non-profit organization established in 1960. With more than 55 years of experience, TSI represents all stakeholders engaged in producing, consuming, trading, handling, and adding value to sulphur. Recently, TSI expanded its programs and now is actively representing sulphuric acid interests in North America and expanding activities to include membership and participation in the European Sulphuric Acid Association. We seek to provide a common voice working in concert with both segments of industry and to promote leading practices in the handling and transportation of all sulphur products while protecting the environment and communities in which we operate.

Acknowledging the role of sulphuric acid

Sulphuric acid is the most widely used chemical for manufacturing a myriad of products and in numerous other applications. Over the last century, its use is extensive in production of nearly all manufactured goods consumed around the world. More than half the sulphuric acid

consumed is to manufacture phosphoric acid for use in phosphate fertilizers and soft drinks, other sulphuric acid based fertilizer materials, and ore leaching for recovering copper, nickel and uranium. It also has roles in petroleum refining and in production of sulphate salts, medications, munitions, and a variety of dyes and pigments. Sulphuric acid also is important in metals processing (cleaning steel and iron before plating) and as an electrolyte in lead acid batteries used in vehicles. Recognized in many references as one of the most important industrial chemicals, production of sulphuric acid is increasing every year.

Working together for safety

TSI established a working group on transportation regulations and logistics to promote appropriate regulations for sulphur and subsequently established a working group on environmental health and safety. Both working groups provide opportunities for TSI member company representatives with common interests in the supply chain to share information that improves safety and handling practices and addresses industry issues. These working groups

meet face-to-face twice a year and also via teleconference and at other times during the year as needed. Meetings and teleconferences provide forums for interface and networking across supply chain sectors.

Over the last five years, TSI developed three key documents. "Molten Sulphur Rail Tank Car Guidance" document, now referenced in North American regulations, assists industry in addressing concerns about sulphur residue on exterior surfaces of rail tank cars. "Molten Sulphur Rail Tank Car Loading and Unloading Operations: Leading Practices in Industry" contains a summary of industry practices collected from multiple sites that provides facility managers with opportunities to customize their operating procedures to further improve safety and handling. "Molten Sulphur Truck Transportation" white paper, prepared by a road transportation task group and available only to TSI members, provides a summary of equipment alternatives and handling practices to improve overall cargo tank truck operations and safety. TSI formed a task group that now is undertaking a project to prepare a summary of cargo tank truck leading practices for sulphuric acid.

TSI established a sulphuric acid working group in April 2015. This working group is assisting with a rail tank car loading and unloading study conducted in cooperation with the US Department of Transportation Federal Railroad Administration. Its objective is developing a summary report of leading practices to make further improvements in safe handling and compliance with regulatory requirements. Sulphuric acid working group is meeting monthly via teleconference for sharing information to improve safety and handling operations and reporting from newly formed task groups. One task group is working to better understand and establish positions that will resolve questions, issues, and evaluate impacts of proposals for changes to rail tank car standards under consideration by the Association of American Railroads Tank Car Committee (TCC). An additional task force is assembling cargo tank truck loading and unloading leading practices to develop a document on sulphuric acid road transportation. When issues arise following an incident, greater collaboration between sulphuric acid stakeholders helps with preparing accurate information to resolve common issues.

Forward looking for industry

With greater regulatory scrutiny of all commodities in all modes of transportation, united effort of the sulphur and sulphuric acid industry sectors will be better suited to address and resolve issues. TSI will represent not only sulphur, but also sulphuric acid stakeholder's positions with one voice on future regulatory proposals. For example, TSI will represent both sulphur and sulphuric acid industry on the TCC to address any proposed changes to equipment are justified with a positive benefits-to-costs ratio.

In the future, TSI has plans for expanding programs and services of importance to both sulphur and sulphuric acid industries and for gaining additional support through increasing member companies with interest in these industry segments. One example of this is that TSI recently joined the European Sulphuric Acid Association (ESA) to improve alignment for regulatory changes within the United Nations and the European Union. There are several new projects planned for this upcoming year and other potential projects expressed through working group participation. However, with

out greater industry participation and support, some may not come to completion.

Finding a common voice

TSI fulfils a significant role for the sulphur and sulphuric acid industries by providing venues where participants can share information and experiences to improve safety and handling practices that will reduce potential for incidents and injuries. A variety of issues and opportunities exist that are better addressed when the sulphur and sulphuric acid industries work in concert. On many issues, TSI stands ready to represent industry positions by speaking with a unified voice; opposing unneeded or unworkable changes and guiding needed changes in an appropriate direction with technical and factual information. Through efforts to expand programs and related services for sulphuric acid industry stakeholders, TSI is providing increased support to both sulphur and sulphuric acid sectors for its member companies and is eager to share these opportunities with new member companies. For additional information, please visit www.SulphurInstitute.org

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CONTENTS

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

Improved acid gas removal

COVER FEATURE 4

Enhanced sulphuric acid production

SULPHUR
ISSUE 364
MAY-JUNE 2016

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PHOTO: ABU DHABI FILM COMMISSION

The 2016 Sour Oil and Gas Advanced Technology (SOGAT) conference returned to Abu Dhabi's Beach Rotana Hotel, from March 20th-24th this year.

The start-up of the massive Shah sour gas project deep in the deserts of the Emirate of Abu Dhabi has highlighted the extent to which the centre of gravity of the sulphur industry is slowly but inexorably shifting to the Middle East, and Abu Dhabi's Sour Oil and Gas Advanced Technology (SOGAT) conference, now in its 12th year, brings together industry experts across the region and across the globe to discuss sour gas processing.

Sulphur workshop

Prior to the main conference, a workshop was held focusing on sulphur and its role in the supply chain. **Meena Chauhan** of Integer Research began with a run-down on global sulphur and sulphuric acid markets. On the sulphur supply side, the Middle East has seen over 5 million t/a of capacity additions from 2011-16. Another 3 million t/a has come in East Asia, mainly China, and 1.7 million t/a in the FSU. North America has seen less production as sour gas production declines and refiners take advantage of lower crude prices to switch to sweeter grades, and Europe has also seen production declines. Any oil

price effect is mostly noticeable in north America, where oil sands production forecasts have also been downgraded by 1.1 million bbl/d to 2030. Canadian sulphur production now looks stable at 5.1 million t/a from 2016-21, but elsewhere the sulphur capacity additions are accelerating; 7.3 million t/a over the next five years in the Middle East, 2.7 million t/a in the FSU and 2.3 million t/a in East Asia, with sour gas-based projects adding the majority of new supply

On the demand side, falling DAP prices have led Mosaic and OCP to cut back on production, while the end of the commodity boom has seen slower growth in metal leaching. The bright spot is Africa, where copper and phosphate projects will take sulphur demand from 9.9 million t/a in 2016 to 15 million t/a in 2025, and Tunisia has the potential for more imports if labour problems can be overcome. Moroccan sulphur imports have shifted from Russia towards the UAE in the past two years and a similar trend can be seen in Chinese imports. The UAE is now exporting 4 million t/a, not far short of Canada's 4.8 million t/a. China has imported 10-12 million t/a over the past four years, and in

spite of new sulphur production looks set to continue to import 9 million t/a or so out to 2020.

The global sulphur balance is for a projected surplus of 800,000 t/a this year, potentially rising to 7 million t/a to 2020, and the question remains as to where this excess will go. Canada has the potential to store more sulphur, as do Turkmenistan, Russia and possibly Saudi Arabia. Meena even raised the prospect of major consumers like OCP creating storage blocks.

On the subject of UAE exports, **Anas al Mahmood** of Adnoc illustrated his company's rapidly rising sulphur production – from 2.2 million t/a in 2014 to 5.8 million t/a in 2016 – and the logistical challenges this presents. Sulphur trains of up to 100 cars (12,000 tonnes) travel the 220 km from Shah, via Habshan to Ruwais. There are two export berths at Ruwais, one which can take ships up to 45,000 dwt, and capable of loading 1,000 t/h, and the second can take ships of up to 80,000 dwt and load 4,000 t/h.

Sulphur forming and quality

Moving to the technical presentations, **Uday Parekh** reviewed various sulphur forming techniques; pastillation, granulation, wet prilling, with particular focus on moisture content of the sulphur and its safety implications. He referenced a report by the port of Anacortes in Washington

State, USA, which specifies that sulphur must have a moisture content of 2-3% in order to guard against fire and explosion. Finally, he ran through sulphur blocking, as well as some recent projects such as the Puguang Gas Plant in China and forthcoming Heartland Sulphur Terminal Project in Canada.

The point on sulphur dust was echoed by **Jerry D'Aquin**, who discussed what he called 'volatile sulphur particulate' (VSP) – small, sub-millimetre particles of sulphur which are not really covered by existing SUDIC specifications. These specifications were designed, Jerry said, around the so-called 'Polish prill', which produced particles for a No 16 mesh screen (ca 1.2 mm), different from the typical sizing of pastilles, granules and wet prills, which he had measured at 2.3, 3.4 and 4.8 mm mesh screens respectively. Regardless of the forming technique, handling and transit produces small particles of microscopic sulphur, and the fraction between about 75-150 micrometres is the key issue, he said, as it can drift in the air and irritate lungs, skin and eyes and lead to static discharges which can ignite. This fraction represented 0.5% of a sample he measured at Odessa port, or 150 tonnes of a 30,000 tonne cargo. Spraying water/foam and surfactants can mitigate this problem, but has limited effect on dry sulphur, and increasing moisture content of sulphur limits release of this VSP particulate. Sulphur dust below 300 micrometres in size accounted for 1% of a completely dry sulphur sample tested, but only 0.2% at 1% moisture, and zero at 2% moisture.

Degassing and melting

Thomas Chow of Fluor looked at sour gas treatment in arid environments where there may be high ambient temperatures and little or no cooling water, as well as large scale plants required to deal with high CO₂ concentrations and contamination with ammonia, BTX etc, and in so doing showcased oxygen enrichment technology, including COPE, developed by Fluor in conjunction with Goar Allison Associates (GAA). He also covered degassing, including in-pit and out of pit (such as Fluor/GAA's D'GAASS) process designs.

Jeremy DeLay of Devco described his company's new melting technology, as used in the New Wales melter for Mosaic in Florida. There will be a full discussion of this in our next issue.

Sulphur copolymers

A couple of short presentations looked first at alternative uses for sulphur, presented by Sulphur editor **Richard Hands**, including recent work on sulphur as a carbon copolymer via a so-called 'reverse vulcanisation' process, and this then led into work recently carried out by **Saeed Al Hassan** of the Petroleum Institute in Abu Dhabi, who has been looking at sulphur copolymer composites with low density polyethylene (LDPE), where the addition of sulphur can lead to increased tensile strength of the polythene. Similar effects have been observed with polypropylene. Sulphur will highlight this work in a full paper from Dr Al Hassan later this year.

Project updates

The main SOGAT conference began as usual with updates on the major projects in the region. **Ahmed al Hosani** of Al Hosn Gas reviewed the Shah sour gas project, which processes 1 billion scf/d of highly sour gas (23% H₂S, 10% CO₂) to produce 504 million scf/d of sales gas as well as 3,900 t/d of natural gas liquids, 30,000 bbl/d of condensate and of course 9,700 t/d of sulphur. Liquid sulphur was imported from Gasco to run the sulphur pipelines and granulation facility to ensure they were in working condition before the main plant startup, which occurred in January 2015. Commissioning took longer than expected, but Shah had achieved 100% capacity by July. Ahmed stressed the importance of appointing an integrated commissioning manager to ensure smooth alignment between several different contractors.

Muntazer Alawi of Saudi Aramco described the Wasit Gas Plant, which takes gas from the offshore Hasbah and Arabiyah fields, processing 2.6 billion scf/d of gas. Wasit and the Karan plant will between them increase Saudi Arabia's gas processing capacity by 40%. Wasit will also produce 4,200 t/d of molten sulphur form 99.3% efficient EuroClaus units with a Sulfino-M amine gas treating section. There are four SRU trains. Sulphur is degassed to below 10ppm.

Prosernat discussed their work on Qatar's Plateau Maintenance Project, which treats gas for the Qatargas 1 LNG unit. The H₂S content of the gas, at 1-2%, was edging past the original design specification of the SRU. It was desired to avoid an acid gas enrichment unit because of

cost grounds, and the final option selected was an integrated advanced amine acid gas recovery unit/enrichment/tail gas treatment unit with a common regenerator. Sulphur recovery is via the *SmartSulf* process, and increased from 95% to 99.5%.

Technical papers

Unfortunately there is only space to highlight a few papers from the three-day conference, but it was interesting to see a technical presentation from a Chinese company, or at least the US subsidiary of a Chinese company. US-based Jiangnan Environmental Technology (JET) is the first international subsidiary of Jiangnan Environmental Protection (JNEP) Co., Ltd, headquartered in Nanjing, China, and JET's **Peter Lu** described JNEP's ammonia-based SO₂ wet scrubbing process, which it is offering for use in SRU tail gas treatment – JNEP has already successfully installed 11 such systems at Chinese SRUs.

Angie Slavens' thought-provoking paper on the trade-offs between sulphur recovery efficiency and carbon dioxide emissions is reproduced in full in this issue on pages 50-53.

Sulphur has previously reported on the new Controls Southeast/Phillips 66 pre-pit sulphur degassing system – ICon (see *Sulphur* 358, May/June 2015, pp56-57). **Thomas Willingham** of Controls Southeast presented an update on the process, including results from real world field testing of the system in a 250 t/d SRU installation at a Phillips 66 refinery on the US Gulf Coast. The normal H₂S content of the sulphur exiting the SRU is around 300-400 ppmw. Results from the trial showed consistent degassing to less than 4 ppmw, well below the 10 ppmw that was the design specification, regardless of the input H₂S content of the sulphur itself.

More real world performance data came from **Vincent Wong** of Fluor, in this case the highly topical performance of the *FLEXSORB* tail gas treatment unit at Al Hosn Gas's Shah project in Abu Dhabi. Aside from some initial foaming in the regenerator, start-up proceeded smoothly, and performance testing was completed during August 2015. Inlet gas composition to the TGTU was 1.1% H₂S and 16.6% CO₂ – the higher than expected ratio made selective H₂S absorption more challenging, but outlet H₂S levels were measured independently at 77 ppmv average – well below the 150 ppmv design criterion. ■

CONTENTS

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

Improved acid gas removal

COVER FEATURE 4

Enhanced sulphuric acid production

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Acid gas reinjection

With increasing volumes of sulphur from sour oil and gas projects now beginning to reach the market, will companies have to more seriously consider reinjection of acid gas?

Sulphur production is projected to rise from about 60 million t/a at the end of 2015 to 75 million t/a in 2020, and much of the increase in production (11 million t/a out of the 15 million t/a increase) is coming from sulphur extracted in sour gas processing. With a projected surplus of several million tonne per year by 2020, sulphur will be in considerable excess in the market, and hence prices low. Many producers are already having to think about whether to pour sulphur to block. That being the case, the other option – if you are a sour gas producer – is to inject the acid fraction of the gas from your gas processing plant back down the well.

History

Although there were some early experiments in the US, it was Canada which began significant reinjection of acid gas at gas plants in Alberta and British Columbia during the 1990s. This began at Edmonton in 1989, after Alberta emission limits for sulphur dioxide were lowered in 1988, and it no longer became acceptable to flare acid gas as had previously been the case. Although these operations were typically fairly small scale, there were 48 different injection sites, and it was estimated that 4.5 million tonnes of acid gas (about 40% of it H₂S) had been reinjected by 2003, at which time injection was running at 1 million t/a, with no leakage detected. This forms the basis of much industry experience of acid gas reinjection, although Poland also experimented with acid gas reinjection at two sites during the 1990s.

Disposal sites

Finding the right place to inject the acid gas is a prime concern, and can decide whether the process is viable or not at any given site. Ideally, where oil production occurs within a reasonable distance, the

gas can be pumped into an oil reservoir for enhanced oil recovery (EOR). If not, the nearby presence of a large aquifer, a depleted reservoir, or a zone producing sour fluids is required, ideally with a pre-existing well; since having to drill a specific disposal well obviously increases the cost significantly, and it is also important from both cost and safety grounds to avoid a long reinjection pipeline to another site. A depleted zone is particularly attractive because reservoir size and original pressure are known, and it is easy to estimate how much gas can safely be injected. Later, if the sulphur price were to increase back to profitable levels, it could also be possible to re-extract the acid gas.

Corrosion

Where water is present in the gas, sour gas can corrode lower grade steels, generating atomic hydrogen, and leading to hydrogen-induced cracking, blistering, or sulphide stress cracking. This can lead to sudden failures, as was experienced at the sour gas line at Kashagan recently. For this reason the gas is usually dehydrated before reinjection. The presence of water can also lead to hydrate formation in the gas. As pressure increases, so the temperature at which hydrate formation occurs decreases. As compression heats the gas, it is usually necessary to compress the gas in stages and cool it between each compression stage.

The balance of carbon steel vs 316 stainless steel is a key consideration on cost grounds, and because it is more expensive stainless steel tends to be avoided where possible. Most units have carbon steel material up to the first compression stage cylinder, and carbon steel downstream of the dehydration facilities, with the majority of the compression and dehydration sections being made of stainless. The coolers, lines, and inter-stage scrubbers should generally be 316 stainless steel. While the cost of equipment is a significant factor, the consequences of failure are serious enough that it is generally wiser to err on the side of caution.

Cost

The dehydration unit and the stainless steel piping are the major cost items, and can be the determinant of the profitability of acid gas reinjection. The most common dehydration system remains the glycol dehydrator, although molecular sieve or silica gel could be used. When glycol dehydrators are installed, all vessels, equipment, and piping on the rich system are usually 316 stainless steel. Compressing the acid gas to higher pressures increases the solubility of water in the acid gas and more than decreases the decrease in solubility due to inter-stage cooling, and so it may be possible to avoid a dehydration step and dehydrate via compression and cooling alone.

Table 1: Additional cost of sour gas processing

	Gas type		
	Sweet	Sour (20% H ₂ S)	Sour (40% H ₂ S)
Sales gas %	98	75	52
Capex	100	140	185
Opex	100	160	200
Gas cost, \$/MMBtu	100%	200%	400%

Source: Prosernat

However, without dehydration it is sensible to make the line to the reinjection well out of stainless, and hence the distance from the processing station to the injection point may determine whether or not it is cost-effective to avoid the dehydration step. Methanol injection is another possible option to avoid corrosion and hydrate formation, but of course again will increase the operating cost.

Table 1 shows some 'ballpark' figures from Prosernat on the additional cost of treating sour gas to remove H₂S, although of course this must be done whether or not the acid gas is eventually reinjected or passed to a Claus plant. Sinopec recently did some work with the Chinese Academy of Sciences on the relative costs of acid gas reinjection and sulphur recovery for the Puguang gas plant in Sichuan province. The gas at Puguang is 14.5% H₂S and 8.8% CO₂. Three different acid gas injection schemes were considered; a best case, which used lower pressures and shorter distance to the reinjection well, a base case, and a worst case, which used the highest compression level (and hence thicker piping etc) and longest distance to the reinjection well. The cases were based on Chinese costs for labour and natural gas – acid gas injection tends to require fewer front line workers than sulphur recovery. The analysis assumed that most of the water could be dehydrated via the compressor – the worst case assumes an additional requirement for methanol injection.

The final results put the capital expenditure of acid gas reinjection at between \$200 million for the 'best case' and \$460 million for the worst case, with \$310 million for the base case (at current Rmb – dollar exchange rates). The Claus recovery cost came to \$700 million for fixed investment cost. Operating costs ranged from \$14-36 million per year for the acid gas injection and \$45 million per year for the Claus plant. On the face of it, the analysis appears to show that acid gas injection is considerably cheaper than sulphur recovery, and conservatively comes in at around 60% of the cost.

However, these costs did not factor in the returns from sale of sulphur. The current Puguang gas plant can process 3 million t/a, and even at a relatively conservative ex-works price of \$50/t of sulphur, that could represent an additional \$150 million in costs recovered. Should realised sulphur prices fall towards zero, or the cost

of long term storage of sulphur need to be taken into account, the sour gas option of course could become preferred.


Production of sulphur in the well

One alternative which has been suggested, by Black & Veatch amongst others, is to oxidise the sulphur/H₂S to sulphur dioxide and then inject that into the well, where the SO₂ reacts with H₂S remaining, creating sulphur in the well. Sulphur dioxide is more easily liquefied and does not require the compression stages of acid gas to inject

it into the well, and the combustion can generate heat recovery and electrical power, while the sulphur formed in the well is a potential resource for future extraction. However, this option does end up requiring a Claus plant or something similar, with attendant costs.

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CONTENTS

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

Improved acid gas removal

COVER FEATURE 4

Enhanced sulphuric acid production

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The Sulphur Institute's 2016 Sulphur World Symposium was held from April 12th-14th, in Vancouver, British Columbia.

Vancouver may not export as much sulphur as it used to, but it did still ship 2.6 million bulk tonnes in 2015, according to Port Metro Vancouver statistics, representing 55% of Canada's total sulphur exports for last year. That being the case, it was a very apposite location for The Sulphur Institute to hold its 2016 Sulphur World Symposium, and a tour of Kinder Morgan's loading terminal was organised for April 12th as part of the conference.

Market papers

For those not on the terminal tour, the conference began with a paper by **John McCall** of BP North America, who reviewed oil and gas markets. He suggested that the oil market would not return to balance until the second half of 2017. There are no further supply side surprises on the horizon after the return of Iran to the market, but inventories are still being worked off. Meanwhile, demand has responded to lower prices, and has risen by a million barrels per day in 2014, and around 1.5-2.0 million barrels/day in 2015.

The outlook for US unconventional oil and gas supplies has been repeatedly revised upwards, and in general output has not fallen as fast as people expected. Natural gas liquids particularly add to the overall liquids supply, with US LPG exports likely to rise from 900,000 bbl/d in 2015 to 1.8 million bbl/d by 2018. New ethane crackers are also under construction, with 450,000 bbl/d of capacity, and another 12 planned or proposed within the US.

On the gas side, LNG supply is growing rapidly, with 33 trains under construction and an additional 143 million t/a of capacity due to come on-stream by the end of 2018, potentially adding 50% to global production. The US and Australia are the major source of new exports, with Europe and China the major destinations. Gas demand growth is mainly in the non-OECD world, for power and industry.

As to whether US LNG exports were competitive, John's analysis looked at different scenarios for crude prices – at \$50/bbl crude, profitability was marginal, but at \$75/bbl the answer was definitely yes.

The general – and generally gloomy – economic outlook was presented by **Richard Koss** of the International Monetary Fund, who began with a look at the steady downwards progression in global growth forecasts since 2011. Growth trends remain slower than experienced in prior recoveries, he said, and although we have become used to a (very) long term growth rate of 3% for the US (since 1950!), since 2008 it has stubbornly stuck at 2% even through 43 consecutive months of job growth. Is this the new normal?

China is moving towards consumption-led growth, with import volumes unchanged year on year for 2014-16, but its growth forecast is now uprated to 6.5% for 2016. Commodities and energy have been a major deflationary shock to the world economy, with headwinds to growth, including low productivity – is the latter down to measurement issues, perhaps in areas like electronic payments? Demographics are also a factor, with ageing populations, and there are systemic risks ahead, such as that of a 'Brexit' – British exit from the EU.

The prospects were similarly gloomy for freight (if you're a shipper, that is...), as described by **Brian Malone** of MidShip Group. The Baltic Dry Index reached the low-

est level in its history in February, at 290, down from 11,000 at its 2008 peak, and has only recovered to about 400 since. The oversupply of ships continues in almost all classes, in spite of increased scrapping, and yet bunker fuel prices remain relatively high at \$175/t. He noted that the rock bottom freight market meant that almost no-one was investing in SO₂ scrubbing technology, which can cost over \$1 million per vessel, leading to the prospect of a price shock come 2020/2025 when everyone would be clamouring for low sulphur marine fuel.

Sulphur markets

Sulphur prices have fallen by \$100/t over the past 12 months, said **Meena Chauhan** of Integer Research. Falling oil prices have had an impact on sulphur production – while US refineries maintained throughputs in 2015, lower oil prices allowed them to switch to low sulphur crudes. Meanwhile Canadian oil sands production has seen a major downward revision in forecasts, and Canadian sulphur production seems set to continue its slow decline, from 5.1 million t/a in 2016 to 4.6 million t/a in 2021. The Middle East meanwhile continues to be the major source of new sulphur, with output rising from 13.4 million t/a in 2015 to 22.7 million t/a in 2020. Additional production will come from Kazakhstan and Turkmenistan and China. Overall global sulphur production will rise from 59.5 million t/a to 76 million t/a in 2021. On the demand side the forecast is lower for metal leaching (as discussed below), although there is some non-fertilizer demand growth in Russia and China, for chemicals production, and fertilizer related growth in Morocco, Saudi Arabia and East Asia. On the face of it this means a sulphur surplus of 1 million t/a in 2015 will rise to 7 million t/a in 2020, with stocks likely to build. The big question, she said, is where that will occur.

CRU's **Peter Harrison** covered the impact of metal leaching on the sulphur and sulphuric acid markets. Metal leaching represents around 10% of sulphuric acid demand and by extension 6% of sulphur demand, but a much larger share of trade, at around 33% of traded sulphuric acid and 18% of traded sulphur, making it proportionately more important. It has also seen strong growth over the past 10 years. However, the fall in metal prices has led to cutbacks in SX/EW production, and while there is some new copper leaching capacity coming in Zambia and the DRC, there is little prospect on the nickel side, where prices remain extremely low, outside of the acid import replacement project at Moa Bay in Cuba. For uranium, Kazakhstan has added around 2.4 million t/a of acid demand over the past decade, and Namibia will see some new demand in 2017 (coinciding with new smelter supply from Tsumeb), but Kazakhstan may see a slight decline going forward as in-situ leach projects switch to less acid-hungry projects.

On the phosphate side, **Jeff Holzman** of PotashCorp considered the strong correlation between phosphate prices and crop and oil prices, albeit with occasional disconnects due to market movements. At the moment the market is seeing moderate but supportive crop prices, but phosphate prices have been under pressure due to record Chinese exports; 11 million t/a of DAP/MAP in 2015, and a forecast of 9 million t/a this year. It remains open to question, though, he said, whether Chinese capacity will remain competitive in the light of new low cost capacity additions in Africa, the Middle East and Russia. Over 40% of new phosphoric acid capacity will be in Morocco and 30% in Saudi Arabia.

On the consumption side India remains the largest importer, but with uneven buying patterns. In the US, imports and speciality phosphates are gaining market share. Overall the forecast is for continuing demand growth around 2% per year, driven by Asia (especially India) and Latin America (mainly Brazil).

Projects

Mosaic's sulphur melter was the topic for a joint paper by **Herman Wittje** of Mosaic and **Mark Gilbreath** of project developers Devco. Herman explained the rationale behind the installation. Mosaic consumes 4.5 million t/a of sulphur and is the largest single importer in the world. Sulphur output from Mosaic's traditional suppliers – US and Canadian sour gas producers – is falling, while shipping costs into Tampa for international sulphur is now considerably cheaper than liquid sulphur from Canada. Mark then detailed the specifics of the installation – there will be a more detailed article about the sulphur melter in the next issue of *Sulphur*, July/August 2016.

Another large sulphur project – this time on the recovery rather than melting side – has been the Shah project in Abu Dhabi, as detailed in the Jan/Feb issue of *Sulphur*, pages 32-34. Enersul have installed 10,000 t/d of sulphur granulation capacity at Shah, and another 10,000 t/a at nearby Habshan, as described by **Pat Worries** of Enersul.

Transportation and safety

On Tuesday afternoon a session on supply chain management and safety was held, chaired by **Duane Abbott** of Chemtrade. **Harold Weber** of TSI updated delegates on transportation regulations for sulphur and sulphuric acid in North America – a fuller discussion of this can be found on pages 20-21. Handling sulphur brings with it the attendant hazard of potential exposure to hydrogen sulphide and sulphur dioxide, and **Chuck Simpson** of Epic Brokers dealt with training workers to work safely, arguing that the Z-390 training standard is now 20 years old and has some shortcomings in areas like SO₂, safety of visitors to sites, fitness standards etc. Likewise sulphuric acid transport brings its own challenges and risks, and **Scott King** of the Westway Terminal Company covered aspects of safe handling of sulphuric acid and issues around storage and transportation. Finally, a discussion panel comprising **Josh Berg** of Savage Services, **Joe McCann** of CSX Transportation, **Amy Blanton** of Chemours and **Josee Boudreau** of Transport Canada considered emergency preparedness as it relates to the shipping and handling of sulphur (especially liquid sulphur) and sulphuric acid – including setting up procedures, who to notify etc.

TSI returns to Europe next year, with Dublin the location, and April 24-26 the tentative dates.



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CONTENTS

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

Improved acid gas removal

COVER FEATURE 4

Enhanced sulphuric acid production

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Sulphur forming plant listing

System manufacturer/ supplier	Operating company	Operating site	Units	Product type	Scheduled throughput	New project/ expansion	Scheduled
BELARUS							
Sandvik Process Systems	Naftan Refinery	Novopolotsk	2	pastille	115 t/d	expansion	2016
CHINA							
Sandvik Process Systems	Sinopec	Qilu	2	pastille	750 t/d	new	2015
ECUADOR							
Sandvik Process Systems	Petroecuador	Esmerleidas	1	pastille	100 t/d	new	2016
FRANCE							
Sandvik Process Systems	Citis	Dunquerque	2	pastille	240 t/d	expansion	2015
INDIA							
Enersul	Reliance Industries	Gujarat	8	granule	2,800 t/d	expansion	2016
Sandvik Process Systems	Bharat Petroleum	Ambalmugal	3	pastille	800 t/d	expansion	2015
IRAQ							
Devco	Mishraq State Sulphur Mine	Mishraq	1	wet prill	1,500 t/d	new	n.a.
Sandvik Process Systems		Karbala	4	pastille	360 t/d	new	2017
Enersul	GazpromNeft	Badra	1	granule	350 t/d	new	2016
KAZAKHSTAN							
Sandvik Process Systems	Atyrau Refinery	Atyrau	2	pastille	175 t/d	new	2015
KUWAIT							
Enersul	KNPC	Mina al Ahmadi	5	granule	6,000 t/d	expansion	2015
MALAYSIA							
Enersul	RAPID	Pengerang, Johor	5	granule	2,000 t/d	new	2017
MEXICO							
Sandvik Process Systems	PEMEX	Coatzacoalcos	4	pastille	1,080 t/d	new	2016
OMAN							
Sandvik Process Systems	SOHAR Refinery	Liwa	3	pastille	300 t/d	new	2015
PAKISTAN							
Enersul	ARL	Rawalpindi	1	wet prill	100 t/d	new	2014
RUSSIA							
Enersul	Atpinsky Refinery	Tyumen	1	granule	350 t/d	expansion	2015
Enersul	Syzran Refinery	Samara	1	granule	350 t/d	expansion	2017
Enersul	Total/Globalstroy	Kharyaga	1	granule	350 t/d	new	2017
Sandvik Process Systems	Orsk Refinery	Orsk	2	pastille	200 t/d	new	2016
Sandvik Process Systems	TAIF-NK	Nizhnekamsk	1	pastille	100 t/d	new	2016
Sandvik Process Systems	MAVEG	n.a.	5	pastille	576 t/d	new	2018
SAUDI ARABIA							
Devco	SAMREF	Yanbu	1	prill	750 t/d	new	2014
Enersul	Aramco	Yanbu	2	wet prill	200 t/d	new	2015
SPAIN							
Enersul	Petroleos del Norte	Muskiz	1	granule	350 t/d	expansion	2016
Sandvik Process Systems	Repsol	Coruna	2	pastille	290 t/d	expansion	2016
Sandvik Process Systems	Repsol	Puerollano	4	pastille	520 t/d	expansion	2017
TURKEY							
Enersul	Aegean Refinery	Aliaga	3	granule	1,050 t/d	new	2016
TURKMENISTAN							
Enersul	Turkmgas	South Yolotan	7	granule	2,800 t/d	expansion	2014
Sandvik Process Systems	Turkmgas	South Yolotan	1	pastille	400 t/d	expansion	2015
VIETNAM							
Enersul	Nghi Son Refinery	Nghi Son	3	granule	1,380 t/d	new	2016



A twice yearly review contributed by
Alberta Sulphur Research Ltd

ASRL REVIEW

The chemistry and technology of sulphur degassing

Peter D. Clark, Director of Research, Alberta Sulphur Research Ltd and Professor Emeritus of Chemistry, University of Calgary

Technologies for removal of trace amounts of hydrogen sulphide from liquid sulphur were investigated and implemented in some Claus plants as long as 35 years ago. However, such technology was not applied extensively until the late 1990's. Systems were configured in which either air or steam was blown through the sulphur in the run-down pit or in an external vessel. These techniques were able to achieve the desired result of producing odour-free sulphur with <10 ppmw H₂S, greatly reducing the hazards of handling H₂S-laden product. The reasons why an air or steam purge actually worked were not understood in detail, but it was assumed that H₂S dissolved in the sulphur was removed by the purge gas.

Work at Freeport Sulphur¹ had shown that H₂S in sulphur existed as H₂S_x, a series of polymeric compounds, as well as being in solution, but not until the use of IR spectroscopy for analysis of liquid sulphur² did it become clear that removal of H₂S was the limiting factor for successful sulphur degassing. IR spectroscopy took a great leap forward when desktop computers became powerful enough to conduct Fourier transforms in a few seconds (now microseconds), allowing high resolution spectra to be

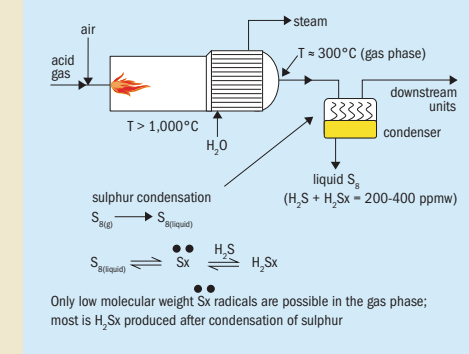
obtained for H₂S and H₂S_x even at very low concentrations. These developments enabled the study of the kinetics of degassing, with the consequent unravelling of the chemical mechanisms by which H₂S_x was decomposed³.

Today, sulphur degassing technology is an important component of reducing total emissions from a Claus plant, and also in eliminating some of the hazards of handling sulphur in the transportation and marketing chains. The objective of this article is to review sulphur degassing research conducted at ASRL illustrating how this fundamental work has facilitated new technology and improved safety and emissions control as a consequence.

H₂S and H₂S_x in liquid sulphur

Since liquid sulphur is in contact with H₂S – containing process streams until it flows through the lock system, it is not surprising that some H₂S dissolves in the sulphur. The reason for the presence of H₂S_x is complex and hence more interesting from a chemical viewpoint. S-S single bonds are unstable until the temperature drops below 400°C, so it is not possible to have H₂S_x in the furnace. Only in the waste heat boiler (WHB) when the tempera-

Fig 1: Formation of H₂S_x in Sulphur



ture drops below that value can H₂S_x be produced. Since there is no evidence of H₂S_x in the gas phase (many groups, including our own, have looked in vain), it can be argued that H₂S_x is formed as sulphur condenses from the gas phase, a suggestion that makes sense because of the presence of high concentrations of sulphur radicals in liquid sulphur at 300°C (Figure 1). The mechanism of formation of H₂S_x predicts that more should be present in the liquid sulphur

produced in the condenser downstream of the WHB, because there is more H₂S in the process gas, and also because the initial sulphur condensation temperature is at its highest value; a condition which favours sulphur radical formation. Because the WHB produces as much as 70% of sulphur from the plant, the obvious approach to reducing degassing needs would be, somehow, to prevent or lessen formation of H₂S_x in the WHB condenser. As will be

Fig 2: Mechanisms of air degassing

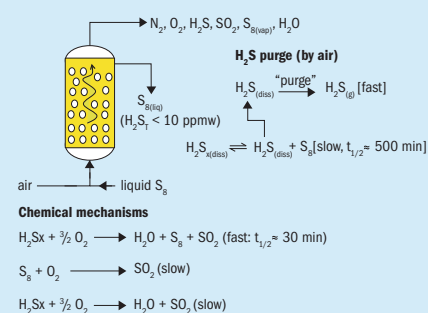
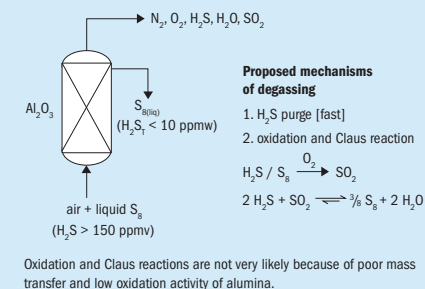


Fig 4: Degassing with solid catalysts eg: alumina



explained later, a new Claus process configuration designed by ASRL has achieved that goal.

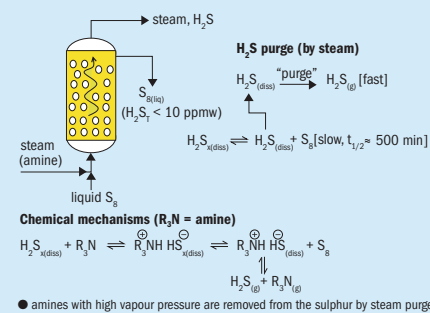
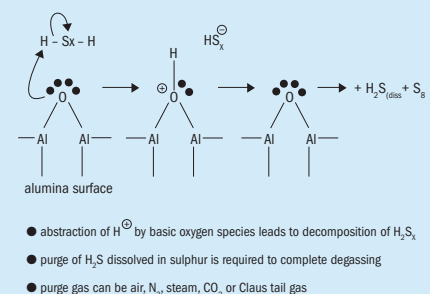
Of course, release of H₂S from liquid sulphur is a safety concern, as un-degassed sulphur can easily result in lethal quantities in the head space of tanks and run-down pits. Even degassed sulphur with <10 ppmw total H₂S should be treated as a hazardous liquid in a non-vented tank. Although H₂S in sulphur is a safety concern, H₂S reduces the liquid viscosity at WHB condenser operating temperatures (180°C). Indeed, if it were not for the presence of H₂Sx in sulphur at 180°C, a Claus condenser could not be operated at that temperature. This observation suggests that H₂Sx polymers have a relatively low molecular weight range, although no measurements have been conducted to determine the nature of H₂Sx species in liquid sulphur.

How does air degassing work?

There are numerous technologies for sulphur degassing which involve purge of air through the liquid. All kinds of mechanical wizardry has been applied to dispersing air through sulphur, and all have the problem of what to do with the air purge stream after the degassing unit. That stream contains H₂S, SO₂, H₂O and sulphur vapour, as well as lots of air. Formerly this off-gas was routed to the incinerator, but this practice decreases total sulphur recovery by as much as 0.1%, which today precludes attainment of emission limits in most jurisdictions.

The chemistry of air degassing, like most sulphur chemistry, turns out to be more complex than one might first think, as it not only involves purge of H₂S from the liquid, which might have originated from decomposition of H₂Sx, but also involves chemical reaction of H₂Sx with O₂, forming SO₂ and H₂O (Figure 2).

Fig 3: Mechanisms of steam degassing

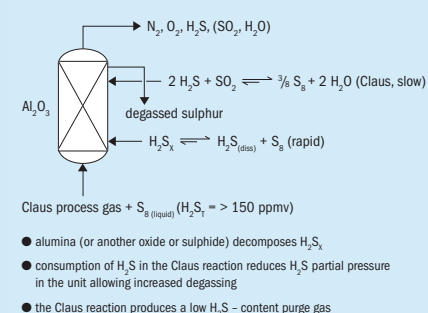
Fig 5: Decomposition of H₂Sx over solid oxides

Thus, if air is replaced by N₂, the SO₂ in the off-gas disappears. However, the rate of degassing decreases dramatically when N₂ or other O₂-free purge gases are used. The message from the chemical mechanism is that O₂ is a chemical reactant in air degassing, and that SO₂ formation cannot be avoided. The other important aspect of the chemical action of O₂ is that because H₂Sx is dissolved in the liquid phase, the engineering of air degassing must be such so as to facilitate mass transfer of O₂ to the liquid phase. This feature of degassing has been solved by use of rapid mixing devices and by operation at elevated pressure, which increases the solubility of O₂ in sulphur. This last adaptation has the advantage of decreasing air purge rates, so decreasing the volume of off-gas that must be dealt with in the plant. Furthermore, if the off-gas air stream is at elevated pressure, it is easier to com-

Degassing with steam (and a catalyst)

Preliminary research at ASRL in the late 1980's showed that steam purge degassing did not work any better than N₂, but local sulphur plants seemed to have great success with steam degassing. Discussion with operators at these plants revealed that industrial steam is not the same as clean laboratory steam. The key difference was that industrial steam boilers use volatile amines (morpholine, cyclohexylamine, amongst others) to prevent corrosion in the kettles. Addition of just 1-2 ppmw of these compounds to our laboratory steam resulted in sulphur degassing at rates exceeding ambient pressure air degassing

Fig 6: Degassing with Claus process gas

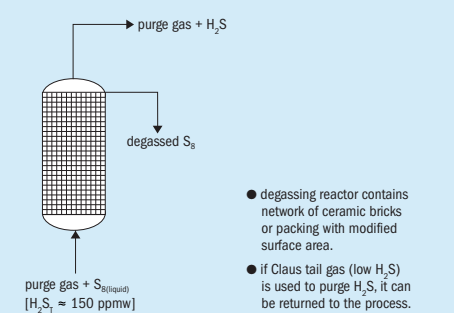


(Figure 3). From a chemical viewpoint, all of the ducks fall nicely into line for amine-catalysed sulphur degassing, as the active agent for H₂Sx decomposition is soluble in sulphur (Figure 3) and is readily removed at the end of the process. If steam or another inert purge gas (N₂) is used in combination with amines, only H₂S appears in the off-gas, but use of air still results in some SO₂ because of O₂-promoted H₂Sx decomposition, which proceeds alongside the amine promoted reaction. Commercially, this information was used to develop new degassing technology and enhance existing air degassing methods.

Degassing with solid catalysts

Amoco USA introduced a degassing technology in which liquid sulphur and air flow through a bed of alumina catalyst. It was assumed that the process worked by in-situ formation of SO₂ and Claus reaction of that product with H₂S and H₂Sx in liquid sulphur on the alumina catalyst (Figure 4). Thus the process would be a version of sub-depoint sulphur production akin to the tail gas process introduced by Amoco and others. Although this explanation may be part of the liquid sulphur degassing mechanism, research conducted at ASRL showed that it was not the major process, as simply passing sulphur and N₂ over alumina resulted in rapid removal of H₂Sx from the liquid as H₂S. Consideration of the nature of an alumina surface shows that basic sites - essentially any bound oxygen atom at the surface - should result in decomposition of H₂Sx by chemistry very similar to

Fig 7: Degassing liquid sulphur in ceramic reactors



that of amine-assisted decomposition of H₂Sx (Figure 5). The observation of H₂Sx decomposition at solid surfaces was a very important one, as it allowed us to propose new approaches to degassing, some of which have already been introduced at a commercial scale.

Ramifications of solid catalyst degassing chemistry

Decomposition of H₂Sx by bound oxygen atoms at an alumina surface suggests that any solid oxide will degas sulphur as it is the lone electron pairs on the oxygen atoms that promote the initial step of H-abstraction from H₂Sx (Figure 6).

This mechanism means that solid sulphides will also catalyse decomposition of H₂Sx. Thus, laboratory research at ASRL found that silica and oxides of iron and copper, which form sulphides in situ, are effective catalysts for sulphur degassing^{4,5}. The other important aspect of the research was that any purge gas should work, as its function is to remove the H₂S from the liquid, so driving the system to degassed sulphur. So N₂, CO₂, steam and Claus tail gas should all be effective purge gases.

A very interesting set of experiments performed as part of the ASRL Core Research Program showed that Claus process gas with a composition similar to that flowing from the first Claus converter condenser resulted in very effective (~1 ppmw H₂S/H₂Sx) degassing of liquid sulphur. This result was unexpected as the H₂S in the process gas should have resulted in greater retention of H₂S and H₂Sx (ca. 25 ppmw) in the

low flow of process gas is required relative to the total flow in the plant, the degassing off-gas could be compressed back into the first converter. Another adaptation would be placement of ceramic tubes or coated tubes inside all of the Claus condensers, although heat transfer considerations and expense might preclude this option. Only partial degassing of sulphur in the WHB condenser would be expected because of the relatively high H₂S partial pressure in the process gas.

New technology for sulphur degassing

Studies on the mechanisms of solid degassing allowed consideration of new technology and adaptation of existing methods^{4,5}. One possible adaptation is simply to line the vessels used for sulphur degassing with low surface area solid alumina brick, as contact of the H₂Sx-laden sulphur with the basic sites on the solid surface would accelerate the decomposition of H₂Sx. This lining could be the type of ceramic bricks used in furnaces, with some modification to increase surface area of the ceramic. More usefully, the ceramic could be part of the inner structure of the degassing vessel (Figure 7). Although this system would have to be designed carefully to avoid mass transfer limitations, some reduction of degassing residence time would be expected compared to a carbon steel vessel. If this modification is coupled with use of Claus process gas as the degasser purge gas, some conversion of the remaining H₂S and SO₂ would be expected. Since only a

low flow of process gas is required relative to the total flow in the plant, the degassing off-gas could be compressed back into the first converter.

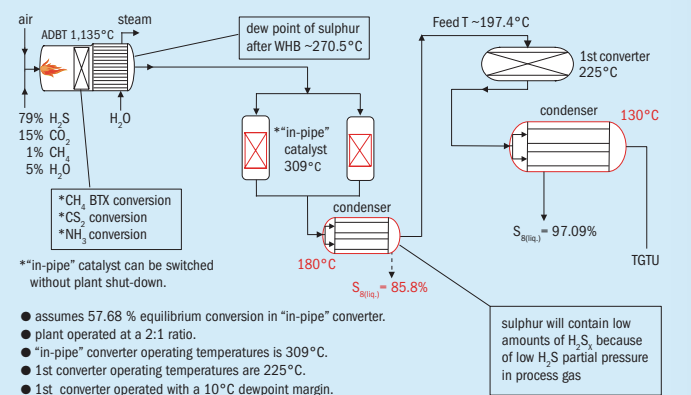
Another adaptation would be placement of ceramic tubes or coated tubes inside all of the Claus condensers, although heat transfer considerations and expense might preclude this option. Only partial degassing of sulphur in the WHB condenser would be expected because of the relatively high H₂S partial pressure in the process gas.

Recently, ASRL has examined a simplified Claus process in which the product gas from the furnace and WHB is passed directly to a small converter operating at around 300°C before condensation of any sulphur (Figure 8). The main aim of the converter is to produce more sulphur, enabling reduction of equipment for the downstream units. However, since the process gas entering the condenser now has much less H₂S compared to a normal plant (ca. 3% compared to 8%), the amount of H₂Sx that could form in the condenser would be reduced very considerably. Moreover, if H₂Sx is present in the gas phase (probably unlikely), it would react with SO₂ in the small catalytic converter, so eliminating that source of H₂Sx in the product. Adoption of this type of Claus process would have a very significant effect on the degassing requirement in a Claus plant, as it is calculated that the sulphur from the first condenser, which will be as much as 85% of the plant production, will have <50 ppmw residual H₂S, compared with >250 ppmw for a standard Claus plant.

Concluding comments

Sulphur degassing is an integral component of a sulphur plant for both emissions control and for increasing the safety of handling of liquid sulphur and the solid derived from it. The fundamental research conducted in our laboratories since the early 1990s has enabled deduction of the chemical mechanisms of air and catalyst degassing. This knowledge has been used to enhance existing processes and for development of new technology. Although these commercial technologies were not described in this short article, their implementation has made a major contribution to enhancing the efficiency of Claus sulphur recovery. ASRL continues to work in this area: stay tuned.

Fig 8: A simplified Claus process



- assumes 57.68 % equilibrium conversion in "in-pipe" converter.
- plant operated at a 2:1 ratio.
- "in-pipe" converter operating temperatures is 309°C.
- 1st converter operating temperatures are 225°C.
- 1st converter operated with a 10°C dewpoint margin.

sulphur will contain low amounts of H₂S, because of low H₂S partial pressure in process gas

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CONTENTS

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

Improved acid gas removal

COVER FEATURE 4

Enhanced sulphuric acid production

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Improvements in acid gas removal

Acid gas removal has been improved over the years with the development of new solvents and novel process line-ups, tailored to specific project requirements. In this article **J. Rolker**, **M. Irfan** and **R. Steglich** discuss a new class of amines for acid gas removal from Evonik, **S. Kobussen** reports on the first results from new acid gas removal designs from Jacobs and **M. Rameshni** discusses recent developments from RATE.

The most common process for acid gas removal in the industry is the chemical absorption process utilising an aqueous amine solution (Fig. 1). The sour gas and the lean amine are brought in contact in counter-current mode in the absorber at higher pressures (10-100 bar) and lower temperatures (lean amine inlet temperature at the top: 40-65°C). The CO₂ and H₂S loaded rich amine leaves the absorber at the bottom of the absorber and is introduced to a first flash vessel where the pressure is decreased and co-absorbed gas components are predominantly released (high-pressure flash) and a second flash at lower pressure to release a part of the acid gases (low-pressure flash). The remaining amount

of acid gases is drawn from the stripper, which is equipped with a reboiler to generate stripping steam and provide the regeneration energy for desorption of the acid gases. The desorber is operated at lower pressure (1-2 bara) and higher temperatures (110-125°C). Finally, the regenerated lean absorber is fed back to the absorber.

There are numerous amine-based absorption processes in operation worldwide utilising different kinds of amines. The proper choice of amine depends on various conditions starting from the feed gas composition (CO₂ removal, removal of sulphur components or both), the required clean gas specification (bulk removal or ppm range) or on specific

design considerations (e.g. the availability of cooling utilities). Mostly however, these processes use aqueous amine solutions (typically 30-50 wt-% of amine) based on MEA (monoethanolamine), DEA (diethanolamine), AEE aminoethoxyethanol) DIPA (di-isopropanolamine) or MDEA-based formulations that contain a rate-promoter like piperazine for more efficient CO₂ removal.

Despite the long history of acid gas removal utilising amines and the maturity of the gas treating process, gas operators still suffer from a number of drawbacks.

Capacity limitations

The acid gas removal unit often represents the bottleneck if the throughput of the processed gas is about to be increased. The design of the plant is made for a certain amine and a respective rich loading which should not be exceeded due to higher corrosion.

Degradation and corrosion

The aqueous amine solution is corrosive by nature, but furthermore degradation products like heat stable salts that are formed between the amine and trace components of the feed gas, sometimes even CO₂ or oxygen that is introduced to the plant severely enhance corrosion in the plant. In addition to this chemically induced degradation, it is also possible that the amine degrades with high temperatures, e.g. hot spots in the reboiler or high surface temperatures. Degradation mainly traces back to a low chemical and thermal stability of the amine.

Fig 1: Typical acid gas removal process

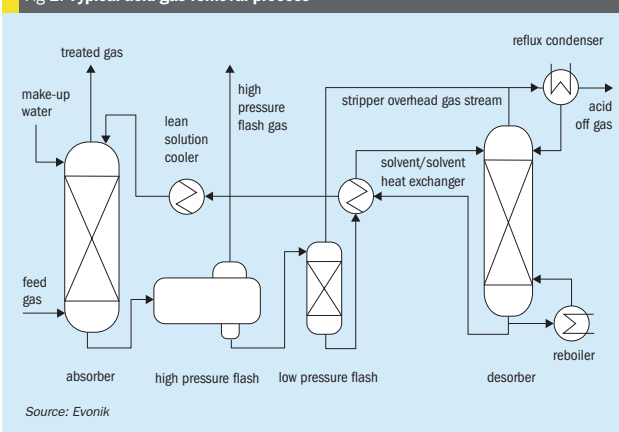


Fig 2: Deep removal of H₂S

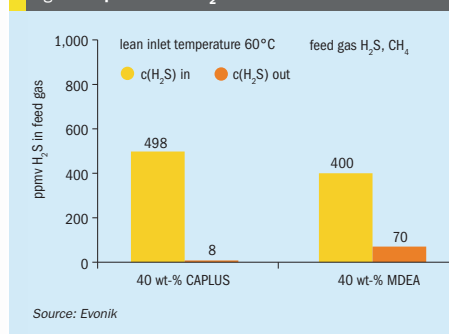


Fig 3: Deep removal of H₂S

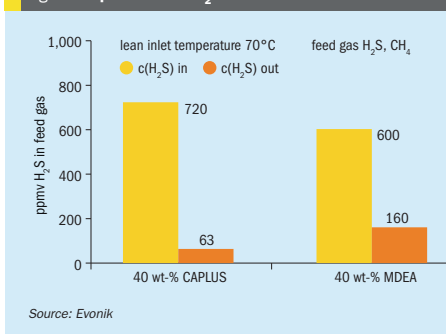


Fig 4: Deep removal of H₂S

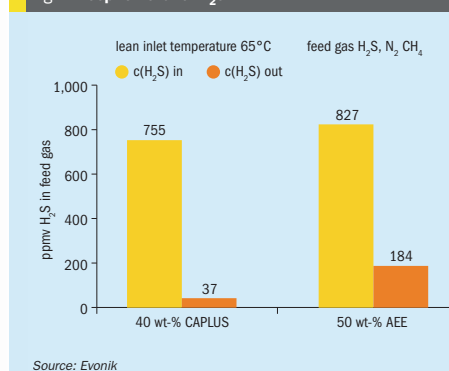
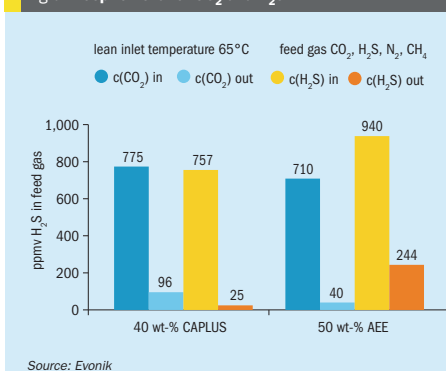


Fig 5: Deep removal of CO₂ and H₂S



Foaming

A lot of amines tend to cause foaming, especially if the amine system is not kept clean and the typical filter units (e.g. particle and carbon filters) are not used properly. If excessive foaming occurs, solvent monitoring has to be intensified and anti-foam addition is the method of choice to prevent a reduction in processing capacity or even a shutdown.

Energy intensiveness

The exothermic reaction of the acid gases with the amine in case of primary or secondary amines or due to the formation of Hydrogen Carbonate (tertiary or sterically hindered amines) that is released in the absorber (absorption enthalpy) leads to an increase in temperature during absorption and has to be supplied in the desorbing step at higher temperatures to strip the

acid gases from the loaded absorbent and receive again the lean amine solution. If the heat is provided from a gas burner using the treated or untreated gas, a high consumption of regeneration energy is directly related to the operating expenditures of the gas treating unit.

The above mentioned pain points are not true for all gas processing units, but are being reported from many gas operators. These issues lower the plant availability, cause high maintenance efforts and lead to higher operational expenditures and therefore decrease the economic performance of an AGR unit.

CAPLUS® – a new high-performance absorbent

In 2012, speciality chemicals company Evonik introduced a new class of amines for acid gas removal applications, such

as natural gas treatment, the purification of synthesis gas, biogas upgrade as well as flue gas scrubbing where the efficient removal of CO₂ and/or H₂S is required.

The new amines are not based on the typical alkanolamines currently in operation and offer significant benefits over conventional amines.

They were developed as a drop-in solution for existing acid gas removal units for a complete exchange with the existing amine, but could also be used as an additive to boost the performance of a plant. The new amines are called CAPLUS® (CApture PLUS or CApacity PLUS). The more robust molecular architecture leads to a higher chemical and thermal stability compared to conventional amines. As a result less degradation and less corrosion are observed. CAPLUS® allows for higher acid gas loadings in operation due to a higher solubility for CO₂ and H₂S and subsequently a higher cyclic capac-

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

Improved acid gas removal

COVER FEATURE 4

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ity. This behaviour originates from the amine molecule carrying more than one amine functionality.

Since the new absorbent is not based on existing amines like MDEA or AEE, several existing drawbacks of state-of-the-art absorbents such as low absorption capacity, high regeneration energy, high make-up streams and their corrosive nature as well as foaming can be addressed and significantly improved with CAPLUS®. Due to the higher capacity for acid gases, an average decrease of 20% in absorbent flow rate can be achieved compared to state-of-the-art amines. Depending on the overall operational goal of a gas plant, this benefit might translate into savings in operational expenditures (less regeneration energy, less electricity costs for utilities) or an increase in gas throughput or in a higher flexibility of plant operability (e.g. feed gas fluctuations).

Pilot plant tests

In pilot plant tests CAPLUS® has demonstrated its superior ability to attain deep removal of H₂S compared to MDEA and aminoethoxyethanol. Figures 2 and 3 show the results for a synthetic natural gas feed of 800 Nm³/h at an absorber pressure of 5 barg treated with 40 wt-% CAPLUS® versus 40 wt-% MDEA at a lean inlet temperature of 60°C and 70°C respectively. Figures 4 and 5 show the results for a synthetic natural gas feed of 800 Nm³/h at an absorber pressure of 5 barg treated with 40 wt-% CAPLUS® versus 50 wt-% AEE at a lean inlet temperature of 65°C. Figure 5 shows that CAPLUS® can achieve much deeper removal of H₂S compared to 50 wt-% AEE even in a feed gas stream containing CO₂.

The pilot plant results, although not representing real life plant data, show on a qualitative basis that CAPLUS® significantly improves the efficiency of H₂S removal compared to state-of-the-art amines, even at a challenging higher lean amine temperature of 70°C.

Commercial status

CAPLUS® is currently in the market entry phase and is already being utilised in commercial plants for CO₂ removal from natural gas, biogas and flue gas. The first reference for the treating of H₂S is expected to come on stream later this year. As a next milestone CAPLUS® will be introduced to a world scale natural gas plant in Asia with the target to remove CO₂ and H₂S by mid 2016.

RATE acid gas processing schemes

Rameshni & Associated Technology and Engineering (RATE) has been involved in several sour gas field development projects in recent years. Selecting the solvent for acid gas removal and proper design criteria are crucial for meeting pipeline gas specifications according to the latest standards and have a significant impact on the sulphur recovery operation. The acid gas removal unit provides the acid gas feed to the sulphur recovery units, therefore, the evaluation, technology selection and design criteria for acid gas removal should be made in conjunction with the entire sulphur block. The sulphur block consists of acid gas removal, sulphur recovery and tail gas treating technologies as well as possible requirements for acid gas enrichment, sulphur degassing and incineration.

Compared to refinery applications, acid gas removal for sour gas field developments is more challenging due to the presence of impurities such as BTEX and mercaptans. However, recent developments in acid gas removal provide a range of technology solutions. They include:

- the development of more selective formulated solvents such as hybrid solvents;
- improvements to molecular sieve technologies to remove mercaptans and by combining with dehydration to reduce the number of operation units, resulting in lower capital costs;
- improvements to towers/columns internal for more efficient packing and trays;
- the addition of pre-conditioning/pre-treatment units upstream of the acid gas removal to remove some of the impurities so that expensive materials of construction for acid gas removal can be eliminated which is again a cost saving factor;
- the addition of polishing or after treatment units downstream of the acid gas removal to remove remaining impurities and to meet pipeline sales gas specifications;
- technology developments in downstream units like the sulphur recovery unit to achieve better and more stable performance, to increase sulphur recovery and to reduce the emissions keeping down capital costs;
- RATE partial acid gas enrichment (Rich "S-MAX") is a solution for acid gas

removal where the feed to the SRU contains a low H₂S concentration and impurities that require a high combustion temperature (see *Sulphur* no. 350, pp. 38-45).

An example of a recent gas project is described below.

The project was for a new gas plant that consists of acid gas removal and a sulphur recovery unit.

The H₂S concentration to the acid gas removal varies from 2.3% to 5%, the CO₂ concentration varies from 3% to 6%. The treated gas from the absorber overhead or the sales gas must meet the following specifications:

- H₂S, 4 ppmv
- CO₂ less than 1.7% max
- mercaptans such as COS 4 ppmw maximum,
- organic sulphur 50 ppmw maximum, total sulphur 60 ppmw maximum

RATE carried out the evaluation for the solvent selection to meet the criteria for the treated gas based on commercially proven solvents in three categories: chemical solvents, physical solvents and hybrid solvents. Both proprietary solvents and generic solvents, such as MDEA from worldwide solvent suppliers, were considered. The generic solvents and the physical solvents were unable to meet the specification and many formulated proprietary solvents were also eliminated.

Although the results revealed a number of chemical solvents, especially MDEA based solvents, that can easily meet the H₂S and CO₂ specifications, most of the commercially available solvents have difficulty in meeting the criteria for mercaptans such as COS less than 4 ppmw. The focus of the evaluation moved on to hybrid solvents that have the capability to meet the product specification and it was concluded that hybrid solvents such as the "Hybrid series" from Dow or "equivalent" would be able to achieve the following specs: H₂S <4 ppmv, COS <4ppmv, mercaptans <50 ppmw. The preliminary amine unit is designed based on 4% H₂S up to 5% H₂S from the well gas composition.

By selecting the proper solvent, the need for more expensive acid gas removal schemes such as hot flash, lean/semi lean absorber configuration, and 2-stage amine regeneration schemes were eliminated.

Jacobs AGR + SRU optimisation

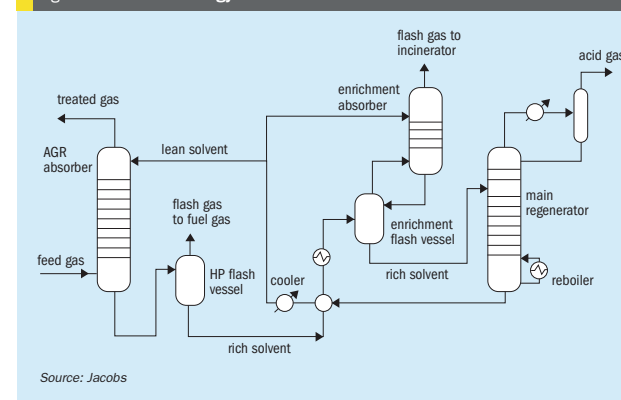
In *Sulphur* no. 355 (pp. 37-40) Jacobs presented some case studies for new developments in acid gas removal. Two approaches for treating lean acid gas have now been built and are in operation. The first results are presented below.

Hot flash technology and Sulfinol-M

Recently a gas plant started up using a novel approach from Jacobs for acid gas removal. At this plant, considerable savings could be made by improving on the standard design, which would have consisted of a standard acid gas enrichment with DGA and would have supplied gas containing only 35% H₂S to the downstream SRU. Jacobs approach was to apply a hot flash enrichment step and to use Sulfinol-M (Fig. 6).

The gas plant is operating successfully processing 1.4 million Nm³/hr of natural gas containing considerable quantities of CO₂ and heavy hydrocarbons. Applying a line-up with Sulfinol-M and hot flash allows for more CO₂ slip, thus increasing the amount of H₂S in the acid gas. An H₂S concentration of 61 mol-% to the SRU can be achieved. Because of the richer gas flow to the SRU, one complete SRU train did not have to be built, so the cost savings were considerable. The SRU itself achieved a sulphur recovery efficiency of 99.3%, meeting the emission criteria

Fig 6: Hot flash technology and Sulfinol-M



Source: Jacobs

of the government easily. These results confirm the validity of the combined Jacobs design.

Tuned enrichment

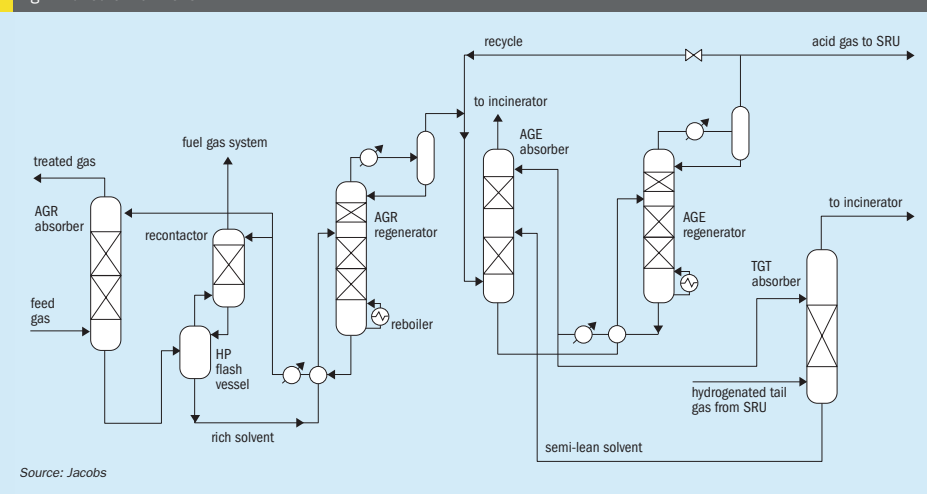
For another gas plant Jacobs made a design that can operate with two different feeds, one with a high H₂S content and another with half the amount of H₂S. A recycle is used so that in both cases a sufficiently high H₂S concentration to the SRU can be achieved. The recycle operates from the enrichment regenerator back to the enrichment absorber (Fig. 7).

The two operating cases are:

- high H₂S feed case: 3.2% H₂S and 12% CO₂
- low H₂S feed case: 1.6% H₂S and 12% CO₂.

The actual feed composition at start-up was 1% H₂S and 8% CO₂, which produced a stream of acid gas to the SRU containing 39% H₂S. Because of the low CO₂ content this concentration was achieved without the need to operate the recycle. Further news can be expected when more sour gas wells will be taken on stream and the recycle will be taken into operation. ■

Fig 7: Tuned enrichment



Source: Jacobs

Combining technologies for enhanced acid production

New sulphuric acid plant designs are being proposed that combine innovative technologies in new process line-ups to optimise the economics of sulphuric acid production and reduce emissions.

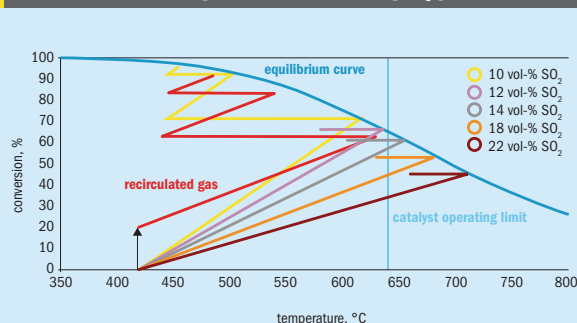
Outotec sulphuric acid technologies

Outotec has been providing technologies for the production of sulphuric acid for more than 80 years and is a leading supplier of solutions for the sulphuric acid industry. Outotec's LUREC™ and HEROS™ technologies can be combined to provide highly efficient acid production.

Outotec LUREC™ process

Modern copper smelting processes use oxygen enrichment and produce a strong SO₂ off-gas. The LUREC™ process was developed to process these strong off-gases from continuous processes such as Outotec flash smelting or flash converting. The more the total gas flow can be reduced in an acid plant, the lower the opex and capex cost will be from power savings in the main blower and from smaller equipment sizes.

Fig 1: Conversion and bed 1 exit temperature for different SO₂ concentrations with red line showing the effect of recirculating SO₃ gas



Source: Outotec

Low gas flow can be obtained by operating an acid plant at high SO₂ concentrations which leads to the challenge illustrated in Fig. 1. A conventional acid plant with an inlet temperature of 420°C is limited to a SO₂ concentration of 12 vol-% by the maximum catalyst operating temperature.

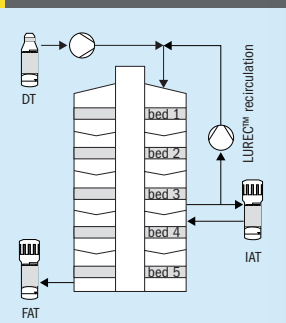
An additional opportunity arising from high SO₂ concentrations is the production of high pressure steam. For a lower gas flow the heat of reaction and absorption is constant, while less heat will be lost for heating the gas to operating temperature after the intermediate absorption and also less gas heat is lost in the final absorption. This excess heat is useable for steam production. With increasing SO₂ concentrations above 12 vol-% the amount of excess heat that must be removed from the system increases significantly and is suitable for stand-alone power generation from high pressure steam.

The Outotec LUREC™ technology limits the outlet temperature of bed 1 by recirculating some of the SO₃-rich gas from the exit of bed 3 to the feed gas to bed 1 (see Fig. 2). Figure 1 shows the effect of this recirculation: The additional SO₃ at the inlet of bed 1 is acting as a "preconversion", so the chemical equilibrium conditions are reached after a lower temperature increase. The rate of recirculated gas controls the outlet temperature of bed 1.

This allows operation at much higher SO₂ inlet concentrations than conventional plants with all its benefits.

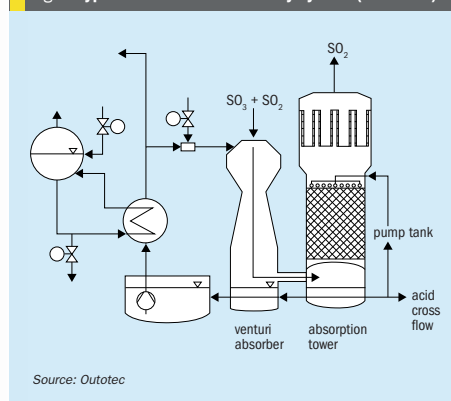
Recirculation of SO₃ gas allows in principle the processing of SO₂ gas of up to 25 vol-%. This high SO₂ concentration requires a sufficient amount of oxygen for conversion,

Fig 2: Principle of LUREC™ recirculation



Source: Outotec

Fig 3: Typical Outotec heat recovery system (HEROS™)



Source: Outotec

so in the case of copper smelter off-gas a practical concentration range is between 16 and 18 vol-% SO₂.

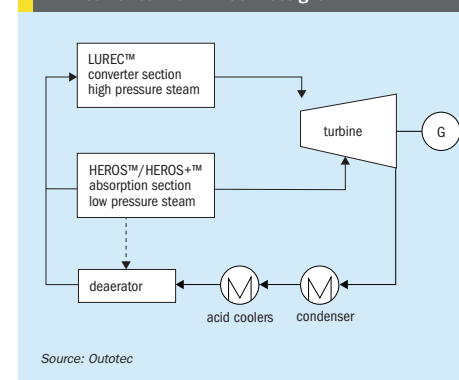
Outotec HEROS™ Process

A large amount of heat is released by the absorption of SO₃. The application of the Outotec HEROS™ process (Fig. 3) enables the generation of saturated low pressure steam from the absorption energy released at the intermediate absorption step.

Most of the SO₃ absorption takes place in a co-current venturi at high temperatures and is used to produce low pressure steam in the HEROS™ boiler. The remaining SO₃ is absorbed in the intermediate absorption tower downstream of the venturi.

The design of the intermediate absorption tower is a conventional absorber design for the full capacity so that it is capable of handling all SO₃ when the HEROS™ is not in operation.

Fig 4: Enhanced power generation in a LUREC™ acid plant combined with HEROS™ designs



Source: Outotec

In addition, energy is recovered in the acid coolers and is available for boiler feed water pre-heating.

Combining both sources in a synergetic way leads to a concept of even higher efficiency. This concept integrates heat from the standard HEROS™ system into a possible high pressure steam system by pre-heating the boiler feed water to even higher temperatures. On the basis of this design the so-called Outotec HEROS+™ process increases the production of valuable high pressure steam for maximised power generation.

Combining LUREC™ and HEROS™

A combination of LUREC™ and HEROS™ technology is beneficial for treating off-gas from a continuous Outotec flash smelter and Outotec flash converter. This is a perfect gas source for heat integration because of its strong and continuous gas.

The design basis for the described 4,250 t/d LUREC™ acid plant is a strong 18 vol-% SO₂ gas with 14 vol-% O₂.

Figure 4 shows the key elements of the combined technologies: High pressure steam from a LUREC™ converter section and low pressure steam from a HEROS™ are fed into a turbine and this is combined with a boiler feed water pre-heating in the acid coolers.

Compared to a conventional plant the low gas flow rate of a LUREC™ plant reduces all equipment sizes for an extra recirculation blower and reduces the overall power consumption of the plant. Table 1 shows this difference in gas flow between a conventional (330,000 Nm³/h) and a LUREC™ plant (220,000 Nm³/h). The reduced specific power consumption per tonne of sulphuric acid for the LUREC™ design is a direct consequence of this lower gas flow.

Table 1: Technical comparison of a conventional plant with different solutions for power generation (All LUREC™ process solutions in the table use 18 vol-% SO₂)

Basis 4,250 t/d	Conventional 12 vol-% SO ₂	LUREC™	LUREC™ with HEROS™	LUREC™ with HEROS+™
Gas flow to converter, Nm ³ /h	330,000	220,000	220,000	220,000
Power consumption, kWh/t H ₂ SO ₄	55	43	45	46
LP steam generation: 100 kPa, saturated, t/h	-	-	62	72
HP steam generation: 400 kPa, 480°C, t/h	-	46	46	53
Power generated, MW	-	12	21	24
Net power export, MW	-	4.5	13.1	16.1
Emissions, kg SO ₂ /t H ₂ SO ₄ (basis 250 ppmv)	1.1	0.75	0.75	0.75

Source: Outotec



TurboScrubber installation.

Table 1 also shows the potential in steam production when combining a LUREC™ plant concept with HEROS™ or HEROS+™.

Further advantages with LUREC™ technology include reduced SO₂ emissions (based on SO₂/t H₂SO₄), lower cooling water consumption and increased net power export for each combination indicating clearly the efficiency surplus compared to a conventional plant.

The tailored plant design for a specific project is defined by the customer's individual target settings to gain the most economic plant concept. The LUREC™ process with HEROS™ or HEROS+™ fit perfectly together to optimise plant efficiency.

NORAM's TurboScrubber® process line-ups

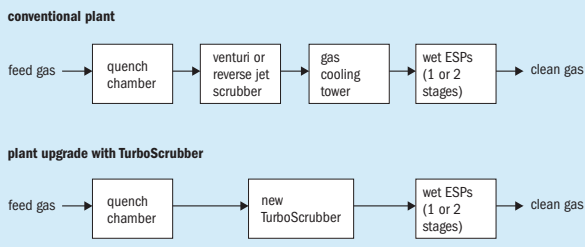
The TurboScrubber® fluidised bed technology licensed by NORAM has been successfully applied to a wide range of SO₂ applications and can potentially be used with great effect in new process line-ups for the sulphuric acid industry to eliminate sub-micron sulphuric acid mist as well as to scrub SO₂ gas. The TurboScrubber can be used for both gas cleaning and tail gas scrubbing.

Gas cleaning

NORAM's TurboScrubber system can replace the conventional venturi scrubber and the conventional cooling tower and/or one stage of wet electrostatic precipitation (WESP) in the gas cleaning section of a sulphuric acid regeneration or metallurgical acid plant to simplify the process line-up (see Fig. 5) and provide net savings in pressure drop. Additional benefits include:

- provides continuous as well as start-up

Fig 5: Gas cleaning process line-ups



Source: NORAM

scrubbing of particulates, dust, condensed metals, and sub-micron sulphuric acid mist.

- the scrubber is non-fouling.
- offers cost savings from elimination of the expensive WESPs.
- can have different operating modes depending on the mist and dust loads.

The following common combinations of gas cleaning equipment can be replaced by the TurboScrubber system:

- high pressure drop fixed-throat venturi scrubber and cooling tower;
 - high pressure drop variable-throat venturi scrubber and cooling tower;
 - reverse-jet scrubber and cooling tower/ froth column;
 - radial flow scrubber and cooling tower.
- This replacement is possible because the TurboScrubber:
- achieves particulate and aerosol removal with high efficiencies;
 - is countercurrent, which is important for heat transfer, cooling and water removal;
 - does not foul in dirty service;
 - has a potentially lower pressure drop of about 20"WC (compared to 25 to 50"WC for other equipment combinations).

Tail gas scrubbing

NORAM's TurboScrubber system can also be installed as a tail gas scrubber at the tail end of a sulphuric acid plant. Environmental regulations regarding SO₂ emissions are continuously being tightened around the world. This holds true for both start-up and continuous operating modes. During start-up, acid plants often experience an acid plume from the stack due to cold acid not being able to fully absorb SO₃. Installing a

TurboScrubber after the final absorption tower of an acid plant significantly reduces stack emissions during both start-up and continuous operation. The operation of the TurboScrubber is flexible such that the liquid to gas ratio can be modified for either start-up or normal operations. This flexibility allows using one piece of equipment for two very different operations:

- SO₂ and acid plume removal during start-up,
 - SO₂ removal during normal operation
- In addition to removing SO₂, the TurboScrubber can also remove fine acid mist coming from the upstream final absorption tower. This feature allows replacement of the high efficiency mist eliminator (typically candles) in the final absorption tower with a low pressure drop mesh pad. The TurboScrubber can therefore be installed without adding pressure drop to the plant.

Case study: TurboScrubber acid mist reductions

The following case study is based on a sulphur burning plant producing up to 600 t/d of sulphuric acid. The stack emissions during continuous operation are approximately 310 ppmv SO₂.

The plant has an upstream final absorption tower (FAT) with Brownian diffusion (BD) candles. The acid tower operates with an acid inlet concentration of 98.5 wt-% and inlet temperature of 80°C. The BD candles operate with a 10 inch W.C. pressure drop. The purpose of the BD candles is to remove the majority of the acid mist formed to meet the legislated emission limit on sulphuric acid, which in general in the USA is 0.075 kg H₂SO₄/t H₂SO₄ (as 100%).

There are three sources of acid mist emissions through the stack:

- acid spray and mist;
- H₂SO₄ vapour;
- SO₃ slippage.

Acid spray is generally formed by mechanical splashing or by spray nozzles and are >3 micron. The mist (or fog) is generally <3 micron and is produced by gas cooling which results in gas phase condensation. Mists can also be formed by gas phase reaction which results in the smallest particle sizes.

The process gas leaving the final absorption tower will be close to equilibrium with the incoming sulphuric acid. Hence, the partial pressure of H₂SO₄ in the feed acid to the final tower would be the absolute minimum acid emission possible from an absorption tower with perfect mist elimination and 100% SO₃ absorption. The last source of acid emissions is indeed from SO₃ slippage. In a correctly designed and operating acid tower the absorption efficiency should be 99.9% or higher.

In a final absorption tower of a sulphur burning double absorption plant the acid spray and mist load is up to 1,000 mg/m³, with an approximate distribution by weight of 30% <1 micron, 40% 1-3 micron and 30% >3 micron. Using these numbers, but with a mist load of 700 mg/m³ and a FAT absorption efficiency of 99.99% for this case study provides the results shown in Table 2.

The predictions in Table 2 show that the plant operating with a final absorption tower equipped with high efficiency Brownian diffusion candles will be pressed to meet the general US acid emission limit of 0.075 kg H₂SO₄/t H₂SO₄ (as 100% H₂SO₄). In fact the prediction is that the emissions would be 11% too high. The problem is that the outlet gas, if saturated with acid and SO₃ vapour will be very close to the limit, which leaves very little room for upsets due to mist eliminator candle or SO₃ absorption performance excursions. The reason for the high relative acid vapour load is that the plant operates at a "low" SO₂ concentration to the first pass of about 9.5 vol% SO₂.

The acid emissions can be lowered by the use of a tail gas SO₂ scrubber, since the aqueous scrubbing agent will be able to react with the acid vapour and SO₃ slippage. As the outlet gas from the final absorption tower is cooled further to 50°C and mixed with water vapour in the scrubber, the SO₃ and H₂SO₄ will readily react with water and condense. Most of this condensation will likely take place homogeneously or on already existing acid mist particles not removed in the upstream FAT. To remove this newly formed mist in the scrubber and take advantage of this phenomenon to lower the acid emissions, it is necessary to remove the mist efficiently. The TurboScrubber fluidised bed system

can achieve this without the use of costly Brownian diffusion candles.

NORAM proposes replacing the FAT BD candles with a low pressure drop mesh pad, followed by a TurboScrubber downstream. Removing the BD candles will free up about 10 inch W.C. pressure drop with about 2 inch W.C. being used in the replacement mesh pad. The net 8 inch W.C. saved can be used in the scrubber for mist removal. Removing the BD candles will result in more acid carry-over to the scrubber which will increase the chemical consumption for scrubbing. As shown in Table 2 the total acid mist carry-over with a mesh pad in the FAT is about 7.5 kg/h vs. 0.3 kg/h with BD candles. The additional 7.2 kg/h acid mist carry-over will only add about 10% to the alkaline chemicals consumption as the SO₂ flow rate of 46 kg/h corresponds to 71 kg/h of H₂SO₄.

The gas leaving the final absorption tower mesh pad will have acid mist, acid vapour and SO₃ vapour from slippage. These gas-phase species will start condensing in the scrubber. Due to the inherent high heat transfer rates of the fluidised bed it can be assumed that a large fraction of these vapours will condense homogeneously and on existing acid mist aerosols, which forms the basis for the calculations in Table 2.

The result is that about 96.3% of the acid mist entering the fluidised bed scrubber

Table 2: Comparison of estimated acid emissions

	FAT with BD candles			FAT with mesh pad			FAT with mesh pad + TurboScrubber		
	Inlet to FAT mist eliminator	Removal efficiency	Outlet of FAT BD candle	Inlet to FAT mist eliminator	Removal efficiency	Outlet of FAT mesh pad	Inlet to TurboScrubber	Removal efficiency	Outlet of TurboScrubber
Acid mist	700 mg/m ³	-	4.2 mg/m ³	700 mg/m ³	-	112 mg/m ³	138 mg/m ³	-	11.7 mg/m ³
<1 micron	30 wt-%	98%	4.2 mg/m ³	30 wt-%	60%	84 mg/m ³	75 wt-%	89%	11.4 mg/m ³
1-3 micron	40 wt-%	100%	-	40 wt-%	90%	28 mg/m ³	25 wt-%	99%	0.3 mg/m ³
>3 micron	30 wt-%	100%	-	30 wt-%	100%	-	-	100%	-
Overall removal efficiency	-	99.4%	-	-	84.0%	-	-	96.3%	-
Total acid mist	47 kg/h 1.940 kg/t	-	0.3 kg/h 0.012 kg/t	47 kg/h 1.940 kg/t	-	7.5 kg/h 0.310 kg/t	9 kg/h 0.382 kg/t	-	0.8 kg/h 0.032 kg/t
Acid vapour	1.5 kg/h 0.06 kg/t	-	-	1.5 kg/h 0.06 kg/t	-	1.5 kg/h 0.06 kg/t	-	-	-
SO ₃ slippage	0.3 kg/h 0.011 kg/t	-	-	0.3 kg/h 0.011 kg/t	-	0.3 kg/h 0.011 kg/t	-	-	-
Total acid emission	-	-	2.0 kg/h 0.083 kg/t	-	-	9.2 kg/h 0.382 kg/t	-	-	0.8 kg/h 0.032 kg/t

Note: Unit kg/t refers to kg H₂SO₄ emitted per tonne H₂SO₄ produced (as 100% H₂SO₄).

Source: NORAM

CONTENTS

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

Improved acid gas removal

COVER FEATURE 4

Enhanced sulphuric acid production

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Table 3: Advantages of the Cansolv SO₂ scrubbing system for metallurgical off-gas and acid plant tail gas applications

Metallurgical off-gas applications

- Ability to handle inlet gases with variable SO₂ concentration (load levelling)
- Ability to handle gases at low SO₂ concentration below 1,000 ppmv
- Ability to handle multiple sources of gases
- All captured SO₂ is recycled to converted to sulphuric acid

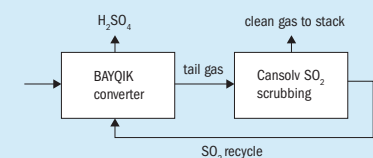
Source: Shell Cansolv

Acid plant tail gas applications

- Low pressure drop (typically less than 3 kPa)
- Ability to handle peaks in SO₂ concentration that usually occur during upsets and start-ups
- All captured SO₂ is recycled to the acid plant and converted to sulphuric acid

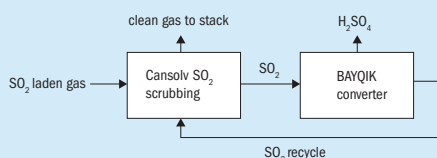
Fig 6: Cansolv + BAYQIK configurations

a) BAYQIK + Cansolv standard configuration



Source: Shell Cansolv

b) Cansolv + BAYQIK concentrator configuration



is removed. Simultaneously, the SO₂ can be scrubbed from 310 to 2 ppmv (99.4% removal) with a scrubber pressure drop of only 8 inch W.C. However, this 8 inch W.C. pressure drop of the scrubber system is compensated for by replacing the BD candles in the FAT with a mesh pad. In this way, the TurboScrubber system can be added to an existing plant without adding pressure drop to the acid plant.

In conclusion, by the use of the TurboScrubber system and compared to the original FAT, the acid emissions have been reduced from 0.083 to 0.032 kg H₂SO₄/t H₂SO₄ (as 100% H₂SO₄), well below the regulatory limit. In addition, the SO₂ removal efficiency of 99.4% provides a large margin for the SO₂ emission requirements, which for some clients may be used for SO₂ credit trading.

Cansolv SO₂ and BAYQIK technologies

Sulphuric acid production presents many challenges for smelter operators including variable concentration of SO₂ in the off gases, fugitive emissions from multiple sources with weak SO₂ concentrations, off gases with high concentrations of SO₂ that must be diluted with ambient air and environmental regulations that impose increasingly reduced SO₂ emissions. These last

two points are also relevant to sulphur burning operations, especially those using oxygen enrichment.

Bayer Technology Services (BTS) has developed the BAYQIK® process for the catalytic oxidation of SO₂ that can be easily integrated into an existing plant. The BAYQIK converter enables sulphuric acid production from constant or fluctuating gas streams with up to 50% SO₂. The resulting acid plant has a smaller footprint, lower catalyst demand and a higher capacity for steam production when compared to single absorption (SA) and double absorption (DA) sulphuric acid plants.

Since 2009, an industrial scale plant has been operating in a metallurgical application treating a process gas with fluctuating SO₂ concentrations peaking at up to 23 vol-%. The next industrial scale plant is scheduled to start operation in 2016. Several other plants are under design.

The ability to cope with gases of almost any technically relevant SO₂-concentration and its flexibility in terms of varying gas conditions make the process ideal for applications in challenging environments such as metallurgical plants.

Shell's Cansolv SO₂ Scrubbing system enables sulphuric acid production from lean gas streams by concentrating SO₂ into a pure gas stream, with the added value of reducing emissions to levels

lower than double absorption plants with a smaller pressure drop.

Aside from its ability to meet stringent SO₂ emissions targets (as low as 10 ppmv in some locations), the Cansolv SO₂ Scrubbing system offers several specific benefits in metallurgical and acid plant applications that are summarised in Table 3.

The combination of the BAYQIK and Cansolv technologies generates synergies that amplify the added value of each individual technology.

The Cansolv unit can be located downstream of the BAYQIK unit in a traditional tail gas treatment configuration (Fig. 6a). However, in many applications the value of the combination is brought by a configuration where the Cansolv unit is located upstream of the BAYQIK unit and serves as an SO₂ concentrator while still treating the BAYQIK tail gas as shown in Fig. 6b.

The combination of the two technologies brings the following added value:

- The BAYQIK system can be designed with the optimum SO₂ conversion efficiency (from a capex perspective), as the Cansolv unit can easily and cost-effectively manage the emissions resulting from limited conversion of higher SO₂ concentrations.
- By acting as an SO₂ concentrator, the Cansolv unit helps maximise the SO₂ concentration at the BAYQIK inlet, thus

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CONTENTS

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

Improved acid gas removal

COVER FEATURE 4

Enhanced sulphuric acid production

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minimising the size and cost of the sulphuric acid production unit.

- The steam produced as a result of the net energy production of the BAYQIK unit can be used in the regeneration step of the Cansolv unit.

The added value of the Cansolv + BAYQIK combination is illustrated in the following case studies.

Case study 1: BAYQIK + Cansolv compared to conventional acid plant line-ups

This case study compares different process line-up options for a 530 t/d sulphuric acid plant processing 11 vol-% SO₂ gas. The gas flow is 45,000 Nm³/h, and it is assumed that in all cases the gas is clean and dry. Table 4 shows a comparison of the BAYQIK + Cansolv line-up versus other traditional line-ups. The line-ups compared are:

- a single absorption (SA) acid plant;
- a single absorption plant followed by a hydrogen peroxide (H₂O₂) tail gas scrubber;
- a double absorption (DA) acid plant;
- a BAYQIK acid plant followed by a Cansolv SO₂ scrubbing system. The BAYQIK system is designed to convert 95% of the incoming SO₂.

The resulting SO₂ emissions and net acid production from the Cansolv + BAYQIK line-up is comparable to that of a single absorption unit coupled with a hydrogen peroxide tail gas scrubber, while the pressure drop is slightly lower for the Cansolv + BAYQIK due to a higher number of heat exchangers in the gas path in the latter case. However, the former line-up consumes far less in terms of reagents with increasing SO₂ concentration in the inlet gas. Moreover, the Cansolv + BAYQIK unit does generate the most additional steam. Overall comparison in terms of net present cost depends on availability and cost of utilities which vary greatly from project to project.

Sensitivity to SO₂ concentration

For applications where the SO₂ concentration is higher than 12 vol-% (for example copper flash furnace off-gas), the BAYQIK + Cansolv line-up has an even bigger advantage in terms of total cost, as it will be designed to operate at the higher concentration without dilution, while a traditional acid plant will require dilution of the inlet gas. The BAYQIK unit alone can result in a 40% capex reduction when compared to conventional acid plant technology.

Table 4: Comparison of sulphuric acid production technologies with and without tail gas scrubbing

	SA	SA + H ₂ O ₂	DA	BAYQIK + Cansolv
SO ₂ emissions, ppmv	< 3,000-6,000	< 50	< 150 - 400	< 50
Net steam production kg/t acid (t/h)	530 (12)	530 (12)	445 (10)	830 (15)
Pressure drop, mbar	290	330	350	240
Main blower energy consumption, kW	510	580	615	420
H ₂ O ₂ consumption (50 wt-%), t/d	-	13	-	-
Catalyst filling, m ³	115	11	100	40

Source: Shell Cansolv

The BAYQIK + Cansolv line-up would also show a better environmental performance in terms of emissions intensity (kg of SO₂ per tonne of sulphuric acid produced), which is the metric commonly used to set acid plant emissions targets. Since it is operating at higher concentration, it is processing less gas for the same acid production, and a given SO₂ concentration in the tail gas will result in lower emission intensity.

For example, a BAYQIK + Cansolv unit operating at 20 vol-% SO₂ will generate a tail gas flow rate about 40% lower than a traditional acid plant operating at 12 vol-%; so its emission intensity will be about 40% lower for the same SO₂ concentration in the gas emitted to the stack. Also the energy efficiency of the plant increases due to the reduced amount of energy (in terms of warm gas) that is released to the atmosphere.

When the concentration of SO₂ falls below 5-6% traditional acid plants cannot operate in a sustained way without an external energy input. With a BAYQIK unit in an in-line configuration followed by a Cansolv unit, auto-thermal operation is possible even when the inlet SO₂ concentration falls to less than 3 vol-%.

This is due to the fact that the cooling loop operating parameters can be adjusted in a way that none of the reaction heat is extracted and the temperature in the cooling loop is raised with less SO₂ entering the BAYQIK converter. The dissipated energy of the cooling air blower also supports the temperature level in the converter.

The traditional Cansolv + BAYQIK line-up thus provides greater flexibility with respect to turndown ratio when compared to conventional sulphuric acid technology since both units can operate at extremely low SO₂ concentrations without the use of any fuel gas to maintain the converter temperature.

However it is then interesting to send the weak gas directly to the Cansolv unit, which will serve as a concentrator for the BAYQIK unit.

Case study 2: Cansolv as a concentrator for low SO₂ concentration

This case study focuses on a line-up where a Cansolv + BAYQIK line-up will be used to treat off-gas from a metallurgical operation and produce sulphuric acid with the captured SO₂. The sulphuric acid will be used on site.

The site produces a gas flow of approximately 200,000 Nm³/h. The concentration varies from less than 1% to 4%.

The gas will first go through pre-cleaning steps including dust removal, quench tower, cooling tower, and WESP. It will then be treated in a Cansolv unit to meet emissions of less than 200 ppmv.

The Cansolv unit will deliver pure SO₂ to the acid plant (up to an equivalent production of 780 t/d sulphuric acid at maximum SO₂ concentration in the off-gas). The SO₂ stream from the Cansolv unit is sent to a drying tower to remove the water which is present in the SO₂ stream.

At the inlet of the BAYQIK unit the SO₂ will be diluted with atmospheric air to a concentration of around 20 vol-%, to achieve a sufficient O₂:SO₂ ratio of 0.8.

The BAYQIK unit is designed for a capacity of 800 t/d with a conversion efficiency of 90%, which in this case has been determined as the overall economic optimum. The resulting SO₂ concentration in the BAYQIK tail gas will thus be about 2.2 vol-%; this tail gas will be recycled at the inlet of the quench tower of the pre-cleaning system.

The SO₂ concentration in the gas being treated by the BAYQIK plant is 20 vol-% which is approximately 65% greater than the maximum acceptable SO₂ concentration in conventional adiabatic converters.

Thus the gas flow rate and the size of all equipment in the BAYQIK plant is significantly reduced.

The Cansolv system has been designed with an overhead mechanical vapour recompression (MVR) system that reduces the steam requirements of the reboilers up to 50%, by recovering energy from the compressed overheads in a primary reboiler. To best fit with the plant energy infrastructure, the MVR compressor will be driven by a steam turbine, which will operate with sufficient backpressure for the exhaust steam to be used in the secondary reboiler to supply the rest of the required energy.

In conclusion, the variable inlet SO₂ concentration of the process results in periods of extremely low SO₂ concentration (less than 1 vol-%) that would be impossible for conventional double absorption technology to process. Furthermore, the integration of the Cansolv-BAYQIK line-up results in lower capital investment for the sulphuric acid plant, enhanced process flexibility as well as less dependence on natural gas due to the net energy production from the BAYQIK unit. Finally, the mechanical vapour recompression system further reduces the Cansolv energy requirement for the regeneration step.

Case study 3: Integrated multi-source management

Sites often face more complex SO₂ management challenges, involving several gas sources of different concentrations, some of them highly variable or cyclical. This is the case of a metallurgical application, for which a study for the implementation of an integrated solution has been performed. The aim of this case was to reduce the emissions of an existing single absorption acid plant processing gas from a flash furnace with an inlet SO₂ concentration between 5 and 9%, and producing up to 150 t/d of acid.

In addition, a solution is needed to treat gases from a converter and a furnace. The furnace gas has a low SO₂ concentration, while the converter gas fluctuates during an 8 hour converter cycle. Characteristics of the different gases are given in Table 5. The converter only generates off gas containing SO₂ intermittently inside an 8-hour cycle.

Averaged over a converter cycle, the combined SO₂ content of the gases can reach up to 5 t/h. This represents an additional sulphuric acid production of 180 t/d, which could exceed the capacity of the existing sulphuric acid plant.

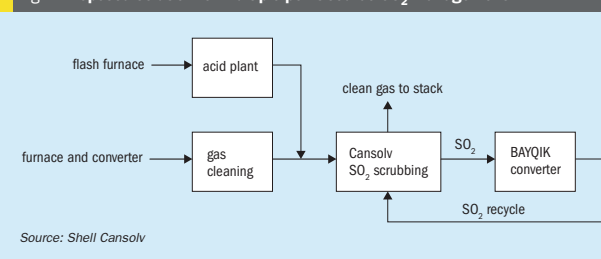
Table 5: Gas flow rate and SO₂ concentration from multiple point sources

	Acid plant		Slag furnace		Converter	
			Slag blow*		Blister blow*	
Flow rate, Nm ³ /h up to	15,000		10,000		40,000	
SO ₂ vol-% (dry)	≤ 1		1		up to 5	
					up to 6	

* Slag and blister blowing steps occurring intermittently during converter cycle.

Source: Shell Cansolv

Fig 7: Proposed solution for multiple point source SO₂ management



Source: Shell Cansolv

The use of a Cansolv-BAYQIK system addresses the different challenges of this application (multiple gas sources, variable SO₂ concentrations, and need for additional conversion capacity) in a simple and cost effective way.

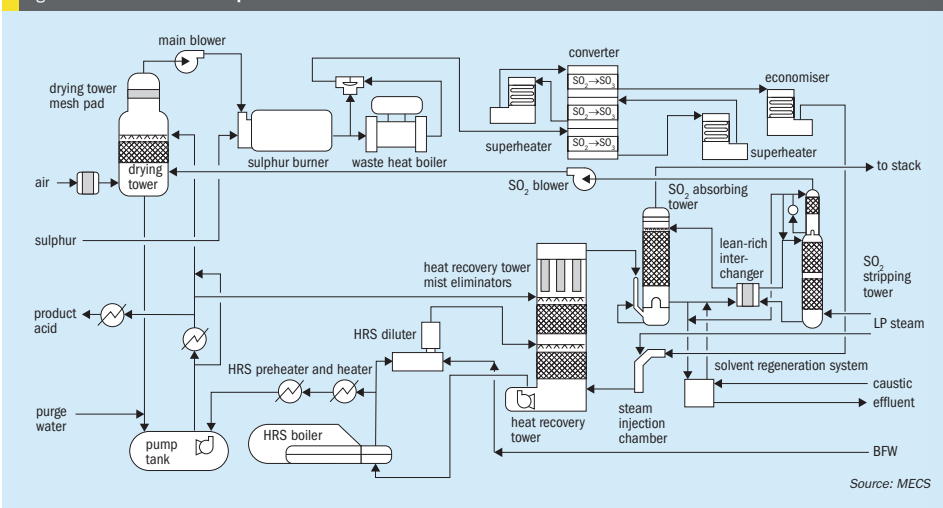
The proposed solution for multiple point source SO₂ management is shown in Fig. 7.

The gases from the converter and slag furnace go through a standard metallurgical gas cleaning system before both entering the Cansolv absorber, while the sulphuric acid plant tail gas is fed directly to the same absorber.

The Cansolv unit captures SO₂ from all gas streams and delivers it as a pure SO₂ stream to the BAYQIK unit for conversion to sulphuric acid. The BAYQIK unit tail gas is sent back to the Cansolv absorber. The BAYQIK unit could be sized to process the resulting SO₂ during peak conditions and still run at a low turndown ratio (less than 1,000 ppmv SO₂). However, this would result in a larger BAYQIK unit comparable in size to conventional acid plant technology. Placing a Cansolv unit upstream of the BAYQIK enables the management of peak conditions with a smaller BAYQIK unit since the SO₂ is first concentrated by the Cansolv system and then sent to the BAYQIK unit at a steady flow rate.

To this intent the Cansolv system is designed in a load levelling configuration with two buffer tanks in order to regulate the lean absorbent flow to the absorber while

Fig 8: The MECS® Maxene™ process



MECS's integrated solution

Incremental innovation in the sulphuric acid plant is an on-going process, such as, better catalyst for reduced emissions and improved heat recovery technologies to attain small improvements in energy efficiency. But, these small, incremental improvements will not meet the market's overall demand to keep up with the world's most critical needs in the future: food, energy and environmental protection. The MECS® Maxene™ process does what incremental improvements cannot by combining two innovative technologies (HRS™ and

SolvR®) into a single technology to provide an integrated solution that addresses the future cost, energy recovery, and emission needs of sulphuric acid plants.

The Maxene™ sulphuric acid plant process simplifies the conventional sulphuric acid plant flow scheme while recovering more energy than conventional HRS™ technology and achieving best-in-class stack emissions. Maxene™ combines MECS' proprietary SolvR® regenerative SO₂ absorption system with the HRS™ technology to shift to a single absorption plant arrangement (Fig. 8), eliminating equipment and reducing cost.

The Maxene™ process also moves past the historic approach of maximising intermediate pressure (e.g. 10 bar) steam in favour of producing more high pressure steam. By optimising energy recovery, the Maxene™ process reduces cooling water consumption and can even eliminate the need for cooling water consumption in the acid system. Finally, MECS's proprietary SO₂ regeneration solvent provides a significant improvement over existing technologies, especially in terms of steam consumption, materials of construction, and effluent treatment. Table 6 summarises the key data for Maxene™ compared to conventional sulphuric acid plant technology.

Table 6: Key data for Maxene™ compared to conventional sulphuric acid plant technology

Export / import	Double absorption	Double absorption with HRS™	Maxene™
HP steam (40 barg, 400°C), kg/h	133,700	132,800	146,500
t/t	1.3	1.3	1.5
IP steam (10 barg, saturated), kg/h	13,000	29,000	19,000
t/t	0.13	0.29	0.20
SO ₂ emissions, ppmv	140	140	30
Cooling water, m ³ /h	3,200	850	1,200
Power use, kWh	5,500	5,500	3,200
Relative TIC	100	1.10	100
Chemicals, \$	0	0	250,000

Source: MECS

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Sulphur recovery from waste metallurgical gases

In recent years the urgency to solve the problem of sulphur utilisation from waste metallurgical gases has increased dramatically. **O.G. Eremin** and **A.V. Tarasov** discuss laboratory investigations that have been conducted by the State Research Institute of Non-Ferrous Metals (Gintsvetmet) in Moscow, Russia, to study the process of catalytic reduction of SO₂ using producer gas (carbon monoxide). When using an alumina catalyst at a temperature of 400°C and a space velocity of 250 h⁻¹ the SO₂ conversion to sulphur was 96-98%. Further conversion to achieve air quality standards for sulphur emissions to the atmosphere can be achieved by adding a single Claus stage.

The production of non-ferrous metals by pyrometallurgical methods generates significant amounts of SO₂ gases with different concentrations, depending on the stage of metal production. Off-gases with higher SO₂ concentrations (more than 4.5%) are typically used for sulphuric acid manufacture. However, in some cases, when there is no demand for sulphuric acid, it is more appropriate to recover sulphur in the form of elemental sulphur. Compared to sulphuric acid, sulphur is easier to transport and can be stored in the open.

For these reasons, in the 1980s, Gintsvetmet developed a novel sulphur recovery technology for the Russian mining and metallurgical company, Norilsk Nickel, which is located in a remote polar region of Russia. The sulphur recovery technology is based on the reduction of sulphur dioxide by natural gas in a hollow reactor at high temperature (1,200-1,300°C) and subsequent processing of the reduced gas by the Claus method^{1,2}.

This process has been used on an industrial scale in two units at Norilsk Nickel's copper plant since 1987. The units have a design capacity of 85,000 t/a sulphur. The long term operation of the plant has confirmed that it can produce elemental sulphur of high quality suitable for sulphuric acid manufacture. The technology

is characterised by its simplicity and high reliability of the equipment.

During times when natural gas prices are high and sulphur prices relatively low the high temperature methane technology becomes uneconomical and has only been continued for environmental reasons. i.e. the need to protect the environment and prevent emissions of SO₂ into the atmosphere.

To improve the methane technology Gintsvetmet recommends reducing the temperature of the catalytic reduction of SO₂ to 700-900°C. In so doing, the consumption of natural gas is decreased by 25-30% compared with the high temperature method and the sulphur recovery efficiency will be significantly higher and can correspond to the common values of typical Claus units used for the treatment of hydrogen sulphide. For cases where the process still remains uneconomical, Gintsvetmet has been looking at cheaper and more effective reducing agents as an alternative to natural gas, in particular, pulverised coal.

Using coal instead of natural gas for the reduction of SO₂ has a number of technological advantages and is particularly attractive for countries with little natural gas but abundant coal resources such as in China and Mongolia. Since the coal process does not form water it achieves a higher yield of sulphur in the Claus stage.

This technology was developed by the Finnish company Outokumpu Oy and was tested at full commercial scale at Norilsk from 1982-1985. The long term operation of the industrial plant confirmed that coal is a very good reducing agent for the production of sulphur.

As Norilsk already uses the methane method for the production of sulphur, Gintsvetmet is of the opinion that it would be more simple and efficient to use carbon monoxide produced from coal for the reduction SO₂^{3,5}.

Lab results for SO₂ reduction using producer gas

Laboratory studies to investigate the catalytic reduction of sulphur dioxide using producer gas were conducted by blowing air through one litre of crushed coke (10-20 mm size pieces) at a temperature of 1,000-1,100°C. The use of coke instead of coal produces a substantially pure carbon monoxide in the absence of any secondary components. This allowed the main technological process parameters to be determined for the recovery of sulphur using carbon monoxide.

The apparatus included a generator, the catalytic reactor and a sulphur condenser. The generator consisted of a ceramic tube with an inner diameter of 70 mm and length

CONTENTS

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

Improved acid gas removal

COVER FEATURE 4

Enhanced sulphuric acid production

SULPHUR
ISSUE 364
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Fig 1: Formulae used for calculations

$$\eta_{SO_2} = \left(1 - \frac{C_{SO_2}^K}{C_{SO_2}^H} \cdot K_N \right) \cdot 100\%$$

Where $C_{SO_2}^H$ is the concentration of SO₂ in the initial gas and $C_{SO_2}^K$ is the sum of the concentrations of SO₂, H₂S and COS in the recovered gas.

$$K_N = \frac{C_N^H}{C_N^K}$$

is the reduction coefficient considering change of gas volumes.

C_N^H and C_N^K are the concentrations of nitrogen in the initial and reduced gas.

$$K_V = \frac{C_{CO} + C_H}{C_{SO_2}^H}$$

For each test the reduction coefficient was calculated using the formula:

Where C_{CO} and C_H are the concentrations of CO and H₂ in the initial gas.

of 650 mm. The reactor was also made of a ceramic tube with a tube length of 650 mm and a tube inner diameter of 127 mm. Electric heaters were used to heat the generator and reactor and to maintain the set temperature. The catalytic reactor was loaded with a granulated alumina catalyst, which was heated to a temperature of 350 to 800°C. The experiments were conducted as follows. After heating the coke layer in the upper part of the generator a calculated amount of air heated to 1,000°C was applied. At this temperature, oxygen and carbon react to form carbon monoxide according to the following reaction:

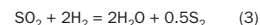


The resulting carbon monoxide was then mixed with a calculated amount of sulphur dioxide and air and then the resulting gas mixture was fed into the reactor with

pre-heated catalyst. As the gas mixture is passed through the catalyst, sulphur dioxide is reduced by the carbon monoxide and elemental sulphur is formed according to the following reaction:



It should be noted that producer gas contains small quantities of hydrogen, which reduces sulphur dioxide to sulphur according to the following reaction:



The amount of air and sulphur dioxide supplied to the generator and the reactor was estimated based on the desired concentration and flow rate of the recovery process. During the research, the temperature in the catalytic reactor was varied in the range of 300-800°C. The concentration of SO₂ in the source gas was 10-30%. The

experiments were conducted at the following reactor space velocities: 125, 250, 500 and 1000 h⁻¹. The composition of the source gas and reduced gas was determined by chromatography.

The initial and reduced gas were analysed to determine the conversion of SO₂ to sulphur η_{SO_2} %. η_{SO_2} % was calculated as shown in Fig. 1.

The first series of experiments for the catalytic reduction of sulphur dioxide with carbon monoxide was conducted to determine the effect of temperature on the conversion of sulphur dioxide to sulphur. The coefficient of reduction in accordance with reactions 2 and 3 were maintained constant at about 2 by changing the flow rate of sulphur dioxide. The results of the research conducted at a space velocity of 250 h⁻¹ and in the temperature range 290-500°C is presented in Table 1. Space velocity was defined as the amount of the gas mixture, which is passed through one litre of catalyst. The data obtained shows that the reduced gas contains H₂S and COS, as well as residual amounts of SO₂ and CO.

The data in Table 1 shows that carbon monoxide is a better reducing agent than methane for the reduction of sulphur dioxide to elemental sulphur.

By analysing the results it is possible to conclude that a catalyst layer in the temperature range of 400-500°C and a space velocity of 250 h⁻¹ gives a 95-96% conversion to sulphur. If the temperature is decreased to 370°C, the degree of conversion decreases to 89.9% with a corresponding increase in the concentration of SO₂, H₂S, COS in the reduced gas. The effect of temperature on conversion at various space velocities is presented in Fig.2. It follows that in the range of temperatures

Fig 2: Effect of temperature on conversion of SO₂ to sulphur

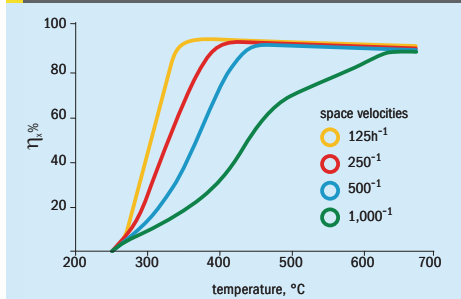
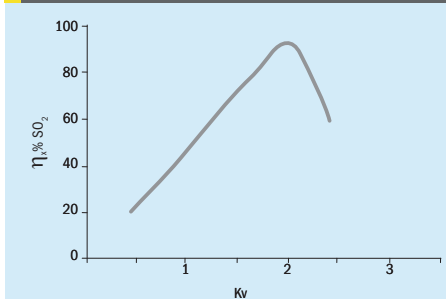


Fig 3: Effect of reduction coefficient (Kv) on conversion of SO₂ to sulphur



250-450°C process of reduction SO₂ by the producer gas proceeds in diffusive-kinetic area as degree of conversion depends both on temperature of carrying out process and volume velocity. The obtained results allow to conclude that the maximum yield of sulphur is achieved at a volume rate 125-250 h⁻¹ and as mentioned above at temperatures of 370-420°C. As a result of processing the obtained experimental data were determined the optimal parameters of the process of recovering sulphur dioxide gas generator, in which is provided the maximum yield of sulphur. The obtained dependences show that at a volume velocity of 500hour-1and a temperature of 480°C is provided a maximum degree of conversion of 96.5%. At lower volume velocity to 250 h⁻¹ and a temperature of 400°C the degree of conversion increases to 98%. Apparently these parameters are optimal for the reduction of sulphur dioxide using producer gas and can be recommended for use in the design of the semi- industrial plant.

A second series of experiments was conducted to determine the effect of the coefficient of reduction Kv on the degree of conversion of sulphur dioxide to sulphur. The experiments were carried out at a catalyst temperature of 400°C to 800°C and a space velocity of 125-1000 h⁻¹. The SO₂ concentration in initial gas mixture was varied in the range of 13-34%. The coefficient of reduction Kv varied by adjusting flow of sulphur dioxide supplied to the reactor in mixture with the generator gas. The results of these experiments were performed at 600°C and a volume velocity of 125 h⁻¹ and are presented in Table 2 and Fig. 3.

From the data obtained it was concluded that the maximum yield of sulphur is attained when the coefficient of reduction is equal to 2. This result corresponds with previously known data obtained during the development and exploitation of methane method for producing sulphur. It should be noted that increasing the coefficient of reduction Kv by more than 2 leads

to the increased formation of sulphurous compounds such as H₂S and COS and a corresponding decrease in the yield of elemental sulphur.

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Table 1: Results of SO₂ reduction to sulphur (12-14%) at a space velocity of 250 h⁻¹ and a temperature interval of 290-500°C

No	T, °C	Composition of initial gas,%							Composition reduced gas,%							ηx,%
		H ₂	O ₂	N ₂	CO	CO ₂	SO ₂	H ₂	O ₂	N ₂	CO	CO ₂	H ₂ S	COS	SO ₂	
1	500	0.52	1.12	57.28	27.88	0.40	12.80	-	1.16	69.24	-	28.98	0.44	0.17	0.01	95.99
2	450	0.42	1.17	56.56	27.05	0.57	14.23	0.16	1.17	69.28	0.05	29.22	0.06	0.03	0.03	99.31
3	420	0.40	1.18	57.00	26.89	0.37	14.16	0.10	1.03	70.70	0.30	27.09	0.20	0.55	0.03	95.56
4	400	0.38	1.20	57.45	26.72	0.17	14.08	0.10	1.12	71.03	0.68	26.50	0.03	0.40	0.14	96.73
5	370	0.19	1.12	59.69	26.76	0.15	12.09	0.13	1.09	71.51	1.30	24.51	-	1.31	0.15	89.92
6	360	0.39	0.93	58.05	26.20	1.6	12.82	-	0.94	67.79	0.33	28.19	0.04	2.70	-	81.70
7	350	0.21	1.00	59.40	26.15	0.49	12.75	0.13	1.06	65.97	3.50	26.71	-	0.78	1.85	81.42
8	330	0.21	1.00	59.40	26.15	0.49	12.75	0.24	1.02	68.15	9.03	17.31	-	0.53	3.72	70.94
9	290	0.24	0.88	59.10	25.54	0.84	13.40	0.15	0.90	61.83	22.57	3.78	-	0.28	10.49	23.17

Table 2: Results of SO₂ reduction to sulphur at a space velocity of 125 h⁻¹ and temp. of 600°C for different initial gas compositions

No	Composition of initial gas,%						Composition reduced gas,%						ηx,%	K _v		
	H ₂	O ₂	N ₂	CO	CO ₂	SO ₂	H ₂	O ₂	N ₂	CO	CO ₂	H ₂ S			COS	SO ₂
1	0.50	0.84	41.33	23.03	0.38	33.91	-	0.89	46.52	-	24.83	0.09	-	27.69	27.22	0.69
2	0.47	1.20	47.04	25.63	0.56	25.10	-	1.18	57.00	-	29.76	0.11	-	11.94	60.38	1.04
3	0.36	0.93	53.06	27.49	0.32	17.85	-	1.00	61.66	-	32.70	0.28	0.02	4.35	77.58	1.56
4	0.87	1.48	53.52	26.90	0.32	16.91	-	1.32	65.90	-	30.24	0.39	0.04	2.11	87.80	1.64
5	0.36	0.83	54.04	28.61	0.26	15.90	-	1.33	64.16	-	32.40	0.43	0.12	1.56	88.82	1.82
6	0.32	1.65	56.01	27.93	0.28	13.82	-	1.49	64.52	-	32.65	0.65	0.33	0.35	91.65	2.04
7	0.38	0.90	55.32	29.44	0.33	13.64	-	0.88	63.38	0.08	31.44	2.38	1.82	0.01	73.06	2.18
8	0.38	0.91	55.60	29.59	0.33	13.19	-	1.47	63.14	0.09	30.38	1.84	3.07	-	67.22	2.27



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Sulphur recovery, energy efficiency and carbon management

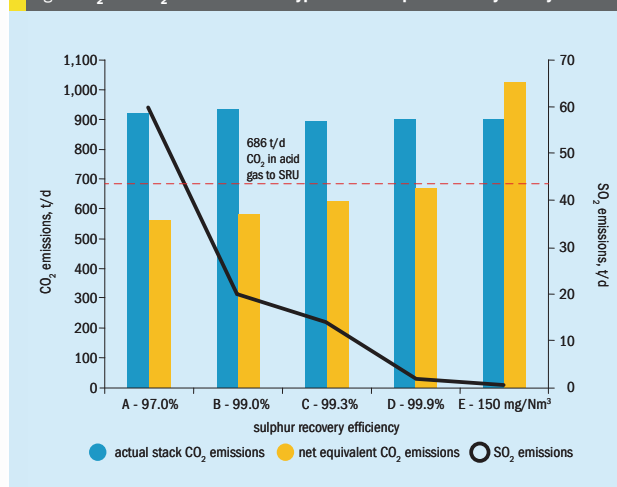
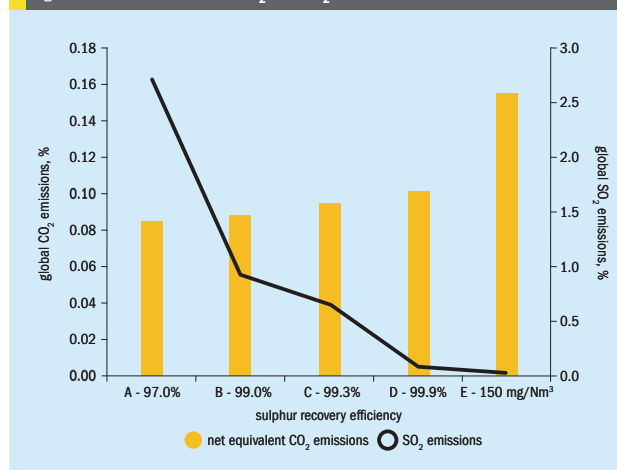
A recent study by UniverSUL Consulting explores the relationship between SO₂ and CO₂ emissions in sulphur recovery facilities and investigates whether there is a point at which further increases in sulphur recovery efficiency results in diminishing returns, in terms of energy consumption and associated CO₂ footprint. Real world data is presented using the sulphur facilities in Abu Dhabi as a specific regional example.

Since the late 1980s, growing concerns that acid precipitation was damaging forests and aquatic ecosystems resulted in governments worldwide adopting increasingly strict clean air regulations on sulphur emissions from processing facilities. Flue gas from coal-fired power plants was, and still is, the primary source of SO₂ emissions contributing to these concerns. Nevertheless, sulphur recovery facilities in refineries and gas plants also came under scrutiny to substantially reduce their SO₂ impact on the environment. As a result, increased sulphur recovery emissions regulations have been imposed over the past three decades, via a stepwise approach.

Initial reductions in allowable SO₂ emissions from sulphur recovery facilities made a fairly significant impact on the global environmental landscape, as sulphur recovery efficiencies (SRE) increased from that which is achievable with a standard Claus sulphur plant (95-97% SRE), to 99% and

above, which is achievable using various tail gas treating technologies. The current industry recovery efficiency benchmark is around 99.9%. However, this figure is on the rise with a greater number of facilities designing for higher sulphur removal rates, as evidenced by the World Bank Standard (WBS), which currently sits at 150 mg/Nm³ (equivalent to approximately 99.98% recovery efficiency).

While striving for increasingly lower sulphur emissions may be beneficial, it does not come free of cost. As sulphur recovery efficiency increases, the energy required to remove each additional kilogram of sulphur escalates. As energy consumption increases so too do CO₂ emissions, an undesirable outcome in a time when carbon emissions reduction is among the top objectives for corporate environmental management programs. Not only is the environmental impact of greenhouse gas familiar and visible to the public, it also carries a high potential for future regulation.

Fig 1: SO₂ and CO₂ emissions from hypothetical sulphur recovery facilityFig 2: Global contribution to SO₂ and CO₂ emissions from SRUs worldwide

In a recent study, UniverSUL Consulting explored the relationship between SO₂ and CO₂ emissions in sulphur recovery facilities and investigated whether there is a point at which further increases in sulphur recovery efficiency results in diminishing returns, in terms of energy consumption and associated CO₂ footprint. The study explored the following questions:

- How does increasing SRE positively impact global SO₂ emissions?

- What is the corresponding negative impact on global CO₂ emissions?

Typical sulphur recovery facility

To consider the impact that sulphur recovery facilities have on overall SO₂ and CO₂ emissions requires examination of the composition and flow of stack gas from a typical sulphur recovery unit. Thus, a hypothetical 1,000 t/d sulphur recovery train

was considered, over a range of sulphur recovery efficiencies.

Considering that most refineries produce rich acid gas (H₂S > 85 mol-%) and most gas plants produce relatively lean acid gas (40-50% H₂S), an average global concentration of 60 mol-% was assumed.

To compare relative SO₂ and CO₂ emissions, simulations using SulSim^{®7} and ProTreat[®] were generated for a range of sulphur recovery efficiency requirements.

Impact of SRUs on global SO₂ and CO₂ emissions

Fig. 1 illustrates the SO₂ and CO₂ emissions from the hypothetical SRU for each of the cases studied. When considering the carbon footprint of a sulphur recovery facility, it is important to look beyond the obvious CO₂ content of the stack gas. It is also essential to take into account the equivalent CO₂ emissions associated with all of the major energy producers and consumers in the facility. The sum of actual CO₂ emissions and equivalent CO₂, based on the energy balance, is termed "net equivalent CO₂" in this article. As shown in Fig. 1, SO₂ emissions decrease substantially from Case A to D, while net CO₂ emissions only increase by about 20%. However, in increasing sulphur recovery from Case D to the WBS specification, there is only a very minor decrease in SO₂ emissions with a significant corresponding CO₂ increase of more than 50%. The dramatic increase in CO₂ emissions for only a marginal decrease in SO₂ emissions can be more clearly illustrated with the following correlations: When increasing SRE from 99.0% to 99.9%:

- Every 1 tonne of SO₂ reduction results in 5 tonnes of CO₂ emissions, or
- Every 1 tonne of S reduction results in 10 tonnes of CO₂ emissions

When increasing SRE from 99.9% to 150 mg/Nm³ (99.98%):

- Every 1 tonne of SO₂ reduction results in 240 tonnes of CO₂ emissions, or
- Every 1 tonne of S reduction results in 480 tonnes of CO₂ emissions

The impact of increasing SRE to ultra-high values, in excess of 99.9%, clearly has a significant impact on energy consumption and CO₂ emissions, which begs the question as to whether the minor SO₂ reduction benefit is justified. This question can be addressed by looking at how the figures for

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

Improved acid gas removal

COVER FEATURE 4

Enhanced sulphuric acid production

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ISSUE 364

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a single sulphur recovery train translate to the global SO₂ and CO₂ landscape.

Scaling up from the 1,000 t/d hypothetical sulphur plant to a global production of 54.3 million t/a gives SO₂ and equivalent CO₂ emissions (as % of world totals) as shown in Fig. 2.

Assuming a world average sulphur recovery efficiency in the range of 99.5-99.9%, Fig. 2 illustrates that sulphur recovery facilities contribute somewhere around 0.3% of global SO₂ emissions and less than 0.1% of global CO₂ emissions. Increasing recovery efficiency from 99.3% to 99.9% with an amine based TGTU (Case C to Case D) only very slightly increases CO₂ emissions but substantially reduces SO₂ emissions. For this reason, if amine-based tail gas treating is employed, it is certainly worthwhile to design for at least 99.9% SRE, from both an energy efficiency and CO₂ footprint perspective. Similar to what was observed in Fig. 1, increasing SRE to greater than 99.9% achieves little benefit with respect to SO₂ emissions but has a significant detrimental impact on CO₂ emissions.

A specific regional example

To validate some of the regional figures with real world data, an investigation of the sulphur facilities in Abu Dhabi was undertaken. Middle Eastern sulphur production at the end of 2015 was 14.3 million t/a (~24% of world total), making it the largest sulphur producing region in the world. The UAE accounts for roughly 50% of Middle Eastern capacity making it one of the most important countries of focus. Current installed sulphur production capacity exceeds 24,000 t/d and normal production is around 80% of this figure. However, for the purpose of simplifying the analysis, it is assumed that all sulphur recovery facilities are operating at 100% of design rates.

The first sulphur plants in UAE were built in the early 1990s and the most recent plants were started up in 2015. Similar to the rest of the world, sulphur recovery emissions specifications in the UAE have tightened over the years. Yet older plants remain grandfathered and are permitted to continue operating with higher emissions, in accordance with regulations that were applicable at the time of construction. Thus, a wide range of sulphur plant technologies and recovery efficiencies exist throughout the country.

A survey of the major SRUs in the UAE reveals the current operating conditions summarised in Table 1, assuming operation at 100% of design rates. The average sulphur recovery efficiency of these facilities is 99.5%, which is greater than Case C but less than Case D. At this recovery efficiency, total SO₂ emissions are approximately 235 t/d (85,800 t/a), which is less than 0.1% of total global SO₂ emissions. Actual CO₂ emissions are approximately 31,000 t/d, which is also less than 0.1% of total global CO₂ emissions. Equivalent CO₂ emissions are approximately 20% lower than actual due to the fact that at 99.5% SRE, a sulphur recovery facility is a net energy exporter.

Fig. 3 illustrates predicted SO₂ and equivalent CO₂ emissions from UAE sulphur plants if overall average SRE were increased by applying Case D or E technologies. Similar to the trend observed previously, as SO₂ emissions decrease, equivalent CO₂ emissions increase. At recovery efficiencies greater than about

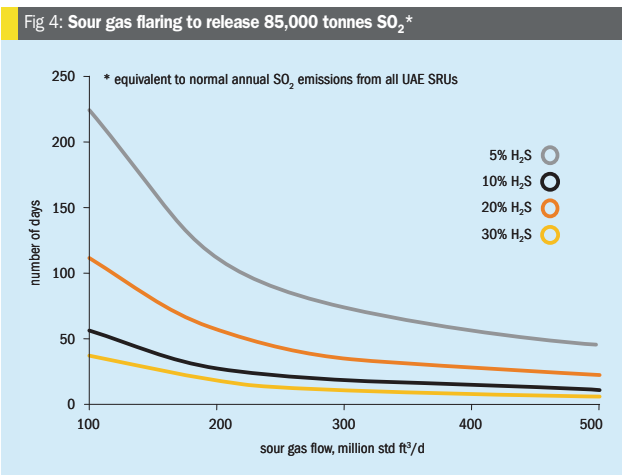
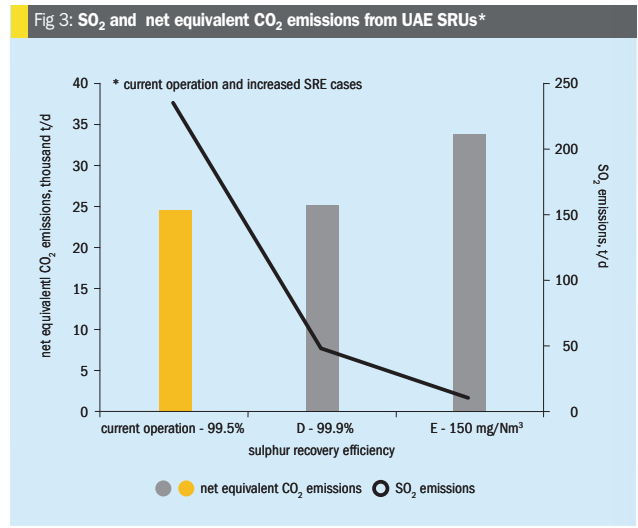
99.9%, equivalent CO₂ emissions increase at a disproportional rate to the corresponding reduction in SO₂ emissions.

A high level analysis reveals that a capital investment of nearly \$1 billion would be required to increase the average SRE of UAE sulphur recovery facilities to roughly 99.9%, which basically involves installation of amine-based tail gas treating on all existing SRUs which are not currently equipped with such facilities. These modifications would decrease SO₂ emissions to about 20% of the current figure, or approximately 50 t/d (18,250 t/a). While this is a substantial reduction, the incremental energy requirements would still require consideration. As a result of the additional energy consumption, for every tonne of SO₂ reduction, approximately 5 tonnes of equivalent CO₂ would be produced.

When contemplating total SO₂ emissions from sour gas treating facilities, SRE achieved in the sulphur plant is not the only area of consideration. Another important aspect is the significant quantity of SO₂

Table 1: SO₂ and CO₂ emissions from UAE sulphur plants

	Total sulphur processing capacity	Average SRE	Emissions at 100% design rate		
			SO ₂	Actual CO ₂	Equivalent CO ₂
Current operating condition	24,065 t/d	99.5%	235 t/d	30,630 t/d	24,550 t/d



that can be released during start-up, shutdown and upset conditions, when sour gas must be flared. Current sour gas processing capacity in the UAE exceeds 7 billion std ft³/d. Fig. 4 illustrates the number of days of sour gas flaring equivalent, at various rates and H₂S concentrations, to match the current equivalent annual SO₂ emissions from UAE sulphur plants (85,500 t/a).

Fig. 4 shows that for a highly sour gas field, it would only take a few days of flaring, at relatively low rate, to release as much SO₂ as is emitted from all UAE SRUs in an entire year. While sour gas flaring isn't something that is planned, it can occur during initial start-up and in facilities that achieve low reliability and/or availability. Thus, in some cases, it may be more beneficial to direct efforts toward improving availability/reliability of existing assets rather than upgrading existing SRUs to achieve higher sulphur recovery efficiency during normal operation. Development and implementation of well management programs that facilitate sour gas diversion or containment, in the case of planned or unplanned outages, would also be highly beneficial for minimising total SO₂ emissions from the facility as a whole.

Possibilities for reducing CO₂ footprint of SRUs

As demonstrated above, sulphur recovery facilities do not contribute a great deal to global CO₂ emissions. However, in large facilities with stringent SO₂ emissions specifications, it is still advantageous to

minimise the quantity of CO₂ emitted for every tonne of SO₂ removed. This is because, in addition to designing and/or operating an environmentally responsible facility, a reduction in carbon footprint also provides an improvement in energy efficiency, which translates to reduced operating cost. Potential measures that might be considered to achieve these objectives include:

- incinerator operating temperature optimisation;
- employment of an incinerator waste heat boiler;
- sulphur pit vent recycle to SRU reaction furnace;
- selective solvents for tail gas treating;
- acid gas injection;
- CO₂ capture for enhanced oil recovery (EOR) or improved acid gas quality.

Summary and conclusions

Revisiting the questions posed at the outset of the study concluded that although SO₂ emissions from sulphur recovery facilities contribute less than 5% of the global total, a significant positive impact is observed as SRE approaches 99.9%. Above 99.9%, energy consumption increases drastically for very little reduction in SO₂ emissions. Even when proprietary, highly-selective solvents are employed, there is a significant energy increase required to achieve the WBS emission standard (99.98% SRE). Therefore, it is questionable whether there is good reason to consider SO₂ emissions specifications in excess of 99.9%.

“The study revealed that sulphur recovery facilities have an essentially inconsequential impact on global CO₂ emissions... but it would be irresponsible to unnecessarily increase the carbon footprint of the facility by not enhancing the design...”

Possible exceptions may be the case of very large sulphur recovery facilities that would have substantial SO₂ point source emission rates (tonne per day basis) and/or facilities that are located in environmentally sensitive regions. Additionally, there may be opportunities to relax SRE requirements below 99.9% for smaller SRUs (<50 t/d), which have only a minor point-source emission impact, even at lower SRE. This philosophy has already been adopted in some parts of the world.

The study revealed that sulphur recovery facilities have an essentially inconsequential impact on global CO₂ emissions. However, it would be irresponsible to unnecessarily increase the carbon footprint of the facility by not enhancing the design via the use of selective solvents, optimised incinerator design/operation or perhaps even considering acid gas injection rather than sulphur recovery. Implementing such measures would also improve energy efficiency of the facility, thereby improving overall project economics.

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CONTENTS

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

Improved acid gas removal

COVER FEATURE 4

Enhanced sulphuric acid production

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MAY-JUNE 2016

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Next issue: July/August 2016

- Extending the life of sulphur recovery units** With many sulphur recovery facilities now into their fourth or fifth decade of operation, operators of these older plants have learned to live with design shortcomings. Newer designs are implementing changes that address long term operating problems.
- Acid cooling in sulphuric acid plants** Acid coolers in sulphuric acid applications fall into two categories – anodic protection stainless steel coolers and alloy coolers. The pros and cons of each type should be fully understood before an informed decision can be made when selecting the most suitable acid cooler. This article compares different acid cooler types and reports on latest acid cooler designs.
- Re-melting sulphur** The addition of a sulphur re-melter to a site can provide flexibility in inventory management as well as a way of reclaiming contaminated sulphur.
- Copper and sulphuric acid** The copper industry has a major influence on sulphuric acid markets on both the demand side, for leaching, and on the supply side, from smelting. With the copper industry in the doldrums, Sulphur looks at the impact on sulphuric acid markets.
- Do oil prices affect sulphur production?** While the precipitous drop in oil prices in 2014-15 has led to many project postponements and delays on upgrading and processing plants in the heavy oil/oil sands sector, will there actually be a significant effect on overall sulphur production?

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CONTENTS

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

Improved acid gas removal

COVER FEATURE 4

Enhanced sulphuric acid production

SULPHUR
ISSUE 364
MAY-JUNE 2016

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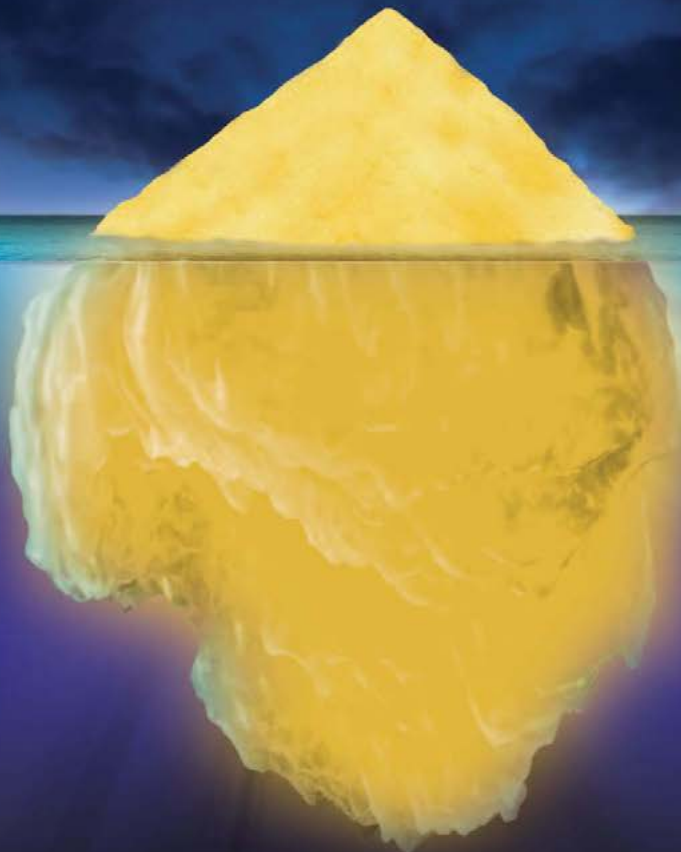
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1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29



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CONTENTS

What's in issue 364

COVER FEATURE 1

Industrial demand for sulphuric acid

COVER FEATURE 2

ASRL review

COVER FEATURE 3

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