

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31

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Number 358

May | June 2015

SULPHUR

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Oil sands update

Sulphur forming project listing

Sulphuric acid materials

Sulphur degassing

■ CONTENTS

What's in issue 358

■ COVER FEATURE 1

Oil sands update

■ COVER FEATURE 2

Sulphur forming
project listing

■ COVER FEATURE 3

Sulphuric acid
materials

■ COVER FEATURE 4

Sulphur degassing

SULPHUR
ISSUE 358
MAY-JUNE 2015

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18 Acid plant maintenance

Approaches to reducing downtime.



22 Sulphur safety

Improvement in degassing techniques.

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SULPHUR

www.sulphurmagazine.com

NUMBER 358

MAY | JUNE 2015

CONTENTS

10 Sulphur from oil sands

The run of high oil prices over the past decade has encouraged the development of unconventional oil resources in many parts of the world, including the heavy oil sands of Canada and Venezuela. But how will production from these high sulphur sources fare now that oil prices have come back to earth?

12 Sulphur forming project listing

Sulphur's annual survey of new forming facilities.

13 TSI comes to Spain

The Sulphur Institute's annual Sulphur World Symposium moved to the historic city of Barcelona this April.

14 Sulphuric acid reclamation

A significant volume of sulphuric acid used in industrial processes generates contaminated acid streams which face increasingly stringent regulations on disposal.

15 SOGAT

A report on the Sour Oil and Gas Advanced Technologies conference, held in Abu Dhabi.

16 HIGHSULF PLUS makes its debut

T. K. Khanmamedov of TTK Company and J. M. Lawrence of Lexington Group International, Inc. compare and discuss some FEED data for an AGE unit based on the HIGHSULF PLUS process and present simulation and design numbers for a commercial unit in the FSU.

18 Maintaining your sulphuric acid plant

M. Salehi and A. Hopp of Steuler-KCH GmbH discuss the importance of engineering, top-quality products and careful installation by highly qualified expert personnel for planning production capacities over the long term.

20 Polymers in sulphuric acid service

In this article we report on fluorinated thermoplastic linings for sulphuric acid services, a unique and innovative approach to the design and inspection of FRP for fabricators and end users as well as recent and ongoing research into plastic materials for sulphuric acid services.

22 Making sulphur safer

Recent improvements to sulphur degassing processes are reported, including the first in-situ sulphur degassing technology for refineries and gas plants.

REGULARS

3 Editorial

4 Price Trends

5 Market Outlook

6 Sulphur Industry News

7 Sulphuric Acid News

9 People/Calendar

CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

Sulphur degassing

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Acid to burn?



Last issue we discussed the coming surplus of sulphur from large-scale sour gas projects and refinery expansions, and the ways in which it might change the sulphur market, but how about sulphuric acid? The global consumption of sulphuric acid is over 260 million tonnes, but the actual merchant market for it remains relatively tiny – perhaps only 7% of this – due to the difficulties inherent in storing and handling such a corrosive material. However, there is some crossover, as noted by Brendan Daly of CRU in his recent presentation to The Sulphur Institute's annual symposium in Barcelona; as every tonne of sulphur produces three tonnes of sulphuric acid when burnt, in theory when the price of sulphur is more than three times higher than that of acid, it makes sense for those operating sulphur-burning acid plants to stop burning sulphur and buy acid on the open market instead. This is a vast oversimplification of course; there are costs to shutting down and starting up plants, transport and logistics considerations, the ability to handle the volumes of acid, health and safety regulations, the money gained from selling power generated by sulphur burning and all of the rest. Nevertheless, prolonged periods of price disconnect in key purchasing markets, as we saw last year, can lead to just such a switch from sulphur into sulphuric acid.

Oversupply is coming to sulphur markets, in theory making sulphur cheaper and hence the preferred option for acid production; there is literally sulphur to burn. But what about sulphuric acid markets? Unlike sulphur, where virtually all production is involuntary, the sulphuric acid market is predominantly based on voluntary production, via sulphur or, in China, pyrites. However, about one third of acid production is also involuntary, from metal smelting, and, being involuntary, it is smelter acid production which dominates the traded acid market. Smelters must sell the acid in order to keep producing the metal, and the price of the acid is fairly irrelevant to them; during a few months in 2008, after the global financial crash, some acid netbacks headed into negative territory – smelters were literally paying people to take the acid off their hands.

Integer Research has recently noted that Chinese smelter acid production has increased by 6

million t/a over the past four years alone, and total acid production in China has increased by 16 million t/a. Demand for acid for phosphates has of course also increased, but Chinese phosphate capacity is now significantly overbuilt and likely to pause. China has traditionally been an importer of sulphuric acid – up to 1 million t/a, mainly from smelters in Japan and Korea – but just as China has turned from a net importer to an exporter of many key commodities, might it be about to become an exporter of sulphuric acid?

Another major importer of acid has traditionally been Chile, to feed copper leaching production. But Chilean acid imports fell by 15% in 2014, to just under 2.5 million tonnes, and are projected to fall further to 1.6 million t/a by 2019 as leaching projects decline and domestic acid production increases. Balancing this, the major growth area in the region was expected to be Peru, where the Tia Maria copper project was due to be consuming 900,000 t/a of acid by 2019. However, while Southern Copper has rowed back from frustrated announcements that it was shelving the project, the latest news from the local area remains grim, with riots against the proposed development and dead protestors. Brazil was forecast to need more acid for single superphosphate production, but here key projects have been shelved or pushed back and the country may depend on plentiful international MAP/DAP production instead. With traditional importers like China and Chile importing less, and forecast new demand in Brazil and possibly Peru failing to materialise, are we about to see oversupply in acid markets as well?

Richard Hands, Editor



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...TO B...



TO SEA.



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CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4


Sulphur degassing

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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

Stability to prevail?

The global sulphur market stabilised somewhat in April, although ample supply led to a downward correction in pricing. Canadian supply is viewed as healthy, the Volga Don waterway reopened in Russia and Middle East spot cargoes all put pressure on the market. Demand has been limited aside from offtake of regular shipments. Buyers in key markets, particularly in China, took to the sidelines, with stock levels stabilising around 1 million tonnes. In the current market, stock levels in China are no longer expected to have significant impact on short term spot pricing as previously seen.

Chinese end users are expected to enter the market in May to replenish requirements for processed phosphates production. The flat rate fertilizer export tax for 2015 is expected to lead to a more stable sulphur market. Prices in the spot market eroded down to \$140/t c.fr in April, although a broad range was seen of \$20/t, up at \$160/t c.fr on the high end.

A period of subdued demand in India has led to a slowdown in purchasing due to plant turnarounds throughout late March and April affecting consumption. IFFCO's complex at Paradip ran a three-week shut-down in April. The company has said that spot demand is not expected before May, with their requirements covered by a contract cargo due to arrive in April. FACT also entered a planned turnaround in March for an estimated 30-35 days.

There are expectations that buyers will return to the market in early May, potentially boosting trade for the weeks ahead. FACT issued a purchase tender for 15,000-25,000 tonnes (+/-10%) of sulphur for May arrival at Cochin. The tender closed on 20 April but was subsequently re-issued to close on 28 April, with offers to remain valid until 5 May. It is understood the lowest offer for the original tender was \$161/t c.fr Cochin, which FACT deemed too high.

In Brazil, Vale was reported to have agreed its Q2 contracts at \$165/t cfr while a settlement in Europe has been noted from a major producer at a rollover from Q1. Contract prices were expected to

remain stable or decrease from Q1 levels following the weaker sentiment in the market through January-March.

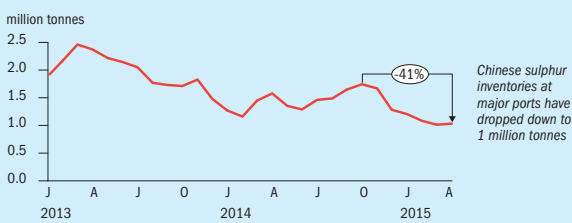
Phosphates demand has been weak in April, with US Gulf DAP prices falling on the back of adverse weather conditions across the Americas. However, as this improves into May, and as China moves its focus to the export market this is expected to pick up significantly and sulphur trade is likely to stabilise.

Price decreases in Middle East monthly price postings characterised the market in April. Lower prices for the month were confirmed by ADNOC and Tasweer at \$140/t f.o.b. and \$145/t f.o.b., respectively. Aramco Trading's price for shipments in

May were meanwhile confirmed at \$140/t f.o.b. Jubail, down \$25/t from April. Some sources suggested the price was not low enough.

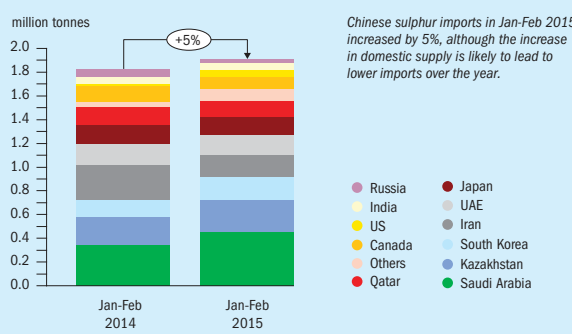
The supply situation in Canada has been stable through the first few months of the year, with oilsands producer Syncrude's operations heard running smoothly. However, 2014 saw a 1% dip in sulphur produced from Canadian oilsands year-on-year. This trend is not expected to continue, as the drop in production is attributed to the disruptions to Syncrude's operations during maintenances. The outlook for oilsands developments does remain in question due to the recent oil price slump, although this is likely to impact on long term investment rather than short term production. Gas based sulphur production continues to decline, due to the depletion of gas as well as challenging economics; further drops are expected for 2015.

Fig 1: Chinese sulphur inventories



Source: ICIS, Integer

Fig 2: Chinese sulphur imports



Source: Integer, GTIS



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CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

Sulphur degassing

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Sulphur exports from Vancouver rose to 185,717 tonnes in February 2015 from 172,705 tonnes in January – but were down 16% year-on-year, with a decline in exports noted to Chile, Mexico and China. China, one of the leading markets for Canadian sulphur in 2014, received no shipments January or February 2015. At the same time, exports to New Caledonia emerged at 78,631 tonnes. The drop in exports to China from Canada is expected to continue in the outlook, due to the increased diversification of Canadian supply to end user markets, as well as the increase of Middle East and FSU sulphur to China.

The Middle East supply outlook remains the main talking point in the solid sulphur market. Sulphur is heard being produced at the Shah gas project in the UAE, albeit the question mark remains over exact quantities and any technical issues with logistics. The second half of the year could see incremental sulphur exports out of the port of Ruwais, although the significant expansion in Morocco is likely to absorb some, if not all of the additional production from the project. This is likely to be dependent upon the rate at which exports grow. A greater impact may be from 2016 in terms of pricing however, as increased production from projects in Saudi Arabia also come to fruition.

In the US, Mosaic's 1 million tonne remelter project is on schedule to come online by the end of the year, with a solid cargo arriving during the summer months for part of the testing process for the project. The North American sulphur trade

flows are likely to see shifts from 2016, particularly as increased production from new projects in the FSU and Middle East regions add to global sulphur trade.

SULPHURIC ACID

Pockets of tightness

Despite the dip in sulphur pricing, the sulphuric acid market has remained stable. NW Europe export spot prices have firmed on the back of trade to Latin America, up by \$5/t to \$35-40/t f.o.b. The price increase has come as smelter inventories remain tight in some areas. The pricing outlook is stable due to the variety of turnarounds expected in the latter part of 2015 in North America and Asia. The price fluctuations in the sulphur market in recent months have been more closely linked to short term supply fundamentals than demand. Should there be any shifts in downstream industrial or fertilizer markets acid prices could also be impacted.

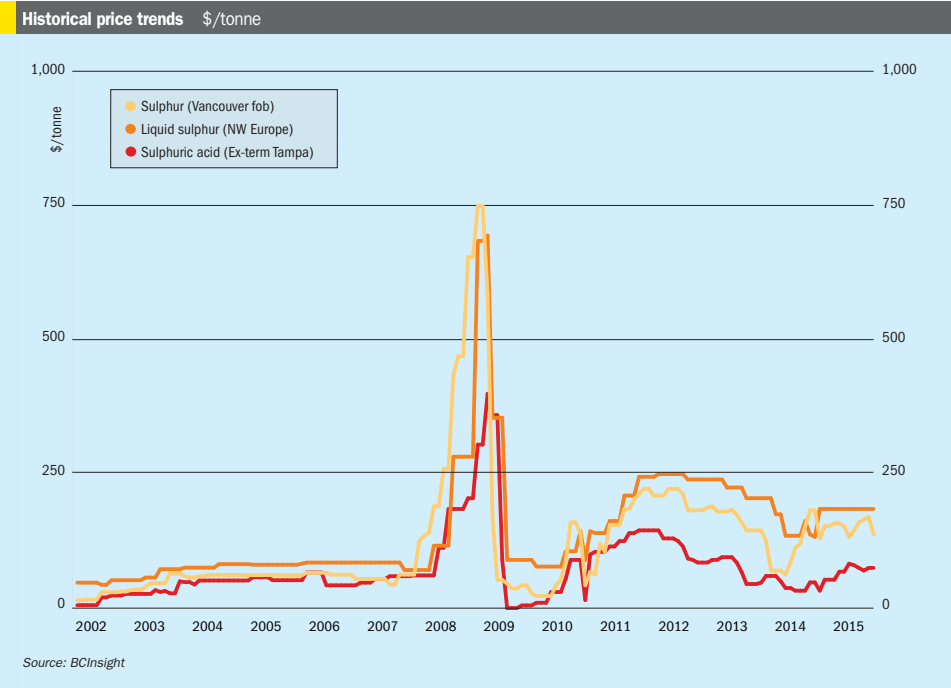
Flooding in Chile led to speculation of acid demand being stimulated and a flux of potential imports. However, metals leaching operations and end users have coped through swapping and inventory management. As a result, spot prices are unchanged in the \$80-90/t cfr range, with expectations for this range through the coming months. A trend seen in the Chile market in recent months is the drop in sulphuric acid imports. This was reflected in the 34% drop in imports in January 2015

compared to a year earlier. Chile imported 59% of its sulphuric acid from Peru in January 2015, and by 25% from South Korea. Looking ahead, Integer expects this trend to continue, posing a question over displaced trade from key supply sources.

In Brazil, spot acid prices firmed following a series of deals, up to \$95/t c.f.r. Yara and Mosaic were in the market to cover its usual requirements. Further business is expected to emerge in May, which will test the price. Due to the tight supply situation, stable pricing is anticipated, although buyers are heard resisting prices above \$90/t cfr. Availability and any trader positions will likely determine the price outlook for upcoming enquiries.

In Japan, spot prices for smelter acid export cargoes firmed to around \$20-25/t FOB, based on healthy demand and tight smelter acid availability. The expectation for the remainder of Q2 is for prices to remain in a similar range, due to the stable demand fundamentals in the short term outlook. For the month of February, sulphuric acid exports from Japan increased by 33% to 237,938 tonnes, compared with 179,234 tonnes a year earlier. For 2014, exports were 2.8m tonnes. We forecast similar export availability in 2015, based on the supply/demand balance. Producer Sumitomo is scheduling a 25-day maintenance at its Toyo Smelter and Refinery in late October, according to its 2015 production schedule. Meanwhile, Mitsubishi was heard completing its month-long turnaround in March.

Market outlook



SULPHUR

- Improved trade in China, as stocks should stabilise around the 1 million tonne level, likely to represent the 'new normal' in purchasing behaviour. The entrance of speculators in end April could have short term impact on pricing, and help reach a floor in price erosion.
- Middle East producers are expected to drop prices further for May, due to pressure from end user markets China and India.
- The official commissioning of Shah is expected in Q3 2015, with increased exports from the UAE likely to move to key market Morocco. Logistics will be a key consideration in bringing the sulphur to the market, with a major focus on the dedicated Ethiad sulphur railway.
- The start up of Mosaic's sulphur remelter later in the year could lead to increased availability from Vancouver and the US Gulf, putting downward pressure on pricing, at a time when supply is due to increase in other key producing regions.

- The NW European molten sulphur market is likely to remain tight to balanced through 2015, in light of declining sulphur production from gas and oil.
- Outlook:** A floor in pricing is likely to be reached during Q2, with China and India expected to enter the market and help stabilise the market further. Chinese speculators could also lead the market to a short term floor. The longer term issue is the increase of supply from key sour gas projects, but pricing in 2015 is unlikely to be affected by this. Trade routes in the latter part of the year and 2016 will see significant shifts, partly due to the new projects adding supply but also as the remelter in Florida comes online.

SULPHURIC ACID

- Stable outlook for demand in the Philippines, with spot purchases expected for nickel leach projects for shipment in second half 2015.
- While supply in NW Europe remains comfortable prices are likely to be supported, with positive netbacks anticipated throughout 2015.

- Producers LS Nikko and Korea Zinc are expected to have limited availability in Q2 owing to turnarounds and contract commitments, supporting the price outlook.
- Moroccan acid demand to remain positive through the year, during the period of transition during the next phase of its process phosphates expansion plans
- Toros sulphuric acid plant delayed start up to end of Q3, leading to continued imports of acid to Turkey to meet demand. Increased imports are expected through 2015 due to the ramp up of Meta Nikel's leaching operations.
- Production from China expected to gain, as new smelter capacity adds to domestic production. Exports could increase in the long term outlook, although this will be dependent on achievable netbacks and logistical infrastructure.
- Outlook:** The year ahead is positive for sulphuric acid, as smelter turnarounds in NW Europe, North America and Asia will continue to support pricing. However, any sustained downturn in the sulphur and downstream markets, could provide a ceiling to any further price increases.

Price indications

Table 1: Recent sulphur prices, major markets

Cash equivalent	December	January	February	March	April
Sulphur, bulk (\$/t)					
Vancouver f.o.b. spot	140-150	155-165	160-170	165-175	135-140
Adnoc monthly contract	150	170	180	140	140
China c.f.r spot	150-180	175-190	170-190	150-160	130-160
Liquid sulphur (\$/t)					
Tampa f.o.b. contract	129	147	147	145	132
NW Europe c.f.r	170-200	170-200	170-200	170-200	170-200
Sulphuric acid (\$/t)					
US Gulf spot	75-85	70-80	60-80	70-80	70-80

Source: CRU

SAUDI ARABIA

Wasit gas plant begins partial commissioning

Saudi Aramco has started testing parts of its Wasit gas plant, according to industry sources, although it is not likely to be fully operational before the end of 2015. Construction of the main gas plant is virtually complete and it is expected to start one train imminently using gas from the master gas gathering system (MGGs) – Saudi Arabia’s collection system for associated gas from oil wells. The aim is to bring the plant up for testing to 20-25% of capacity and begin sulphur recovery unit operations. Wasit, north of Jubail on the east coast of Saudi Arabia, is one of the largest non-associated gas processing plants

built by Aramco. It has capacity to process up to 3 billion scf/d of non-associated gas from the offshore fields at Hasbah and Arabiyah, and will raise gas feed to the MGGs to 20 billion scf/d. Wasit and the Karan gas plant, in operation since 2012, are expected to boost Saudi gas production by up to 40%. Together with Fadhili and another planned plant in Abqaiq they form part of a strategic plan called “Peak Seasonal Production” (PSP), which aims to replace power generation from oil and allow more oil to be exported. The plan is already saving 9 million barrels/year of oil according to Aramco (25,000 bbl/d).

UNITED ARAB EMIRATES

Shah to reach capacity in 2Q 2015

The massive Shah sour gas project is ramping up more rapidly than anticipated, and could achieve capacity during 2Q 2015, according to Saif Ahmed Al Ghafli, chief executive of operator Al Hosn Gas. Speaking at the Sour Oil and Gas Advanced Technologies (SOGAT) conference – see full report elsewhere in this issue – he said: “currently we are in the process of ramping up production to full capacity, which we expect to achieve during the second quarter this year, very soon.”

Production at Shah, 40% owned by US Occidental Petroleum, began in January, and previously estimates were for full processing of 1 billion scf/d of gas by the end of 2015. Shah gas is 23% H₂S, and the sulphur recovery section will produce 10,000 t/d of sulphur at capacity, which is formed on-site and then taken by rail for export at Ruwais on the coast.

Legal challenge to IMO sulphur regulations?

Bunkerworld reports that the International Maritime Organisation’s (IMO) global cap on sulphur in bunker fuel may face a legal challenge. Speaking at the *Fujcon 2015* bunkering and fuel oil conference in Fujairah, Ara Barsamian of the US-based Refinery Automation Institute (RAI), indicated that he may mount a legal challenge to the value of that cap. IMO policy on a global sulphur limit for bunker fuel is for a 0.50% cap to come in 2020 or 2025, subject to the outcome of a review to be concluded by 2018. However, RAI is looking to increase that to 1.0% which Barsamian believes is a much more achievable

target. He explained that the technology used to make 1.00% sulphur capped bunker fuels is already in place, with blend stocks available to manufacture the fuel. However, moving to 0.50% sulphur would mean only half of the available blendstocks would be usable as compared to the case for 1.00%, he argued, costing an “enormous” amount of money. Barsamian said that the case will be taken to the International Court of Justice if IMO is “reluctant” to accept his proposal.

KAZAKHSTAN

Kashagan start-up in 2017, according to Shell.

Production at the Kashagan offshore oil field is expected to re-start in 2017, according to Royal Dutch Shell’s 2014 annual report. The report puts the start-up date, which the Kazakhstan authorities had said would be late 2016, back into the following year. The report, released in March 2015, reads: “After the start of production from the Kashagan field in September 2013, operations had to be stopped in October 2013 due to gas leaks from the sour gas pipeline. Following investigations, it has been decided that both the oil and the gas pipeline will be replaced. Replacement activities are ongoing, with production expected to restart in 2017.”

Saipem is currently replacing two 95km corroded sour gas pipelines at Kashagan at an additional cost of \$1.8 billion on top of the estimated \$40 billion already spent on development.

TURKEY

Major refinery upgrade programme

Turkey is in the process of a major expansion of its refinery capacity to meet rapidly

increasing demand for refined fuels which are currently met mainly by imports. Diesel demand is estimated to rise to 18 million t/a by 2020, up from 14 million t/a in 2010 and an estimated 15.8 million t/a this year. Tüpra, which operates four refineries in the country, is planning to ramp up production to 27.5 million tonnes this year, representing 95% of installed capacity, with a \$2.7 billion upgrade to the residual unit at Izmit, which is expected to start production at the end of 1Q 2015, allowing the refinery to process heavier and higher sulphur content crudes, and allow Tüpra to double diesel output to 11 million t/a and increasing jet fuel and gasoline output by 30%, allowing for substitution of imports.

There is also a new refinery, STAR – the first to be completed in Turkey since 1972 – being built by the State Oil Company of Azerbaijan Republic (SOCAR). This is a \$5.7 billion project near Izmir on the Aegean processing crude supplied by Azerbaijan, with a capacity of 10 million t/a, of which 6 million t/a will be low sulphur diesel and another 1.6 million t/a naphtha for petrochemicals use. STAR is expected to begin operations in late 2017.

FINLAND

Neste takes largest turnaround at Porvoo

Neste Oil’s Porvoo refinery will be down for eight weeks from April 2015 in what the company says is the largest maintenance turnaround in the refinery’s history, costing €100 million and involving 4,500 employees. The turnaround will start with unit shutdowns after Easter and will last into June. Neste Oil says it will sell products from storage during the shutdown, and

the refinery’s oil terminal and road transportation of products will operate normally during the turnaround. As well as normal housekeeping operations like statutory pressure vessel inspections and maintenance, investment projects related to the development of the refinery will also be carried out, such as the installation of new furnaces in the crude oil distilling unit and the replacement of automation in several areas. In addition, a number of connections will be prepared for upcoming investment projects. The turnaround is estimated to involve close to a million man-hours of work and will employ some 3,500 people from outside contractors on site.

EGYPT

Midor refinery expansion

The Middle East Oil Refinery (Midor) is being expanded to increase its capacity from its existing 100,000 bbl/d to 160,000 bbl/d. Annual gasoline production will rise to 1.3 million t/a, according to the company. Midor recently signed an agreement with UOP to supply licenses and engineering design for the refinery

upgrade, with a total investment cost of \$1.4 billion. With the project’s completion, the production capacity of the facility will increase to reach 245,000 t/a of butane, 3.2 million t/a of diesel fuel meeting European specifications, 570,000 t/a of petroleum coke and 135,000 t/a of sulphur, according to the CEO of Midor, Mohamed Abdel-Aziz. Midor, sited at El Amriya near Alexandria, is 78% owned by the Egyptian Oil Company (EGPC) and 10% each by Enppi and Petrojet.

FRANCE

Total to close La Mede, add desulphurisation at Donges

Total’s loss-making La Mede refinery looks to be another casualty of overcapacity and overseas competition in the European refining sector. Total says that it will stop will cease crude refining at the 160,000 b/d refinery by the end of 2016 and convert it instead into a 500,000 t/a biofuels facility. However, Total says that it will continue to operate the 222,000 bbl/d Donges refinery, and as part of its strategic refinery plan will invest €400 million (\$416

million) in the facility in order to “capture profitable new markets with low-sulphur fuels that meet the evolutions of EU specifications”. As part of this investment it will construct a 2.6 million t/a vacuum gasoil desulphurisation facility and develop hydrogen production at Donges. Total also said that its 105,000 bbl/d Feyzin, 240,000 bbl/d Gonfreville and 93,000 bbl/d Grandpuits refineries have “demonstrated their ability to withstand the deteriorating economic environment in 2013 and 2014 and generate ongoing income streams”, and will remain open.

La Mede will instead produce 55,000 t/a of biodiesel from waste oils and renewable feeds, as well as propane and naphtha, similar to the 156,000 bbl/d Dunkirk refinery, which is earmarked to become a 200,000 t/a second-generation biofuels joint venture, BioTfuel in 2016-17. The company aims to begin producing biofuels from organic waste from 2017, although commercial-scale production is unlikely before 2020.

Total says that it has set itself a target of cutting its refinery capacity by 20% by 2017. ■



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CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

Sulphur degassing

SULPHUR
ISSUE 358
MAY-JUNE 2015

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PERU

Southern Copper “abandons” Tia Maria copper project

Peru’s Southern Copper Corp. (SCC) said in late March that it would cancel the \$1.4 billion Tia Maria copper mine project in southern Peru due to ongoing protests and lack of government support, although more recent reports suggest that this was more of a threat than an actual cancellation. The project has been stalled since 2011, and has been the focus for protest by local farmers which turned violent in April, leaving one dead. Protesters have blocked highways in opposition to the proposed mine, saying it could hurt water supplies among other things. SCC has reworked its project several times to gain approval,

and the Peruvian government approved the environmental impact assessment for the project in August 2014. The company had said it would produce 120,000 t/a of copper cathodes over an estimated 20-year lifespan, and had hopes of having the project up and running by 2017. The government has now said that it might ask for “additional changes” to the project, it had hoped would increase copper production to help fuel economic growth, but the government has also given higher profile backing to the project in recent weeks, apparently spurred by the threat of cancellation.

Focus studying Bayovar expansion

Canada’s Focus Ventures Ltd. says that it has begun its Phase 2 drilling program at the Bayovar 12 phosphate project in northern Peru. Approximately 40 holes will be drilled in the eastern part of the original drill grid where the horizontal phosphate beds are closest to surface, in order to increase the confidence of the existing inferred and indicated resources to the “measured” category. Results of preliminary bench scale metallurgical test work by Jacobs Engineering in Florida were positive, according to Focus, and showed that the phosphate beds can be simply processed to concentrate grade via washing and flotation with no milling or grinding. Low levels of impurities make Bayovar 12 concentrates suitable for use in producing phosphoric acid and high analysis fertilizers such as DAP and MAP. Bayovar 12 has indicated resources of over 100 million tonnes of rock at 12.37-12.44% P₂O₅.

Vale currently runs the main Bayovar phosphate mine, a joint venture with Mosaic and Mitsui and one of the largest phosphate deposits in South America. The Bayovar 12 concession, which Focus bought into in 2014, is approximately 15 km east of this.

CHILE

Mines reopen after floods

Codelco, the world’s largest copper producer, says that it is gradually reopening mines in the north of the country that were closed due to heavy rains, but that its Salvador mine remains shuttered and that conditions there do not yet permit safe operation. Some 17 workers were stranded at the site, but had access to shelter, food and com-

munications, Codelco said in a statement. Torrential downpours in northern Chile flooded towns and made roads impassable, forcing a number of mining companies to suspend operations. The worst hit region was Atacama, where villagers had to be evacuated by air. Mines in Atacama include Salvador, Anglo American’s Mantoverde, and JX Nippon Mining & Metals’ Caserones. Antofagasta Minerals said that its Centinela, Michilla, and Antucoya mines were all temporarily closed due to the floods but had since reopened. Codelco said that due to the state of roads it was not transporting sulphuric acid or flammable materials to some mines, but they had sufficient supplies in stock to continue operating.

SOUTH AMERICA

Outotec to deliver solvent extraction technology

Outotec says that it has won an order for delivery of modular solvent extraction technology and services to an unnamed brown-field copper production plant in South America. The contract is worth approximately 30 million euros according to Outotec. The customer is reportedly making changes to their heap leaching operation to enhance copper recovery from secondary sulphide minerals. These changes require an upgrade in the downstream solvent extraction plant washing capacity. Outotec’s solution comprises the VSF[®]X modular solvent extraction technology, including technology license, engineering, proprietary and auxiliary equipment and advisory services for installation, commissioning and start-up. Deliveries from Outotec will take place in 2015.

“This order demonstrates how Outotec’s revolutionary modular plant concept

provides added value in projects”, said Robin Lindahl, head of Outotec’s Metals, Energy & Water business area. “Modular technology enables quick delivery and installation, safe operation as well as high performance and availability even during maintenance, all backed up by performance guarantees. The technology fulfils the strictest environmental and safety standards, minimizes the energy consumption and reduces overall project risks”.

EGYPT

Phosphate barge sinks

A barge carrying 500 tons of phosphate rock capsized and sank in the Nile after striking a bridge at Qena in Upper Egypt. The two boatmen were not injured, and the government said that it although some water stations in the region were closed temporarily as a precautionary measure, samples had revealed no leaching into the river from the rock. Egypt relies on the Nile for 55 bcm of water per year. The barge was travelling from Aswan to Cairo. Qena governorate local authorities are coordinating with the Egypt Aluminium Company to pull the sunken barge and phosphate from the water, according to local Qena Governor Major General Abdel Hamid al-Haggan.

MOROCCO

OCP takes \$1 billion debt facility to fund expansions

OCP has raised \$1 billion from international capital markets with a 10.5 year maturity at a 4.5% coupon in order to fund ongoing work on the company’s ambitious expansion programme – the company is looking to triple its fertiliser output in 10 years. OCP anticipates that the extra

production capacity will nevertheless be swallowed by rising demand, especially by rapidly growing African fertilizer markets.

FLSmith recently received a contract worth approximately €30 million from OCP to supply material handling equipment to the Jorf Lasfar port facility and mine site in Morocco. The order covers supply of equipment, supervision of erection as well as commissioning. The equipment to be supplied includes three bucket wheel reclaimers, each with a capacity of 2,000 t/h, two stackers with a capacity of 2,000 t/h, two stackers with a capacity of 1,000 t/h, and associated yard conveyors.

“Office Chérifien des Phosphates is experiencing an increase in fertilizer demand and thereby a need for capacity expansion. The Group is a well-known customer to FLSmidth and we are very happy that they have chosen to place this order with us,” said Group Executive Vice President of the Minerals Division Manfred Schaffer.

NAMIBIA

Heap leach demonstration plant at Etango uranium project

Bannerman, developing the Etango uranium project, has begun pilot scale heap leaching at the site in order to demonstrate the design and projected performance in the definitive feasibility study for the project, as well as building knowledge and enabling the company to pursue value engineering ahead of full production. Etango is 30 km southwest of Rio Tinto’s Rössing uranium mine and has similar alaskite ore to that found at Rössing, with measured and indicated uranium resources of 57,330 tU and inferred resources of 24,600 tU. With much of the resource less than 200 m deep, it is amenable to conventional open pit mining and sulphuric acid heap leaching in what Bannerman describes as “a low technical and environmental risk project”.

From the definitive feasibility study, Bannerman envisages production of around 2,700-3,500 tU per year over the first five years of production and 2,300-3,100 tU per year thereafter, over a minimum mine life of 16 years. This would place Etango within the world’s top ten uranium mines in terms of production. The heap leach demonstration plant will process ore using four 5 metre-high cribs to process individual 40 tonne ore samples as well as simulating the planned heap leach pad operation by circulating the leached solu-

tion between the cribs. A 3,000 tonne sample of ore has been taken from the Onkelo region of the deposit. Crushed and blended to represent the assumed ore feed in the final operation, it will enable up to three years of testing to be carried out.

SOUTH AFRICA

Elandsfontein awards phosphate contract

Emerging phosphate miner Elandsfontein Exploration and Mining has awarded engineering group DRA the contract for the implementation phase of the Elandsfontein phosphate project, on the west coast of South Africa. DRA, which had also completed the definitive feasibility study for the project, will be responsible for the engineering, procurement and construction management, including the processing facility and its associated infrastructure. The commissioning of the project is expected to be complete by August 2016. The process plant, designed to produce about 1.35 million t/a of phosphate concentrate, will comprise screening, classification, milling, reverse flotation, dewatering and product handling.

“The award follows more than 15 months of working closely with the Elandsfontein team on the study of the project, during which a wide range of test work and trials were carried out to develop the optimum flow sheet,” DRA CEO Paul Thomson said in a statement. DRA’s in-house mining division carried out the design and production scheduling of the open pit mining operation, which will be contracted out by Elandsfontein.

KAZAKHSTAN

Study on new smelter

Kazakhstan’s main copper miner KAZ Minerals has signed an agreement with China’s Baiyin Nonferrous Group Co., Ltd. to perform a scoping study on the construction of a copper smelter in Kazakhstan, processing copper concentrate from the Bozshakol and Aktogay mines. The scoping study is only the start of a long process, however, according to KAZ, with further technical and economic evaluation and the availability of suitable financing all still to be determined. Kazakhstan had reportedly been looking at exporting copper concentrate to China, but is now considering smelting the concentrate locally. There are already two smelters in the

country, but Balkhash is already running at capacity, and the high sulphur content of the Bozshakol concentrate makes it unsuitable for the Zhezkazgan smelter. KAZ has plans to increase copper production via expansion projects at Bozshakol, Aktogay, and Koksay. The company’s goal is to achieve 80% of ore output from large scale, low cost open pit mines producing approximately 300,000 t/a of copper concentrate by 2018.

UZBEKISTAN

Acid capacity to increase 40%

Sulphuric acid capacity in Uzbekistan will increase by 50%, from 950,000 t/a to 1.3 million t/a by 2020, according to the government. Plans are in train to increase build two new 650,000 t/a sulphuric acid plants at Ammofos-Maxam JSC and Navoi Mining and Metallurgical Combine. These will be commissioned in 2018 and 2019, respectively. Meanwhile, two ageing acid plants will be decommissioned at Ammofos-Maxam (with a current capacity of 500,000 t/a) and Navoi Mining and Metallurgical Combine (450,000 t/a). The projects will be financed via the Uzhimprom State Joint Stock Company, Uzbek Fund for Reconstruction and Development, loans from local and foreign banks, and the existing funds of Ammofos-Maxam and the Navoi Combine. The cost of the two plants has not been disclosed. Construction contracts on a “turnkey” basis will be issued through closed tenders.

Ammofos-Maxam JSC, commissioned in 1969, is the largest of the three companies producing phosphate fertilizers in Uzbekistan. The company has a design capacity to produce 338,000 t/a of ammonium phosphate, 500,000 t/a of sulphuric acid and 417,000 t/a of wet-process phosphoric. Spain’s MAXAM Corp. bought 49% of the company’s shares for \$18 million and investment commitments worth \$30 million in January 2008. The state retains the remaining 51%. Navoi Mining and Metallurgical Combine is one of the largest gold producers in Central Asia and remains fully owned by the state.

NEW ZEALAND

Chatham Rock Phosphate faces fallout from permit refusal

Chatham Rock Phosphate (CRP), which saw its share price tumble after the refusal of a license for offshore phosphate mining

CONTENTS

What’s in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

Sulphur degassing

off New Zealand, is now looking at other options, according to CEO Chris Castle. Speaking to local media, he said that; "a decision has been made for CRP to evolve from its single project focus into a more diversified company, principally involving other phosphate projects, both on and offshore. Other marine mining opportunities involving other commodities will also be evaluated by our team".

CRP applied for a Marine (environmental) Consent to Mine in July 2014 and was declined in February 2015. The company has said that it is likely to re-submit its Marine Consent application and has recently announced that it intends to raise NZ\$1.38 million by a rights issue to its existing shareholders in order to advance this project. The company has also applied for five marine phosphate prospecting licences offshore Namibia and has recently sought to accelerate the licensing process, although a moratorium is currently in place on offshore phosphate mining there.

Meanwhile, the company is facing a potential takeover by Antipodes Gold Ltd, via a deal with CRP's major shareholder Aorere Resources.

CANADA

Arianne Phosphate looks to additional finance this year

Junior mining company Arianne Phosphate says it anticipates securing strategic partners and financing this year to advance the Lac à Paul project in Quebec; based on current spending estimates for future project development, Arianne anticipates it will need additional financing before the end of this year.

The Lac à Paul project is sited 200 km north of the Saguenay-Lac-Saint-Jean region of Quebec. It has high quality igneous apatite deposit, which Arianne will use to produce a concentrate containing 39% P_2O_5 with little or no contaminants, according to the company.

In 4Q 2015 Arianne incurred a net loss of C\$1.4 million, compared to C\$1.1 million a year earlier. The company said its net loss and cash burn are consistent with other development stage mining companies.

TUNISIA

Phosphate production down again

Production of phosphate at Compagnie des phosphates de Gafsa (CPG) was

down to 604,000 tonnes in the first quarter of 2015, according to official figures from Groupe Chimique Tunisien (GCT), down from 983,000 tonnes for the first quarter of 2014, and well below the target production for the quarter of 1.56 million tonnes. Sit-ins and protests, and irregular deliveries of rock to processing plants and availability of water have all been blamed for the fall in Tunisia's troubled industry. The Ministry of Industry says that improving output back up to 500,000 tonnes per month is now its top priority for the coming quarter.

NORWAY

Major titanium dioxide project gets approval

The Norwegian government has approved plans to mine rutile titanium dioxide at Engerbø in southwest Norway in spite of opposition from environmental groups about disposal of tailings at sea. The Engerbø mine is considered one of the richest deposits of rutile in the world, with up to 150 million tonnes of rutile-bearing rock, and is expected to produce 90-100,000 t/a of rutile concentrate over its 50-year mine life. During this time, however, operator Nordic Mining is planning to dump nearly six million tonnes of tailings per year into the adjacent Førde Fjord, a spawning ground for cod and salmon in Norway. Nordic says its annual waste production will consist of 1,200 t of sulphuric acid, 1,000 tonnes of sodium, 1,000 tonnes of phosphoric acid, 360 tonnes of carbonic acid and 90 tonnes of acrylamide. Commencement of production is expected at the end of 2017 after completion of final feasibility studies.

RUSSIA

Rosneft moves to Euro V standard

Rosneft's oil refineries at Kyubyshevsky, Novokubyshevsky and Syzransky in Russia's Samara region have completed the necessary upgrades to produce Euro V specification gasoline products. The large scale upgrade projects were completed ahead of schedule. In 3Q 2014, the Kyubyshevsky refinery commissioned an isomerisation unit to produce high octane components for gasoline. As part of the modernisation programme, the facility had previously installed a benzene concentrate recovery unit, a hydrogen generation unit with a swing adsorption machine, a vis-

cosity breaking unit, a nitrogen production module, as well as overhauled its distillate hydro treatment and light hydrocracking units.

In February 2015, the Novokubyshevsky refinery commissioned two key facilities, a continuous catalytic reforming unit and a low temperature isomerisation complex as part of the modernisation programme. The Syzransky refinery has commissioned a hydrogen generation unit, a wet process sulphuric acid plant, a low temperature isomerisation complex and a benzene concentrate recovery unit.

AUSTRALIA

Study prefers nitric acid for leaching

Australian-based Direct Nickel, which is attempting to commercialise a new hydrometallurgical process for nickel extraction from low grade laterite ores, has received academic backing for its Direct Solvent Extraction (DSX) process in the form of research conducted by Mike Hutton Ashkenny of Curtin University, recently published in *Phys Org*. Hutton-Ashkenny believes that DSX will benefit Direct Nickel in terms of producing a purified nickel solution instead of a nickel-rich precipitate. "At the moment they'd sell the precipitate to a refinery, they'd just give it to someone else to deal with," he commented. "We could use a process like DSX to selectively extract the nickel and cobalt, then purify and concentrate that out." Hutton-Ashkenny suggested that the right combination of reagents – in this case pyridine carboxylate and an organic acid called Versatic TM10 can improve existing efficiencies by treating a leaching solution generated with nitric acid instead of sulphuric acid. Using nitric acid allows greater recovery of nickel from the ore. This will lower costs and lead to recycling of reagents, which will ultimately reduce negative impacts on the environment. Nitrate-rich tailings can also improve plant growth when nitrogen is added to the soil.

DSX, was first developed by the Commonwealth Scientific and Industrial Research Organisation (CSIRO), and is now being licensed by Direct Nickel in Perth. Direct Nickel is currently working with Indonesian mining partner PT Aneka Tambeng to start its first nickel ore processing plant, as well as with Regency Mine's Mambare laterite asset in Papua New Guinea. ■

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CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

Sulphur degassing

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People



Chet M. Thompson

The American Fuel & Petrochemical Manufacturers (AFPM) has announced that it has named **Chet M. Thompson** as president effective from May 4th, 2015. Thompson has previously been a partner in the Washington DC office of Crowell and Moring LLP, and will succeed Charles T. Drevna, who is retiring after eight years as AFPM's president.

"The refining and petrochemical industries are important contributors to the nation's economic outlook and while we face extraordinary regulatory challenges,

Chet Thompson brings more than 20 years of experience in the energy and environment sector to his new role as president," AFPM Chairman Greg Goff said in making the announcement. "We are confident in Chet's ability to lead AFPM as the voice and vision of the refining and petrochemical industries throughout the coming years."

Thompson has represented AFPM as external counsel for nine years at Crowell and Moring, where he is chairman of the Environment & Natural Resources Group. He will help to amplify the importance of the refining and petrochemical industries and their positive impact on US manufacturing, jobs growth, energy independence and national security.

Prior to joining Crowell and Moring in 2006, Thompson served as deputy general counsel at the Environmental Protection Agency (EPA), where he provided legal advice to the Agency's administrator, general counsel, and program offices.

The Gulf Petrochemicals and Chemicals Association (GPCA) has announced the appointment of **Rashed Saud Al Shamsi** as its new chairman. Formerly vice chairman of GPCA, Al Shamsi replaces

Mohamed Al Mady, who was recently appointed as the chairman of the General Organisation for Military Industries in Saudi Arabia. "The legacy left by Eng. Mohamed Al Mady is a superb example to follow, and I am honoured to have been selected to continue driving the influential nature of the Association to further establish its position as a predominant authority in the petrochemicals field," said Rashed Saud Al Shamsi.

As Director of Petrochemicals at the Abu Dhabi National Oil Company (Adnoc), Al Shamsi has nearly 30 years of experience in the region's downstream sector. He is currently the chairman of Fertil (Ruweis Fertilizers Industries), and Borouge Pte Ltd which represents the marketing arm of Abu Dhabi Polymers Company (Borouge).

Victaulic has appointed **Ian Lawless** as Vice President, Oil and Gas, Europe. Lawless moves from his previous role as manager of Victaulic's UK business. To working with owners, installers and engineers in the growing European oil and gas market. Lawless has eight years' experience at a senior level within Victaulic, and has worked in Europe, Canada, Australia and Asia Pacific.

Calendar 2015

MAY

18-20

SYMPHOS 2015, 3rd International Symposium on Innovation and Technology in the Phosphate Industry, MARRAKESH, Morocco.

Contact: SYMPHOS Technical Committee
Tel: +212 5 23 34 51 22

Email: symposiumoc@ocpgroup.ma
Web: www.symphos.com

25-27

83rd IFA Annual Conference, ISTANBUL, Turkey.

Contact: IFA Conference Service
Tel: +33 1 53 93 05 25
Email: conference@fertilizer.org
Web: www.fertilizer.org

JUNE

5-6

Clearwater 2015, 39th Annual International Phosphate Fertilizer and Sulphuric Acid Technical Conference, AlChE Central Florida, CLEARWATER, Florida, USA.
Email: chair@aiiche-cf.org
Web: www.aiiche-cf.org

8-11

1st Annual Middle Eastern Brimstone Sulphur Recovery Symposium, ABU DHABI, UAE.

Contact: Brimstone STS Ltd
Tel: +1 909 597 3249
Web: www.brimstone-sts.com

10-11

European Sulphuric Acid Association General Assembly, MALAGA, Spain
Contact: Patricia De Hertogh, Cefic
Tel: +32 2 676 72 53
Fax: +32 2 676 72 41
Email: pdh@cefic.be

24

ASRL Chalk Talks, CALGARY, Alberta, Canada.
Contact: Patricia Alegre, Alberta Sulphur Research Ltd
Tel: +1 403 220 5346
Fax: +1 403 284 2054
Email: asrinfo@ucalgary.ca

SEPTEMBER

21-23

IFA Production and International Trade Conference, TAMPA, Florida, USA.
Contact: IFA Conference Service,

28 rue Marbeuf, 75008 Paris, France.

Tel: +33 1 53 93 05 00
Email: ifa@fertilizer.org

OCTOBER

18-20

2nd Annual Middle East Sulphur Plant Operations Network (MESPON) Forum, ABU DHABI, UAE.

Contact: UniverSUL Consulting,
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NOVEMBER

9-12

Sulphur 2015, TORONTO, Canada.
Contact: CRU Events
Tel: +44 20 7903 2167
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17-19

European Refining Technology Conference, ROME, Italy.
Contact: Eliot Morton, GT Forum
Tel: +44 20 7316 9832
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CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

Sulphur degassing

SULPHUR
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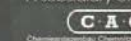


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Sulphur from oil sands

The run of high oil prices has encouraged the development of unconventional oil resources in many parts of the world, including the heavy oil sands of Canada and Venezuela. But how will production from these high sulphur sources fare now that oil prices have come back to earth?

The oil sands of Venezuela and Canada represent two of the largest concentrations of hydrocarbons in the world, on a par with Saudi Arabian crude reserves. The heavy, bituminous oil is trapped in a sandy lay close to (or occasionally on) the surface. It is viscous (completely solid in northern Canada) and high in sulphur, and so requires extensive processing to make it usable. This raises the cost of production, but the run of high oil prices ensured that the economic incentive was there to exploit them.

Venezuela

Two years on from the death of populist 'Bolivarian' president Hugo Chavez, his successor Nicolas Maduro is presiding over an economy and political settlement that are both crumbling in the wake of the falls in oil prices. Oil is vital to Venezuela, representing 95% of foreign earnings and more than half of government income, but production has been falling from a peak in 2005-6. It was reckoned by outside observers that Venezuela required oil prices of over \$100/barrel in order to fund its various commitments, and with oil now at \$60/bbl the country is suffering economically.

Oil sands have been Venezuela's great hope of increasing oil production and exports. Production fell from 3.3 million bbl/d in 2006 to 2.6 million bbl/d in 2013, with oil sands output representing 680,000 bbl/d of production in 2013, but belatedly, there are signs that Maduro is attempting to grapple with reforming state oil company Petroleos de Venezuela SA (PDVSA), which under Chavez had become a tool of state welfare. Last year he appointed Eulogio del Pino to head the company, replacing decade-long oil czar Rafael Ramirez, who had also been oil minister (this latter portfolio is now with Asdrubal Chavez, cousin of the former president). Del Pino has reportedly replaced the red shirts of the Chavistas with business suits, and begun laying off



Table 1: Venezuelan oil sands production 2013			
Company	Ownership	Block	Production, bbl/d
PetroAnzoategui (Petrozuata)	PDVSA 100%	Junin	111,000
Junin Sur	PDVSA 100%	Junin	12,000
PetroCedeno (Sincor)	PDVSA 60%	Junin	114,000
	Total 30.3%		
	Statoil 9.7%		
PetroPiar (Hamaca)	PDVSA 60%	Ayacucho	161,000
	Chevron 30%		
	CITIC 10%		
PetroMonagas (Cerro Negro)	PDVSA 83.3%	Carabobo	142,000
	Rosneft 16.7%		
Sinovensa	PDVSA 60%	Carabobo	136,000
	CNPC 40%		
PetroCarabobo	PDVSA 71%	Carabobo	2,000
	Repsol 11%		
	ONGC Videsh 11%		
	IOC/Oil India 7%		
PetroMiranda	PDVSA 60%	Junin	2,000
	Rosneft 32%		
	Gazprom 8%		
Total			680,000

Source: PDVSA

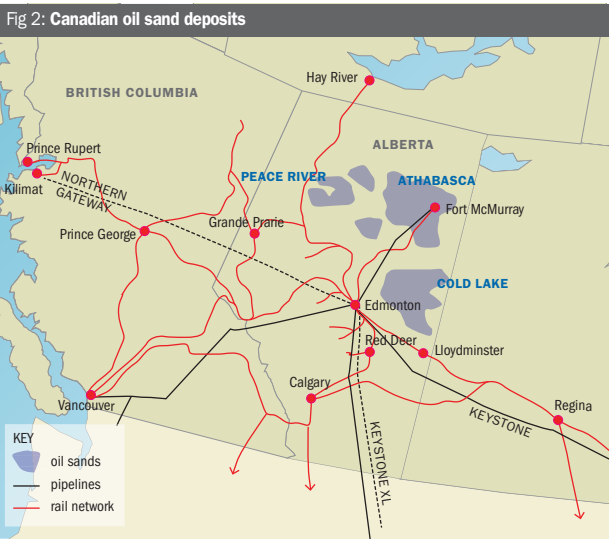
staff whose only purpose was political. He has also been allowing minority partners in PDVSA's joint venture more of a free hand and even offering a potential increase in ownership (most JVs are restricted to 40% foreign ownership at present).

Although government figures are not always the most reliable, it seems that there has been an effect, at least on the joint ventures of the Orinoco heavy oil belt or 'Faja', as it is known. Venezuela's total oil production reached 2.85 million bbl/d in 2014, and much of the increase over 2013 was down to the Faja, where output rose to 1.25 million bbl/d in 2014, and is set to reach 1.37 million bbl/d by the end of 2015, according to PDVSA, although this represents total production of syncrude/dilute crude oil (DCO) rather than the amount of heavy oil actually extracted, and thus includes the 30% dilution with naphtha and light oils – some of which is now imported from Algeria and other overseas sources. Actual oil sands production is currently put by PDVSA at around 830,000 bbl/d. Even so, it is a sign that output is –for once – moving in the right direction for Venezuela, as this has risen by 35% in just two years. Overall, Venezuela is looking to reach 3 million bbl/d of production by the end of 2015 as Faja production expands, and of this production, around 2.45 million bbl/d will be exported, mostly to China and India, with 500,000-550,000 bbl/d earmarked for the domestic market.

The Faja

Venezuela's oil sands cover a 600km long belt along the Orinoco valley, known as the Faja Petrolifera del Orinoco (Orinoco Petroleum Belt). Reserves there are estimated at over 270 billion barrels, representing 90% of Venezuela's oil reserves and over 15% of all global oil reserves – a figure comparable to Saudi Arabia's total. As Figure 1 shows, the region is divided into four major development regions, running from west to east: Boyaca, Junin, Ayacucho and Carabobo. Within these regions there are a total of 36 exploration and production blocks; 9 in Boyaca, 14 in Junin, 8 in Ayacucho and 5 in Carabobo. Most of the existing productive blocks are in the northern Ayacucho and Carabobo and northeastern Junin regions.

Initial development during the 1990s was conducted in partnership with international oil majors like Chevron, BP, Total and Repsol-YPF, but following the accession of Chavez and a partial nationalisation



of the ventures most western companies backed out, to be replaced with national oil companies from more politically 'friendly' countries, including Brazil, Belarus, Iran, China, India, Russia, Argentina, Uruguay and Vietnam. The most recent breakdown of production from these ventures for 2013 is given in Table 1.

Production is rising rapidly in in the Carabobo block, reaching 560,000 bbl/d in 2014 according to PDVSA. The major producer is PetroMonagas, which operates an upgrader which is being debottlenecked to raise dilute crude oil output from 157,800 bbl/d to 187,500 bbl/d between February and October 2016. Extra-heavy crude throughout will rise from 120,000 b/d to 145,000 b/d and synthetic crude output from 108,000 b/d to 130,000 b/d. The other major project at present is Sinovensa, which blends the oil sands with Venezuelan light crude for export, a model which is gaining increasing favour with PDVSA as a way of avoiding the need to build costly new upgrading capacity.

Three more projects are under development in the Carabobo block. PetroCarabobo, with Repsol YPF and three Indian partners (ONGC Videsh, Indian Oil Co and Oil India), is the most advanced, and began producing commercially at the end of 2012. Output is now increasing rapidly towards a target of 400,000 bbl/d, with plans for a \$4.3 billion down-

stream upgrader to process 1.2 million bbl/d to have a final investment decision taken early next year. Technip has already completed FEED for the complex, and a 90,000 bbl/d central processing facility looks to be the most certain. Of the others, PetroVictoria is a 60-40 PDVSA venture with Russia's Rosneft, and there is also Petrolindependencia, where PDVSA's 60% stake is partnered with Chevron (34%), Inpex and Mitsubishi (5% each) and Venezuelan firm Suelopetrol (1%). Petrolindependencia produced 17,000 bbl/d in 2014. These three between them are targeting 300,000 bbl/d of extra heavy crude which is to be blended and exported via a new terminal at Punta Cuchillo at the mouth of the Orinoco river, where a closed ExxonMobil terminal is being refurbished.

The other major producing block is Junin, where many of the older and more established projects are based. There are also ambitious development plans here, including revamping of the existing upgraders to increase total capacity by 140,000 bbl/d. PetroJunin, a 60-40 partnership between PDVSA and Eni, is also interested in building a naphtha stripper and blending unit to handle up to 200,000 bbl/d, avoiding expensive upgraders. The project is also to supply the planned 350,000 bbl/d PetroBicentenario refinery in Jose – Eni and Saipem are currently working on the FEED for this.

CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

Sulphur degassing

SULPHUR
ISSUE 358
MAY-JUNE 2015

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Canada

Like Venezuela, Canada is a major oil producer which faces declining output from its conventional fields, and which is turning to oil sands production in order to balance this. Like Venezuela, Canada's oil sand s are in a remote and relatively inaccessible part of the country – in this case the wilds of northern Alberta rather than the jungles of the Orinoco. The reserves are also of a similar size; Canada's proved oil reserves stand at around 175 billion barrels, 97% of which is represented by Alberta oil sands of northern Alberta (see Figure 2). However, Canada's oil sands exploitation has a longer and happier history than Venezuela's, and hence of the 3.9 million bbl/d of oil that Canada produced in 2013, about 2.3 million bbl/d or 60% was from oil sands production.

Table 2 shows capacity and production for 2014 of various companies. Total installed mining capacity was 2.9 million barrels/day, from which output is currently running at about 2.2 million bbl/d. Upgrading capacity totals around 1.15 million bbl/d, and runs at 950,000 bbl/d. The older projects tend to be those based on surface mining, and most of the newer ones use a variety of in-situ techniques, with steam injection to melt the bitumen and make it fluid enough to be recovered by pumping. About half of oil sands now comes from in situ techniques, and this proportion continues to increase. Most upgraders, conversely, are integrated with mining projects rather than in situ production.

Canada produces about 3.9 million bbl/d of oil, including oil sands, and the country's domestic oil consumption was 2.4 million bbl/d in 2013, leaving a surplus of 1.5 million bbl/d for export. Historically Canadian exports have generally headed to the US, although there are worries that the tight oil production boom there is reducing the potential for Canadian exports there. According to Canadian government statistics, Canada exported 1.8 million bbl/d of oil in 2014, of which 890,000 bbl/d was represented by 'dilbit' – dilute bitumen (510,000 bbl/d) and upgraded syncrudes (380,000 bbl/d). Almost 99% of this was destined for the USA.

Exports of syncrude and dilbit have been a major bone of contention, particularly over the fate of the cross-border 830,000 bbl/d Keystone XL pipeline, designed to connect the oil sands region

Table 2: Canadian oil sands production 2014

Operator	Site	Capacity, bbl/d	Production, bbl/d	Type
Syncrude	Mildred Lake/Aurora	407,000	311,000	Surface mine
		350,000	262,000	Upgrader
Suncor	Millennium/Steepbank	501,000	275,000	Surface mine
	Base Operations	357,000	296,000	Upgrader
	Firebag	180,000	189,000	In situ
	Mackay River	38,000	31,500	In situ
	Fort Hills	160,000	U.C.	Surface mine
Shell Canada	Jackpine	100,000	111,000	Surface mine
	Muskeg River	155,000	132,000	Surface mine
	Peace River	12,500	4,400	Surface mine
	Scotford	255,000	246,000	Upgrader
CNRL	Horizon	140,000	130,000	Surface mine
		127,000	112,000	Upgrader
	Primrose/Wolf Lake	120,000	124,000	In situ
	Kirby	40,000	24,000	In situ
Cenovus	Christina Lake	138,000	138,000	In situ
	Foster Creek	160,000	135,000	In situ
Statoil	Liesmer	20,000	17,000	In situ
Imperial Oil	Kearl	110,000	79,000	Surface mine
	Cold Lake	180,000	147,000	In situ
CNOOC	Long Lake	72,000	39,000	In situ
		58,000	38,000	Upgrader
Devon Canada	Jackfish	105,000	79,000	In situ
ConocoPhillips	Surmont	28,000	24,000	In situ
Conacher	Great Divide	20,000	15,000	In situ
Husky	Sunrise	30,000	C	In situ
	Tucker	30,000	10,000	In situ
MEG Energy	Christina Lake	60,000	81,000	In situ
Others	Various	58,000	20,500	Various

C= commissioning

U.C.= under construction

Source: Oilsands Review

to the US pipeline network and carry syncrude on to US Gulf Coast refineries for processing. The saga of Keystone has rumbled on for most of the Obama presidency, finally culminating in a presidential veto which the Senate failed to overturn in March. In the meantime, the syncrude is travelling by rail instead, and although there have been problems with cross-border capacity, it is estimated that up to 1 million bbl/d can be transported that way. US Gulf Coast refineries have been set up to deal with heavy Canadian syncrudes, so the economic imperative remains, and in spite of the tight oil boom, the recovery of natural gas liquids (NGLs) from gas fracking has meant that the US has had a surplus of lighter fractions which often need to be blended with heavier crudes for processing.

Beyond Keystone, there have been other pipeline proposals to get syncrude from Alberta to consuming markets, via the \$8 billion Northern Gateway pipeline from Bruderheim near Edmonton, Alberta to Kitimat on Canada's west coast, or via a line east to refineries in eastern Canada (Figure 2). Northern Gateway has also faced considerable opposition, but the Canadian government finally approved it last year. At the moment its projected on-stream date is 2018, but opposition from Canadian First Nation groups continues.

United States

Several other countries have oil sands reserves, including Russia, Congo and Madagascar, but these are all much smaller and less well characterised depos-

its than those in Venezuela and Canada. The only other country where there is current project development activity is in the US. Oil sands resources in the USA are mostly concentrated in eastern Utah, where reserves are put at >30 billion barrels. US Oil Sands Inc is in the process of developing these resources, which it characterises as 180 million bbl of recoverable oil sands in place. All regulatory hurdles have now been cleared, and the company has completed site preparation work and front end engineering and design for its phase 1 development at PR Spring. Off-site fabrication of the process extraction plant modules is under way, and these are due to be assembled at the site by 3Q 2015, followed by commissioning and commercial start-up towards the end of the year. US Oil Sands will initially produce 2,000 bbl/d using hot water separation with a proprietary solvent to recover the bitumen, scaling up to 10,000 bbl/d by 2018 in phase 2, and ultimately 50,000 bbl/d some time next decade.

Oil price impact

Oil prices have fallen from a high around \$110/bbl around this time last year, to below \$50/bbl in early 2015, before finally settling around \$60/bbl. The US tight oil boom has been one major supply side factor for this, with China's economic slowdown another major one, but a key decision has been Saudi Arabia refusing to play swing producer as it has historically done, and instead keeping on pumping oil as prices fell. There has been a great deal of speculation as to the reasons for this, from simply trying to keep market share, attempting to economically damage rivals like Iraq and Iran, or trying to slow down the growth in US tight oil and Canadian oil sands production by forcing higher cost producers to shut down. As we noted above, the impact on Venezuela's state finances has been a disastrous one, but in fact this has not had the effect of slowing down production from the Faja but rather the opposite, as Venezuela tries to push new oil sands production as hard as it can. Indeed, the impact has been to force PDVSA to begin relaxing its chokehold on control of operations and allow its foreign partners more leeway, and possibly put in train much needed reforms within the company. However, the ability of Venezuela to provide or raise financing for some of the expensive

upgrader projects looks far more dubious, and PDVSA is now concentrating on expanding output via the production model developed with CNPC via the Sino-venesa joint venture, of mixing the bitumen with light oil and exporting that. PDVSA has indicated that it may begin importing significant quantities of light oil by the end of the year for this purpose. Even if there is no new upgrading capacity, PDVSA still expects at least an additional 500,000 bbl/d of oil sands crude to be produced over the next few years.

As for Canadian oil sands production, well, while in theory the producing companies ought to be more sensitive to market forces than in Venezuela, so far there has been no noticeable slowdown in production. It is reckoned that the break-even price for mining developments is about \$90-100/bbl and \$60-80/bbl for in situ projects. Still, most oil sands producers whose up-front capital expenditure has already occurred currently seem relatively comfortable with \$60/bbl oil, and even many of the new projects where development costs are already sunk still seem to be going ahead. There have been layoffs and project postponements, such as Total at Joslyn and Statoil at Corner, and Shell has cancelled a 200,000 bbl/d mining project at Pierre River, and the prospects for new upgrading capacity also seem to be badly affected by the falling oil price. However, a fall in the value of the Canadian dollar against the US dollar has also helped cushion Canada slightly, with one Canadian dollar now worth just 82 US cents, and the worst effect so far has been on the province of Alberta's public finances, which are heavily dependent on oil royalties. It has also been suggested that a decision to go ahead with Keystone XL could change the economics of some of the projects and make them viable again, by cutting transport costs from \$25/bbl to \$9/bbl. The IEA has revised down its estimates for increased Canadian oil sands production by 2020, but only from 1.2 million bbl/d to 800,000 bbl/d. In other words, growth will still come, just slower than some of the excitable predictions of a couple of years ago, with surface mining and upgrader projects the worst affected, but several new in situ projects still likely. Around 270,000 bbl/d of new oil sands capacity is still due to come on-stream this year in Canada, and at the moment the 150,000 bbl/d Redwater Upgrader is also still in progress.

Sulphur from oil sands

The impact on sulphur production is harder to quantify. Oil sands bitumen has an average sulphur content of about 5%, and if it is to be used in end products then this sulphur must go somewhere. If Canada is producing 2.2 million bbl/d of bitumen and Venezuela 800,000 bbl/d, that is about 135 million t/a of bitumen, containing 7 million tonnes of sulphur. However, only bitumen passing through an upgrader is likely to see that sulphur extracted at the site.

Canadian oil sands sulphur production in 2014 was 2.06 million tonnes according to figures collected by the Alberta Energy Regulator. Of these, 614,000 t was from Syncrude's Mildred Lake facility, 555,000t from Shell's Scotford Upgrader, and 490,000t from Suncor. Nexen at Long Lake and CNRL at Horizon made up the remainder. Onward sales of sulphur amounted to 1.6 million tonnes, the remainder goes to the huge sulphur blocks at Syncrude – now totalling an estimated 9.65 million tonnes. Some is shipped as formed sulphur, but much is transported molten by rail to the US. Meanwhile, Venezuelan total sulphur production is around 800,000 t/a, of which around 500,000 t/a comes from the Jose complex, most of it from heavy oil upgrading. Even so, this means that only about 2.5 million t/a of sulphur in total is actually being produced from oil sands upgraders, and the remaining 4.5 million t/a of sulphur in synthetic and dilute oil sands-based crudes is making its way to refineries around the world – many of them in the US Gulf, which also handles Venezuelan imports – for processing.

Looking forward, the upgrader revamps in Venezuela look to be reasonably safe, even if the massive PetroCarabobo project does not come to fruition, adding another 140,000 bbl/d of capacity over the next 2-3 years, and probably a couple of hundred thousand tonnes per year of additional sulphur. Likewise the Redwater Upgrader will add additional sulphur recovery to Alberta, with the first 50,000 bbl/d phase due for completion by September 2017. Nevertheless, it seems likely that most of the sulphur will be exported still encapsulated in the bitumen, to be processed by refineries in the US, Asia and elsewhere. If, as currently still seems feasible even in the present oil price environment, oil sands production rises from its present 3 million bbl/d to say 4 million bbl/d over the next five years or so, another 2 million t/a of sulphur will be being extracted somewhere in the world. ■

CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

Sulphur degassing

Sulphur forming plant listing

Sulphur’s regular update of recent and scheduled projects worldwide to supply equipment for the manufacture of formed product.

Acid projects							
System manufacturer/supplier	Operating company	Operating site	Units	Product type	Scheduled throughput	New/expansion	Scheduled
CHINA							
Enersul	PetroChina	Anyue Refinery	2	granule	700 t/d	new	2014
Sandvik Process Systems	Sinopec	Qilu	2	pastille	750 t/d	new	2015
INDIA							
Enersul	Reliance Industries	Gujarat	8	granule	2,800 t/d	expansion	2014-15
Sandvik Process Systems	Bharat Petroleum	Ambalmugal	3	pastille	800 t/d	expansion	2015
INDONESIA							
Enersul	ExxonMobil	Banyu Urip	1	wet prill	100 t/d	new	2014
IRAQ							
Devco	Mishraq State Sulphur Mine	Mishraq	1	wet prill	1,500 t/d	new	On hold
Enersul	GazpromNeft	Badra	1	granule	350 t/d	new	2015-16
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
MEXICO							
Sandvik Process Systems	PEMEX	Coatzacoalcos	4	pastille	1,080 t/d	new	2015
OMAN							
Enersul	OOCEP	Musamdah Gas Plant	1	granule	350 t/d	new	2014-15
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	Rosneft	Samara	1	granule	350 t/d	expansion	2015
Enersul	Total/Globalsestroy	Kharyaga	1	granule	350 t/d	new	2015
Sandvik Process Systems	Afipsky Refinery	Krasnodar	1	pastille	72 t/d	new	2016
Sandvik Process Systems	Lukoil	Korny	2	pastille	200 t/d	new	2015
SAUDI ARABIA							
Devco	SAMREF	Yanbu	1	prill	750 t/d	new	2014
Enersul	Aramco	Yanbu	2	wet prill	200 t/d	new	2015
Sandvik Process Systems	Aramco	n.a.	10	pastille	n.a.	new	2015

Acid projects continued							
System manufacturer/supplier	Operating company	Operating site	Units	Product type	Scheduled throughput	New/expansion	Scheduled
SOUTH KOREA							
Sandvik Process Systems	n.a.	n.a.	1	pastille	150 t/d	new	2015
SPAIN							
Enersul	Petroleos del Norte	Muskiz	1	granule	350 t/d	expansion	2016
TURKEY							
Enersul	Aegean Refinery	Aliaga	3	granule	1,050 t/d	new	2015
TURKMENISTAN							
Enersul	Turkmengas	South Yolotan	7	granule	2,800 t/d	expansion	2014
Sandvik Process Systems	Turkmengas	South Yolotan	1	pastille	400 t/d	expansion	2015
UNITED ARAB EMIRATES							
Enersul	Gasco	Shah, Abu Dhabi	12	granule	14,400 t/d	new	2015
Enersul	Gasco	Habshan, Abu Dhabi	12	granule	14,400 t/d	new	2014
VENEZUELA							
Sandvik Process Systems	Petropiar	Barcelona	1	pastille	130 t/d	expansion	2015
VIETNAM							
Enersul	Nghi Son Refinery	Nghi Son	3	granule	1,380 t/d	new	2015



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TSI comes to Spain

The Sulphur Institute's annual Sulphur World Symposium moved to the historic city of Barcelona this April.



Gaudí's Park Güell, Barcelona.

Catalonian sunshine welcome delegates to The Sulphur Institute (TSI)'s annual sulphur symposium. TSI president Robert McBride gave the opening address, stressing that as the global advocate for sulphur, TSI represents all stakeholders buying, selling, handling, transporting or adding value to sulphur. Also welcoming delegates to Spain, Antonio Portela Estevez of Repsol next gave a brief overview of his own company's sulphur production. Sulphur output at Repsol's refineries is rising from 300,000 t/a to 600,000 t/a as new upgrading capacity is completed. In particular, the newer, more modern refineries at Cartagena and Bilbao are likely to produce 200,000 t/a and 170,000 t/a of sulphur respectively, with the other three refineries about 80,000 t/a each.

Energy markets

Beginning the symposium proper, Francis Osborne of Argus Consulting took a long term look at energy markets. Global GDP continues to increase, to the tune of about 3.5% per year (down from 4.5%), with more than half of this coming from non-OECD Asia. This should double global GDP by 2035 and increase GDP/capita by 75%, but primary energy growth out to 2035 is running much lower at about 1.5% per year, down from 2.5% in previous decades. Fossil fuels are still likely to be responsible for 80% of energy use by then, with power generation the main driver, rising to 55% of energy demand as the world electrifies,

but this masks a decline in coal use and an increase in gas use. Renewables may claim as high as 20-25% of world energy demand by then; renewables are growing at 16.5% per year, with China now installing more wind, solar and hydroelectric power than coal, demand for which fell in 2014. The cost of solar power has declined by 50% in the past five years, and wind 35%.

Oil supply growth is increasingly becoming focused on natural gas liquids (NGLs) and tight oil – especially the latter, and especially in North America – with some biofuel and oil sands supply (depending on the oil price environment) and very little from conventional sources. In the short term however OPEC has clearly decided on a strategic shift and is no longer supporting the oil price – supposedly in order to choke off new supply from tight oil, although the first major impact may be on Iraq as \$60/bbl appears to be enough to support US tight oil production and even Canadian oil shales for now. Longer term a higher oil price may be needed in order to encourage fresh supply into the market. Gas developments, conversely, are more evenly spread, as consumption rises by 50% to 2035. The US and Middle East will be responsible for 55% of growth, but shale will also be making an impact on China by then.

Sulphur supply

Marina Ivanova of Douglas Westwood looked at Europe's refining industry. There are 670 refineries operating worldwide, 102 of them in Europe. Douglas West-

wood has identified 81 capacity expansion projects out to 2019, of which only 2 are in Europe; Total's Antwerp refinery expansion, scheduled for 2016, and ExxonMobil's Antwerp expansion in 2018. Global refining capacity is set to rise from 89 million bbl/d in 2014 to 112 million bbl/d in 2019. The new capacity projects are 35% in Asia, 20% in Latin America and 20% in North America, with only 15% each in the Middle East and FSU. There have also been 29 refinery closures since 2009, about half in Europe.

Moving to regional production, Tom Smith of Sandvik Process Systems gave an update on sulphur output from the Caspian region, which is set to rise from 8.9 million t/a in 2013 to 14 million t/a in 2019. Some of this will come from Kashagan (1.1 million t/a) once it is finally up and running, with Norilsk Nickel's sulphur dioxide to sulphur reduction adding another 800,000 t/a, and various Russian refineries another 800,000 t/a. However, the largest increase in output will come from Turkmenistan, where production is rising from 550,000 t/a to 2.2 million t/a with the start-up of the South Yoloten plant taking gas from the Galkynsh field. Sandvik have installed eight 400 t/d Rotoform units at the South Yoloten project, and Tom took delegates through the sulphur handling and forming facilities at the site. At the moment the project has only 12 days of bulk storage, but it is possible that there may be a need for block pouring here or elsewhere in central Asia in the coming years as the world's output of sulphur rises.

Sulphur demand

Phosphate production remains the largest source of demand for sulphur and sulphuric acid, and Youssef Bouslikhane of Morocco's OCP said that he saw strong long-term demand fundamentals as population rises and arable land falls. Fertilizer growth is likely to be about 2% per year over the long term. However, OCP sees great potential in Africa, where the potential is for demand to increase fivefold in much the same way that Brazil's cerrado region has transformed fertilizer demand in South America. As the owner of 75% of the world's phosphate reserves and 29% of production, OCP aims to capitalise on this by doubling its mining capacity and tripling its fertilizer capacity out to 2025 and optimise the value chain via increased end product and better linkage between stages of the process (such as the recent slurry pipeline to take phosphate from the mines to processing areas). In the \$16 billion first phase, OCP is building four phosphate complexes, the first of which is commissioning now, and the other three of which will be onstream by the end of 2016. Sulphur consumption and imports will rise from their present 4.5 million t/a to 7 million t/a in 2017, and again to 11.5 million t/a in the second phase, which will involve another six production complexes!

In the non-fertilizer sector, one of the major areas of demand for sulphuric acid has been in caprolactam production, with knock-on production of ammonium sulphate. Leon Muijtjens of DSM described this market, noting that the amount of ammonium sulphate produced from caprolactam manufacture depends on the process used, ranging from 1.5 tonnes AS per tonne caprolactam for the phenol-based HPO process to 4.4 tonnes per tonne for hydroxylammonium ammonium sulphate oximation (HSO). Caprolactam demand has mainly been driven by nylon production or textiles, but food packaging is also of increasing importance, and engineering plastics in eg China. China has been the main growth area for caprolactam – virtually all growth in production has occurred there, with other markets stable. New capacity in China is mostly ammonium/HPO based, with lower volumes of ammonium sulphate produced, but there will still be significant volumes of AS, leading to overcapacity in China. The global AS market is about 5 million t/a, but capacity is set to rise to 7 million t/a in 2020, presumably leading to a

shakeout. Utilisation rates are now down to 80% for caprolactam and many producers are not making money.

Drawing these strands of supply and demand together, Brendan Daly of CRU began with the supply of sulphur, which he said would stand at 59.3 million t/a this year. The Middle East region is seeing the strongest supply increase, while China remains the centre for demand and imports. Although Chinese stocks at ports have fallen this year, he thought that they would stabilise around the 1.0 million tonnes region. Demand increases elsewhere include nickel leaching in Cuba, Madagascar and Oceania, copper leaching in Peru and Mexico, and as noted above, caprolactam production in China. The phosphate market has been weaker in 2013 due to the impact of the Ma'aden project, but stronger in 2014 in spite of increased capacity in the Middle East/North Africa due to a stronger market in China. Overall demand is likely to rise from 56.5 million t/a in 2014 to 66.3 million t/a in 2019. This will lead to a surplus rising from about 1 million t/a in 2015 to 4.5 million t/a in 2019. Some start-ups may end up pushed back, but probably not cancelled, and it seems likely that that some will need to be poured to block.

On the trade side, total traded volumes of sulphur in 2014 was 31 million tonnes. Acid markets had been tighter last year, he said, as the price disparity between low acid prices and high sulphur prices had encouraged some sulphur burning acid producers to buy product on the merchant market in China and India during 2014, but this disparity has gone now.

Freight

The seaborne freight market is at historically depressed levels, said Derek Langstrom of SSY. Dry bulk seaborne trade in 2014 was 4.15 billion tonnes, with iron ore representing one third of that and coal 28%. Sulphur, by contrast, is about 0.7%. Chinese coal imports are down by 40% in March 2015 compared to the previous year, with power generation increasingly being replaced by renewables and with lower steel production (which peaked

in late 2013) iron ore shipments are also down. Although Indian coal imports – mainly from Indonesia – are becoming more important, and India is set to become the world's largest coal importer, the demand side is down, while there is still a considerable order book of new ship deliveries for the next couple of years, especially in the 60-65,000 dwt category, and lower oil – and hence bunker fuel – prices may encourage faster sailing, making the existing fleet more efficient and raising capacity. Thus a recovery in freight rates at the moment can only come from supply side adjustments such as increased scrapping of older vessels and slippage of new build orders.

Regulation

Craig Jorgensen of TSI looked at the organisation's work with regulators. MARPOL's Annex V directs shippers to classify cargoes as harmful or not harmful to the marine environment from January 2015. Sulphur has been classified as 'not harmful' thanks to help and advice from TSI and

so shipowners can wash holds at sea, saving time and cost. TSI has also collaborated with the European Maritime Safety Agency to provide marine chemical information sheets for pollution response for both molten and formed sulphur.

In the US, there is work in progress to redesign rail tank cars in the wake of recent crude oil derailments and accidents and generally increased legislative scrutiny, although TSI does not anticipate any immediate impact on molten sulphur rail cars. However, the city of Chicago is trying to minimise airborne particulate matter from storage handling and processing of bulk solid materials, and formed sulphur is currently on the list of substances likely to be controlled. With the risk that this regulation spreads to other areas where sulphur is stored in the open, like Gulf Coast ports, TSI is assisting the local authorities in addressing the matter.

Finally, the increasing supply of sulphur may lead to challenges in terms of long term storage, whether above ground, underground etc, and TSI is developing an inventory management platform to meet the needs of industry, the regulator and the environment. ■

CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

Sulphur degassing

SULPHUR
ISSUE 358
MAY-JUNE 2015

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Sulphuric acid reclamation

A significant volume of sulphuric acid used in industrial processes generates contaminated acid streams which face increasingly stringent regulations on disposal.

In the processing of bulk minerals such as phosphates, and copper, nickel and uranium ores, sulphuric acid is used as a reagent, but in many industrial and chemical processes, the acid acts either as a catalyst (such as in alkylation in refineries) or reaction medium, or (such as in titanium dioxide manufacture) as a temporary complexing agent, and does not form part of the final product. Nevertheless, there is a build-up of contaminant in the acid, and so to prevent too large a build-up of contaminant, 'spent' acid containing the contaminants is withdrawn in a constant stream and topped up with new 'fresh' acid. In this way, many of these processes generate large quantities of waste, dilute acid, which may also be contaminated with organic or inorganic compounds.

Regulations on disposal of sulphuric acid continue to tighten around the world, and simply dumping it into rivers or oceans is now prohibited in most places. Disposal of waste sulphuric acid can therefore be a difficult and expensive process, requiring neutralisation with limestone or hydrated lime, and generating carbon dioxide and solid and liquid wastes such as gypsum sludge, requiring landfilling or sometimes further treatment, where the gypsum is contaminated with toxic compounds. The US Environmental Protection Agency (EPA) in particular has become increasingly stringent in recycling of industrial wastes, and in December last year published its revised Definition of Solid Waste (DSW) rule, under the Resource Conservation and Recovery Act (RCRA). Although the recycling of process sulphuric acid continues to be one of the major exclusions from the act, acidified sludges and recycled acid from lead/acid batteries remain bones of contention and possibly subject to future legislation.

The alternative to this is to 'reclaim' or 'regenerate' the spent acid via re-concentration back up to 'useful' concentrations (75-98%), and this is becoming an increasingly preferred solution from both an environmental and even commercial basis.

Global capacity

Total capacity figures for sulphuric acid regeneration are not always easy to come by. Partially this is a matter of definition, as small quantities of acid can be regenerated on-site by some industrial or petrochemical producers. Broadly speaking, acid regeneration capacity is largest in the traditional heavy industrial regions where large scale chemical production and refining were based (North America, Europe, Japan), as well as some of the newly industrialising countries. In the US in particular, the widespread use of sulphuric acid alkylation in refineries also generates considerable quantities of spent sulphuric acid, to the tune of about 500,000 t/a. The US Geological Survey estimates that between 2.5 and 5 million t/a of spent sulphuric acid from chemical and industrial processes is recycled every year (on a 100% acid basis)

in the US, representing a major segment of US acid production (which totals >33 million t/a). Elsewhere, the European Sulphuric Acid Association (ESA) estimated 2014 European nameplate capacity for regeneration of spent acid at 1.68 million t/a out of a total acid capacity of 26.3 million t/a in Europe, or about 7% of European acid capacity, with 2013 production at 1.2 million t/a out of output of 16.1 million t/a, i.e. again around 7%. CRU estimates Chinese recycling production at about 300,000 t/a, and Japan at slightly lower, representing much smaller segments of these acid markets. Total regeneration of sulphuric acid is thus somewhere less than 5% of the overall market.

Acid regeneration

Briefly, sulphuric acid is regenerated by spraying the acid into a hot (1,000-1,200°C) furnace where the acid decomposes to SO₂, O₂ and H₂O, and organic contaminants are converted to CO₂ and H₂O. The furnace offgas passes through a heat recovery section, and is then cleaned of ash and soot particles and dried, condensing H₂O from the gas stream. From here, the SO₂ is oxidised to SO₃ and thence to H₂SO₄ as in a conventional contact acid process. However, the details can vary widely, as the composition of spent acids is also highly variable (see Table 1).

Pre-concentration

Where acids have a high water content, as in the methyl methacrylate (MMA) spent acid on the right in Table 1, the excess water must usually first be driven off to improve the efficiency of the combustion process. In most commercial acid regeneration plants pre-concentration happens in a pre-heat section which re-uses process heat from elsewhere in the plant. The

extent to which this can be done depends on the solubility of contaminants; normally it stops at the point where these begin to precipitate. In acid concentrations up to 75% H₂SO₄, evaporation will drive off water almost exclusively, but beyond that point the vapour pressure of acid will increase. Some spent acids which contain only metal sulphates can have these precipitated out at this stage and the acid then filtered and re-used. In other processes, such as methyl chloride production, where only volatile organics are present, a steam stripping process can liberate the organic contaminants allowing the remaining sulphuric acid to be simply concentrated back up to 93-96% and returned to the process. However, in cases where these steps are insufficient, a subsequent thermal oxidation step must be used after pre-concentration.

Oxidation

The concentrated mix is now sprayed into the refractory-lined oxidation furnace. The decomposition reaction is endothermic so heat must be provided for the reaction to occur. Hydrocarbons present in the acid can provide part of the heat but the rest must be generated via burners operating on natural gas or other fuels. In acid regeneration plants linked to a sulphur burning acid plant or otherwise near a source of sulphur (such as a refinery) sulphur or even H₂S combustion can also be used as source of heat.

Combustion air required for the process can be enriched with oxygen to varying degrees all the way to 100%. As in a Claus plant, the use of oxygen enrichment reduces the amount of gaseous inerts (i.e. nitrogen) that must be carried through the downstream equipment, and as a retrofit to an existing plant this has the effect of increasing the throughput of spent acid without the need to increase the size of downstream equipment. Oxygen enrichment also increases the SO₂ concentration, allowing for a smaller downstream sulphuric acid plant.

The hot gases leaving the furnace enter a waste heat boiler where high pressure steam is generated for process use (e.g. in the evaporation/pre-concentration section) and/or power generation.

Gas cleaning

The gas cleaning section removes ash and solid impurities from the oxidation section, and includes a final water removal step

to concentrate the acid up to industrial strengths. An adiabatic scrubber reduces the temperature and removes some solids, followed by a section where water removal is often achieved using concentrated (93-96%) acid in a packed bed acid tower or drying tower.

Technologies

All of the major licensors offer spent acid regeneration processes;

MECS

DuPont offers acid regeneration technology via its Monsanto Enviro-Chem Systems (MECS) division. The thermal decomposition section consists of a fuel burner and spent acid atomisation into a large brick-lined decomposition furnace, where the acid is vapourised and decomposed into SO₂, H₂O and O₂ at around 1,000°C. In order to maximise the yield of SO₂ the combustion is controlled at near-stoichiometric quantities of fuel and air. If the ratio of fuel to oxygen is not well controlled, elemental S will be produced which can clog the downstream gas cleaning section. When feeds or fuels contain nitrogen compounds or where low NOx emissions are required, two-stage combustion systems are included. The hot combustion gases are cooled in a high pressure boiler and in some cases a downstream superheater or (generally in smaller <100t/d plants) a radiant heat exchanger. The gas cleaning section of the plant typically includes four or five different units; the first is an adiabatic scrubber using weak acid to saturate and reduce the temperature of the gas from about 300°C to about 80°C, along with some solids removal. Open spray towers, Venturi scrubbers or froth contactors are typically used for this primary scrubber, with MECS offering the *DynaWave* scrubber. Next gas cooling with condensation of excess water is completed in the second unit to further capture dust/ash particles which have been agglomerated in upstream gas cleaning equipment and/or gaseous contaminants like chlorides or fluorides, typically in a second *DynaWave* scrubber. The final gas cleaning unit captures all of the remaining dust.ash and the acid mist formed by the hydration of the small amount of undecomposed SO₃ present. If the dust and ash particles are soluble in weak acid (e.g. iron salts), fibre bed mist eliminators such as MECS Brink series are used. The SO₂ bearing gas is then dried by contact with concentrated acid.

Haldor Topsoe

Haldor Tospoe uses its wet gas sulphuric acid (WSA) process downstream of the thermal decomposition section. The gas is cooled to 400-450°C in a waste heat boiler and after dust removal in an electrostatic precipitator or high temperature filter the filter gas goes to the SO₂ converter and condensation. No drying of the gas takes place, so there is no loss of acid or acidic waste material and no heat lost in process gas reheating. Selective condensation in the WSA condenser ensures the regenerated fresh acid will be 98% by weight.

Outotec

Outotec is the inheritor of Lurgi Metallurgie's processes, one of the pioneers of spent acid regeneration, with their history in developing the thermal decomposition process going back to the 1930s. Outotec's process design for spent acid plants uses a horizontal furnace with a downstream multi-stage wet gas cleaning section and double absorption sulphuric acid plant. The latter section is similar in design to conventional acid production plants based on SO₂ gases from metallurgical processes. Because the volume of combustion gas introduced into the decomposition furnace depends on the required process heat, the total specific gas volume and the resulting SO₂ concentration of the gases at the furnace exit become a function of the spent acid concentration.

Jacobs

Jacobs design and build acid plants using spent sulfuric acid as feedstock ranging in size from 200-1,500 t/d, incorporating Chemetics' proprietary designs for spent acid guns, regeneration furnaces, quench Venturi, variable throat scrubber Venturi, stainless steel converter with multiple internal exchangers, radial flow gas-gas exchangers, anodically protected coolers and SARAMET[®] piping and distributors. These acid recovery and concentration technologies can also be applied to effluent treatment plants, which are being increasingly required to treat the liquid effluent resulting from the wet gas cleaning sections of metallurgical sulphuric acid plants. Jacobs also offer treatment for weak acids which are often contaminated with a variety of heavy metal, separating contaminants from the gypsum to produce a saleable product and an environmentally safe solid effluent, or alternatively, clean and concentrate the weak acid to produce a commercial grade acid. ■

CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

Sulphur degassing

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SOGAT 2015

A report from the Sour Oil and Gas Advanced Technologies (SOGAT) conference, held in Abu Dhabi in April.



Given the volumes of sulphur already coming from the Middle East in particular, the theory and practice of sour gas processing in the Arabian Gulf continues to be a significant topic for the industry, and for 11 years now the SOGAT meeting has provided an arena for such discussions.

Project updates

As the region is home to several of the new large sour gas projects which are changing the dynamics of the sulphur industry, news on how those projects are progressing is always keenly awaited. In his introductory remarks, Saif Ahmed Aghfelli of Al Hosn Gas said that the massive Shah project had begun producing gas in 1Q 2015, and would be ramping up during 2Q.

In neighbouring Saudi Arabia, Ali Dossary of Saudi Aramco described lessons learned with the Karan gas plant in Saudi Arabia, which is currently in its start-up phase. The plant receives gas from five offshore unmanned gas platforms along 110km of pipeline, 85km of it undersea. It can process up to 1,800 million scf/d of feed gas in three 600 MMscf/d trains, producing 1,350 MMscf/d of sales gas and 1,250 t/d of sulphur. The gas brought to the processing plant is 8.5% CO₂ and

2% H₂S – a very high CO₂:H₂S ratio, and the requirement is for the final sales gas to have less than 4ppm H₂S. This has required a special amine formulation from INEOS. Among the challenges the project has faced has been hydrate formation in the undersea pipeline, and foaming in the acid gas rich absorber.

PDO Oman also updated delegates on progress with work on a new brownfield sour gas development there, which is just moving from the design to execution phase. Here the feed gas has 3% H₂S and 5% CO₂. The sulphur recovery target is 99.9% to achieve sales gas with less than 5ppm H₂S, and on top of that Oman's SO₂ emission limits, at 35mg/Nm³, are some of the most stringent in the world. Vijay Kesankurthy and Ahmed Al-Azizi of PDO described the project's choice of a CANSOLV unit to quench flue gas from the incinerator to keep SO_x emissions down, and the dispersion modelling carried out to ensure that ground level concentrations remain below permissible limits – including increasing steam temperature to make the stack gas plume rise faster.

Sulphur

Sulphur markets were covered by Meena Chauhan of Integer Research. China, Morocco and Saudi Arabia continue to lead

Left: New sulphur source: the Shah sour gas project during construction.

global sulphur consumption growth, led by new phosphate capacity there, with total demand projected to rise to 70 million t/a in the early years of the next decade. The impact of sour gas there and a slowdown in phosphate production growth will lead to falling Chinese imports, while the familiar story of sour gas production elsewhere also lifts supply and hence global oversupply to 3-6 million t/a by the end of the decade.

"Never walk over a covered sulphur pit" was the salutary lesson from ASRL's Peter Clark. Detailing the chemistry of sulphur pits, he showed how sulphur vapour permeates void spaces in concrete and – away from the heat of the pit itself – freeze/thaw cycles create pressure which can crack concrete and expose steel rebar, allowing rapid attack by sulphur and water. High silica concrete can help prevent ingress and does not catalyse some of the acidic intermediaries, but roofs remain especially vulnerable, where poor insulation can lead to solid sulphur deposition and increased corrosion if the roof temperature is not kept above 125°C.

Technology

As usual the meeting was a showcase for technologies in the sour gas arena. Unfortunately space precludes more than a couple of edited highlights. Jorn Rolker of Evonik presented a new high performance absorbent for acid gas removal. The CAP-LUS scrubbing agent is not conventionally amine-based, and offers, so Evonik claim, higher capacities, energy efficiency and plant uptime and less degradation and corrosion issues even at high acid gas loadings. In a real world swap-out for an amine absorbent a 10% energy efficiency improvement was noted.

Moving away from chemical absorption altogether, Tecnimont showcased a cryogenic distillation technology for gas sweetening. The technology uses a dual pressure double absorption distillation unit which discharges CO₂ and H₂S at high pressure, suitable for re-injection or enhanced oil recovery.

Ametek CSI also chose SOGAT as the place to launch the company's new degassing process, described by Thomas Willingham – a much fuller description of this can be found in our major degassing article this issue, on pages 43-57. ■

Lewis® Pumps products are right



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CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

Sulphur degassing

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HIGHSULF PLUS makes its debut

HIGHSULF PLUS™, a recent addition to the HIGHSULF™ processes, brings a new dimension to acid gas removal and enrichment. In addition to increasing the H₂S concentration of the SRU feed, this technology allows the amine unit (including TGTU) to control the H₂S concentration in the acid gas feed to the SRU. **T. K. Khanmamedov** of TKK Company and **J. M. Lawrence** of Lexington Group International, Inc. compare and discuss some FEED data for an AGE unit based on the HIGHSULF PLUS process and present simulation and design numbers for a commercial unit in the FSU.

Many natural gas streams contain small concentrations of H₂S (between 10 to 40%), or contain high CO₂ to H₂S ratios. These streams can pose challenges to the designer and the operator because the acid gas produced by processing in a typical unit is sub-quality for Claus sulphur plant feed; however, it cannot be vented or incinerated because of the sulphurous compounds. Even in plants with a moderate CO₂:H₂S ratio of say 4:1, if complete acid gas removal is necessary (LNG for example), using a single contactor will necessarily produce an acid gas stream containing about 20% H₂S on a wet basis. In other situations where total removal of the CO₂ is not required, the resulting acid gas may be too dilute for a Claus sulphur recovery unit with straight through configuration.

One of the ways currently used to produce sulphur from such dilute acid gas feed is the so-called Claus unit with split-flow configuration (Fig. 1). In this configuration, up to 66% of the acid gas feed bypasses the combustion zone (thermal stage) and is fed directly to the first catalytic reactor. Bypassing the thermal stage (where 50 to 60% of the H₂S in a typical unit is converted to sulphur in a straight through design), places additional recovery demand on the catalytic reactors and results in reduced sulphur recovery efficiencies. H₂S conversion to sulphur is most efficient when the feed contains 55% or more H₂S.

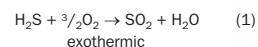
In addition to H₂S, the balance of the SRU feed is CO₂ and water, possibly with a small amount of hydrocarbons or other components. Lower concentrations of H₂S

result in greater sulphur plant complexity, larger equipment, higher cost and most importantly reduced sulphur recovery efficiencies. Streams having less than 32% H₂S are extremely difficult to operate in the straight-through Claus configuration without oxygen assisted combustion. For air only combustion, the lower limit for H₂S composition in the feed gas is closer to 45% for a straight-through Claus unit.

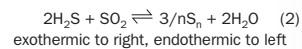
In the following case study, the acid gas produced by a regular amine unit contained 21 mol-% of H₂S and the downstream SRU was designed with split flow configuration (oxygen enrichment was not available for the SRU).

In this SRU at least one-third of the acid gas is directed to the thermal reactor

where one-third of the total H₂S is combusted to SO₂ according to the exothermic reaction (1):



The acid gas that bypasses the thermal reactor is mixed with the thermal reactor effluent and the combined stream is sent to the catalytic reactor(s) (catalyst beds 1 and 2). In the catalytic reactors, SO₂ generated in the thermal reactor reacts with the remained H₂S for formation of sulphur according to the equilibrium reaction (2).



Sulphur that is produced in catalyst bed 1

Fig 1: Simple scheme of SRU with split flow configuration

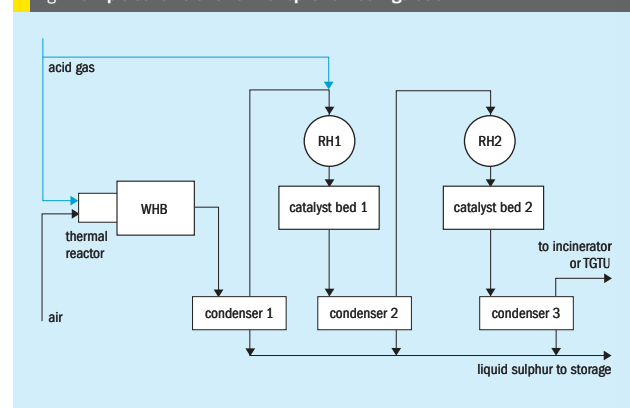
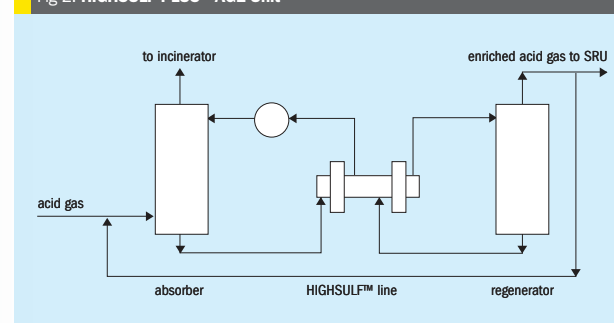


Table 1: Acid gas from regular amine unit, conventional AGE unit and HIGHSULF PLUS AGE unit

Components of acid gas	Fresh acid gas from regular MDEA unit, mol-%	Acid gas from regular MDEA AGE unit, mol-%	Acid gas from HIGHSULF PLUS AGE unit, mol-%
H ₂ O	6.4	6.4	6.4
H ₂ S	21.8	62.0	78.7
CO ₂	71.3	31.5	14.7
Methane	0.37	8.9 x 10 ⁻⁴	2.57 x 10 ⁻⁴
Ethane	0.05	1.9 x 10 ⁻⁴	5.41 x 10 ⁻⁵
Propane	0.05	2.5 x 10 ⁻⁴	7.45 x 10 ⁻⁵
Nitrogen	0.07	4.2 x 10 ⁻⁵	1.18 x 10 ⁻⁵

Fig 2: HIGHSULF PLUS™ AGE Unit



as reaction (2) proceeds to the right is condensed in condenser 2 and removed from the reaction system by draining to the sulphur pit. By removing the produced sulphur from the reaction area, the reverse portion (to the left) of reaction (2) is minimised as the sulphur reactant is removed. The remaining gas is sent to a reheater and then to catalytic bed 2 for further sulphur recovery. Sulphur formed in catalyst bed 2 is condensed in condenser 3 and separated from the remaining gas. The remaining gas (vent gas) is then sent to the incinerator or tail gas treatment unit. Condenser 1 in Fig. 1 is not included in many split flow units, since all the acid gas sent to the thermal reactor will always be converted to SO₂. Without any H₂S remaining in the thermal reactor effluent, reaction (2) will not proceed to produce sulphur.

While split flow sulphur recovery units have a long history for processing low H₂S content acid gas, that history has proven the thermodynamic limitations and the reduced sulphur recovery efficiencies available from that configuration. As the H₂S

concentration decreases, the amount of heat liberated by equation (1) decreases and maintaining stable combustion is increasingly difficult. Another important issue that is related to the acid gas composition is hydrocarbons.

Table 1 shows the acid gas components including hydrocarbons from a regular amine unit, conventional AGE unit and HIGHSULF PLUS AGE unit.

Hydrocarbons in the bypassed stream are sent to the catalytic reactors where they can reduce the life of the catalyst beds and contribute to contamination of the produced sulphur. Hydrocarbons in the thermal reactor feed will consume oxygen and increase the possibility of producing soot which will contaminate the produced sulphur and possibly deactivate the catalyst by plugging.

For these reasons many clients favour the installation of small acid gas enrichment units (AGE) that will raise the H₂S concentration of the feed gas to the SRU to the level acceptable for a Claus unit with straight through configuration.

Acid gas enrichment

There are different ways to enrich acid gas. As discussed in previous articles (*Sulphur No.s 318, 330, 342 and 346*), the patented HIGHSULF processes offer an effective technology for acid gas enrichment (AGE) and tail gas treatment. The technology is based on the use of generic N-methyldiethanolamine (MDEA) or any other solvent selective to H₂S removal. HIGHSULF enriches weak acid gas and makes the feed to the sulphur recovery unit (SRU) more suitable for straight through Claus unit design and operation. In addition to increasing the H₂S concentration of the SRU feed, this technology allows control of the H₂S concentration in the feed of SRU for stable and efficient operation of the SRU.

For new facilities, the HIGHSULF processes can be designed in place of the primary gas treating unit. Existing facilities can benefit from the HIGHSULF processes by installing an AGE absorber and accompanying regenerator on the acid gas from the existing primary amine plant regenerator.

The HIGHSULF PLUS process (Fig. 2) is a recent addition to the HIGHSULF processes and it is most effective for cases like the one described.

A versatile technology

HIGHSULF PLUS has potential application in gas processing, petroleum refining, oil associated gas, shale gas, coal gasification and chemical processing.

TKK Company has just completed the FEED of a HIGHSULF PLUS unit for a client in FSU and is working on another one for the Asian market with its alliance company Lexington Group International, Inc. (LGI). In both cases HIGHSULF has addressed the problem of treating gases containing lower than expected sulphur content.

New HIGHSULF PLUS AGE unit in the FSU

A refrigerated natural gas plant was designed to provide pipeline gas from a previously unproduced natural gas field. Since drilling was still taking place and since the completed wells were shut in, it was difficult to determine the "current" sulphur content of the blocked in field and whether the H₂S or CO₂ content will increase or decrease as the field is produced. Because of the many unknown factors, the plant designer typically designs for the highest concentration possible and accepts whatever turnaround that design allows.

This design approach resulted in an amine unit with the capacity to produce 1,460 Nm³/h of SRU feed with an H₂S content of 68%. The SRU was designed to operate either straight through or split flow. As the gas plant was commissioned, it quickly became apparent that the gas field was sweeter than expected and that field production was one to two years behind schedule.

The amine units were commissioned and initially only produced 960 Nm³/h of acid gas with an H₂S content less than 20%. Because of the low H₂S content, the low acid gas rate, and the harsh winter environment it was recommended by LGI and later by the licensor/designer of the SRU that it not be commissioned as designed.

An additional gas processing unit is being installed as the field production is being increased. The new gas processing unit will contain another amine unit and the acid gas from the two amine units will produce a combined rate of acid gas rate of 2,586 Nm³/h at an average 21% H₂S. To reduce the rate, and increase the H₂S concentration, these streams will be fed to a HIGHSULF PLUS AGE unit (Fig. 2) to produce a SRU feed gas of 750 Nm³/h at 78% H₂S. Additionally, the SRU will undergo mechanical modifications to the heat transfer and flow measuring elements for the design change and the reduced flow of acid gas.

Because of the extreme climatic conditions at the plant site, the AGE unit is designed to be primarily enclosed in a building. A 3-D design view of the AGE unit (without the building) is shown in Fig. 3. This unit is scheduled for detailed design and fabrication in the 4th quarter 2015 and start-up in mid-2016.

HIGHSULF PLUS in Asia

A sulphur recovery unit with HIGHSULF PLUS TGTU (Fig. 4) is currently under consideration for a large AGE unit in Asia for the treatment of effluent gases from coal gasification. Determining the sulphur content of coal not yet mined can be difficult. Also, the gasifier(s) and other catalytic conversion units may require extended initial operation (three to six months) at reduced rates on low sulphur feedstock. While extended operation at reduced rates on low sulphur feedstock may be best for these units, it makes operation of the SRU difficult if not impossible.

Environmental regulations require 99.5%+ sulphur recovery in most cases.

Fig 3: 3-D HIGHSULF PLUS™ AGE unit

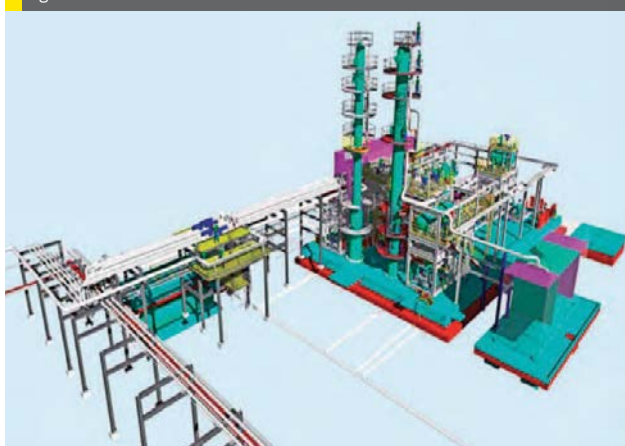
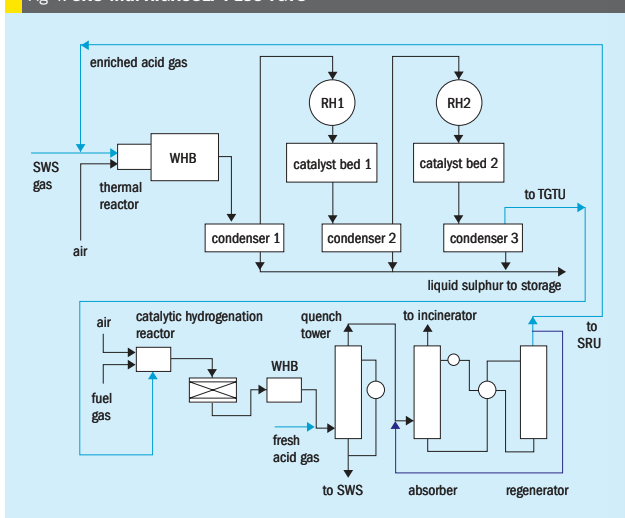


Fig 4: SRU with HIGHSULF PLUS TGTU



This requires SRU effluent treating before incineration. This treating unit is typically an MDEA based tail gas treating unit. In a recent technology proposal for this situation, the design basis for the acid gas clean-up unit (AGCU) was 8,658 Nm³/d at 33% H₂S. This composition is marginal for operation as a straight through SRU even with oxygen enrichment. From start-up and operating experience, it was known that the feed

gas H₂S composition and rate will both be much less during times of extended initial required operation.

HIGHSULF provided the solution to low H₂S composition and varying rate. By feeding the design or fresh acid gas to the TGTU, the H₂S concentration in the feed to the SRU can be increased to 68% H₂S. At the same time the feed rate to the SRU can be decreased by about 50% to 4,354 Nm³/h.



Jeffrey J. Bolebruch Senior Market Manager

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CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

Sulphur degassing

SULPHUR
ISSUE 358
MAY-JUNE 2015

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Maintaining your sulphuric acid plant

Corrosion problems are a common cause of downtimes in sulphuric acid plants. New developments in corrosion resistant materials have led to fewer and shorter downtimes helping to minimise loss of production capacity. **M. Salehi** and **A. Hopp** of Steuler-KCH GmbH discuss the importance of engineering, top-quality products and careful installation by highly qualified expert personnel for planning production capacities over the long term.

Despite the continuous developments in corrosion protection materials, the aggressive operating conditions in sulphuric acid plants lead to regular downtimes. During these downtimes the full gamut of corrosion protection work is carried out, from repairs to floors and ditches, to partial replacement of masonry in absorption towers, heat exchangers and pump tanks, to the switching out of complete components of the plant.

This kind of work is made more difficult by the extremely limited time frame available due to the need to minimise loss of production capacity. In addition, the presence of concentrated sulphuric acid throughout all parts of the plant necessitates comprehensive occupational safety measures to be taken. Masonry materials are virtually saturated with sulphuric acid after a certain time in operation. This means that work, for example within an absorption tower, is only possible with acid resistant rubber suits and external breathing apparatus. Due to the enormous physical strain this places on workers, such work has to be carefully planned in terms of scope, available time and the staffing capacities involved.

From a technical point of view, the work necessary to connect new pieces of masonry to existing linings is very difficult because the surface is contaminated with sulphuric acid. The aging processes induced by the sulphuric acid, such as those encountered on a polyisobutylene sealing strip in a drying tower, create difficulties when connecting the old liner to the new liner.

In sulphur burning sulphuric acid plants, a refractory masonry lining is

required to protect facilities due to the high reaction temperatures (1,200°C to 1,600°C). Any damage occurring in this area during operation is mainly caused by excessive temperature.

For example, if the oxygen content is too high during the combustion of sulphur it can cause an increase in the combustion temperature. Under extreme conditions, this can result in failure of the carefully constructed and finely tuned corrosion protection system. In the event that heat insulation is no longer sufficient, temperature break-outs into the steel and/or sintering processes within the masonry can occur. These can then be observed as changes in the technical properties of the lining which, in the medium term, can make replacement of the lining or even the entire facility, including the steel, unavoidable.

The time that elapses until this occurs, however, depends strongly on the materials used and how well they have been installed. As the mechanism by which the damage occurs is unknown, it is recommended that both the lining thickness

and the materials used for the lining be adjusted to take account of this situation. In other words, it requires the selection of high-quality products and an increased liner thickness.

In sulphuric acid plants, SO₂ gases from roasting or sulphur combustion enter a venturi scrubber, where they are cooled and cleaned. Here, the venturi head with its gas outlet and the nozzle ceiling are the main problem areas with regard to corrosion.

Chemical protection of the steel structure is usually provided by a rubber lining membrane that is either created as an in-plant prefabricated membrane or is applied on-site. To protect the rubber lining from excessive temperatures (the gases in the outlet have temperatures of around 400°C), appropriate protection in the form of masonry has to be applied. Plans will call for an insulating ply of foam glass as a first layer over the rubber lining, the result of a heat penetration calculation that will have to take account of the interior temperatures actually occurring along with such ambient values as

PHOTOS: STEULERKCH



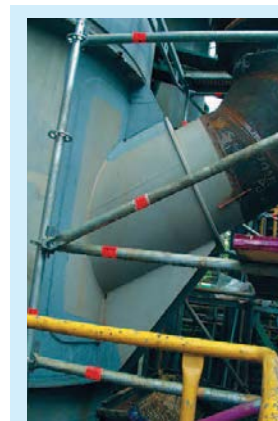
Replacement of the gas inlet nozzle of an existing absorption tower: after removal of the brickwork in the intermediate zone, the damaged nozzle was cut off and replaced.

exterior temperature, solar radiation and wind speed. The remaining structure of the plies can then be made up of one ply of light refractory brick and, as contact layer with the media, one ply of acid-resistant ceramic brick, jointed with potassium silica cement. The nozzle ceiling also has to be lined with temperature-reducing plies. The inner ply facing the media, however, requires a variety of different brick grades to be used, depending on the temperature, in order to withstand the high loads incurred by temperature fluctuations (hot/damp) in this zone. For temperatures up to 400°C, graphite brick is used, for higher temperatures highly refractory grades are used. In the damp area, i.e. the impact area of the cone, the lining will have at least two plies. The first ply consists of acid-resistant ceramic brick and the second, if required (for fluoride conditions) of carbon brick. The lower cone and the lower box usually have a single ply of masonry for cost reasons. Depending on the load, either acid-resistant ceramic brick or carbon brick is used.

Even with careful selection of the materials or material combinations to be used, the cement joints in the upper part of the venturi are often washed out, a commonly observed pattern of damage. Hot gas entering the venturi at temperatures of 350-400°C has to be properly cooled. The actual gas entry point is only exposed to a dry load and can be lined in the conventional manner with acid-resistant brick bedded and jointed in potassium silica cement.

The venturi ceiling connected to the gas inlet requires more complicated technical solutions on the side in contact with the media. In spite of their excellent resistance to acid, even at high temperatures, conventional potassium silica cements only display moderate to poor resistance to washing out. A switch to a potassium cement optimised especially for resistance to washing out is thus imperative.

The maximum temperature resistance of potassium silica cements presently available with the properties described is approximately 450°C, which is still about 50K above the typical temperatures of gas entering this type of equipment. It does not become problematic until a high temperature meets hydrofluoric acid, a combination typical for steelworks. Due to the poor chemical resistance of cements containing SiO₂ (these include potassium silica cements), only SiO₂-free cement materials can be used for those kinds of conditions. This limitation leads to a compulsory resin-bonded system based on furane resins. However, for all the advantages in terms of resistance to washing off and chemical attack, the problem encountered with this alternative is actually the temperature resistance values. At 300°C short-term peak resistance and a value of around 230°C for long-term resistance, all the resin-bonded systems currently on the market have reached their limits. Due to these limits to resistance, the joints in these areas have to be reworked at regular intervals. As a rule, these temperatures



Replaced gas inlet.

initially cause a kind of coking of organic material in the cement joints. The carbon-rich layer builds up and for a certain time acts as a protective layer, but will later be washed out of the joint. Experience over recent years has shown that if servicing intervals are maintained and the joints are repaired regularly, despite its weakness in terms of temperature resistance, the long-term stability and with it the operational safety of these alternatives (even in hydrofluoric acid loads) is preferable over time to the alternative offered by potassium silica cement.

The still damp SO₂ gas leaving the venturi scrubber is dried by coursing through a damp electric filter in a drying tower together with concentrated sulphuric acid and then led into a contact boiler. In principle, both the drying tower and the intermediate and final absorbers are very similar in their operating conditions. The conditions are caused by concentrated sulphuric acid (drying tower 93-98%, absorber 95-98%). Unalloyed steel (C steel) is resistant to sulphuric acid concentrations over 92-93% H₂SO₄ to a maximum of 25°C. The reason for this resistance lies in the formation of a thin layer of iron (II) sulphate. However, this layer is dissolved at higher temperatures and thus loses its protective effect. Carbon steel is also unable to withstand streaming sulphuric acid in the long term, as the thin passive layer is constantly being washed off. On the other hand, if a 2 mm thick ply of polyisobutylene liner is adhered to the steel surface and protected



To reduce the production loss, the bricklining job for a new furnace took place beside the plant while the existing combustion chamber was still in operation.



PHOTO: STEULERKCH

with masonry made of acid-resistant brick and suitable bedding materials, the result is a material composite that has virtually unlimited resistance to hot, concentrated sulphuric acid and attacks to the material from streaming abrasion. The decisive points for durability are the type of lining materials used and above all the correct installation of the masonry work.

Damage to the masonry can result in hot, streaming, concentrated sulphuric acid gaining direct access to the polyisobutylene liner. When this happens, the carbon-rich surface layer building up on the liner is constantly worn down by the current until the acid reaches the steel substrate. The effect of the formation of this protective layer on the liner only exists if this layer is not washed away i.e. if the masonry is intact and free from tears.

As a rule, therefore, the area beneath the cantilevered domed latticework is provided with three layers of masonry, two layers above the latticework around the packed bed and a single layer further above this (40 or 65 mm). This is, however, only a general guideline. In practice, the thickness of the masonry and the number of brick layers can and does vary, and will also depend upon the size of the tower. In order to avoid damage to the masonry and minimise downtimes, finite element analyses are carried out in the planning and construction phase to obtain details on the areas that are under particular threat at the transition points to fittings on the coated masonry, such as acid muffs or gas inlets, and to determine the procedures required to install the corrosion protection system. This type of lining using a membrane is standard for drying towers; intermediate and final absorber, on the other hand, are often provided with only one layer of masonry. In this case, a ply of potassium silica cement is trowel-applied to the blank sandblasted steel plate or adhered to the steel substrate with ceramic paper saturated in soluble potassium. The preliminary masonry, acid-resistant ceramic brick, bedded and jointed in potassium silica cement, is then applied. The adherence of potassium silica cement to steel is relatively poor and over time a gap can appear between the lining and the steel plate in which a thin film of concentrated sulphuric acid unavoidably gathers. Subsequently, a very thin layer of iron (II) sulphate crystals form on the steel plate, initially producing a passive effect. The protective effect is lost

at higher temperatures, however, because the iron sulphate goes into the solution.

Such layers of iron sulphate can grow considerably over time and create such tension in the masonry that a larger portion of the brick lining can break apart during repair work. Unfortunately, such phenomena often does not become apparent until repair or demolition begins, which in turn means that very rapid decisions have to be made with regard to further action to be taken. Depending on the location of the damaged area, it is sometimes impossible to break out large areas without compromising the structure and stability of the remaining masonry. In these cases the iron sulphate will remain on the steel casing as a passive layer. If any new ingress of hot concentrated sulphuric acid is prevented, the protective function of this layer will remain intact.

Regardless of the corrosion protection system used, it is inevitable that, after a certain time in operation, parts of the facility, such as the gas inlet in the drying towers or quenching towers, or even whole sections of the facility, will have to be replaced. The replacement of a gas inlet muff, which experience shows has yet to suffer damage, is, in technical terms, unproblematic. After removal of the old lining in the transitional area from muff to tank, the old muff is separated and lifted out of the plant. The new muff is then lifted into position and welded. After the required pre-treatment of the steel substrate by means of sandblasting, the new lining of this portion of the surface is easy to do. Problems only exist for the transitional area between the old and new corrosion protection system. To save time and thus prevent losses in production, there is, for instance, an opportunity to prefabricate as far as possible the membrane being planned for that area (rubber lining, polyisobutylene liner) so that only the contact points between old and new lining system have to be made on site. If partial repair is no longer possible, complete replacement of the entire facility will be the only possible option. When complete replacement is required, absorption towers and sulphur combustion furnaces pose a challenge due to their size, especially in terms of the downtimes required and actual time available. In order to drastically shorten both downtimes and with them losses in production, for several years facilities have been provided with partial replacement supplies of masonry (e.g. half the

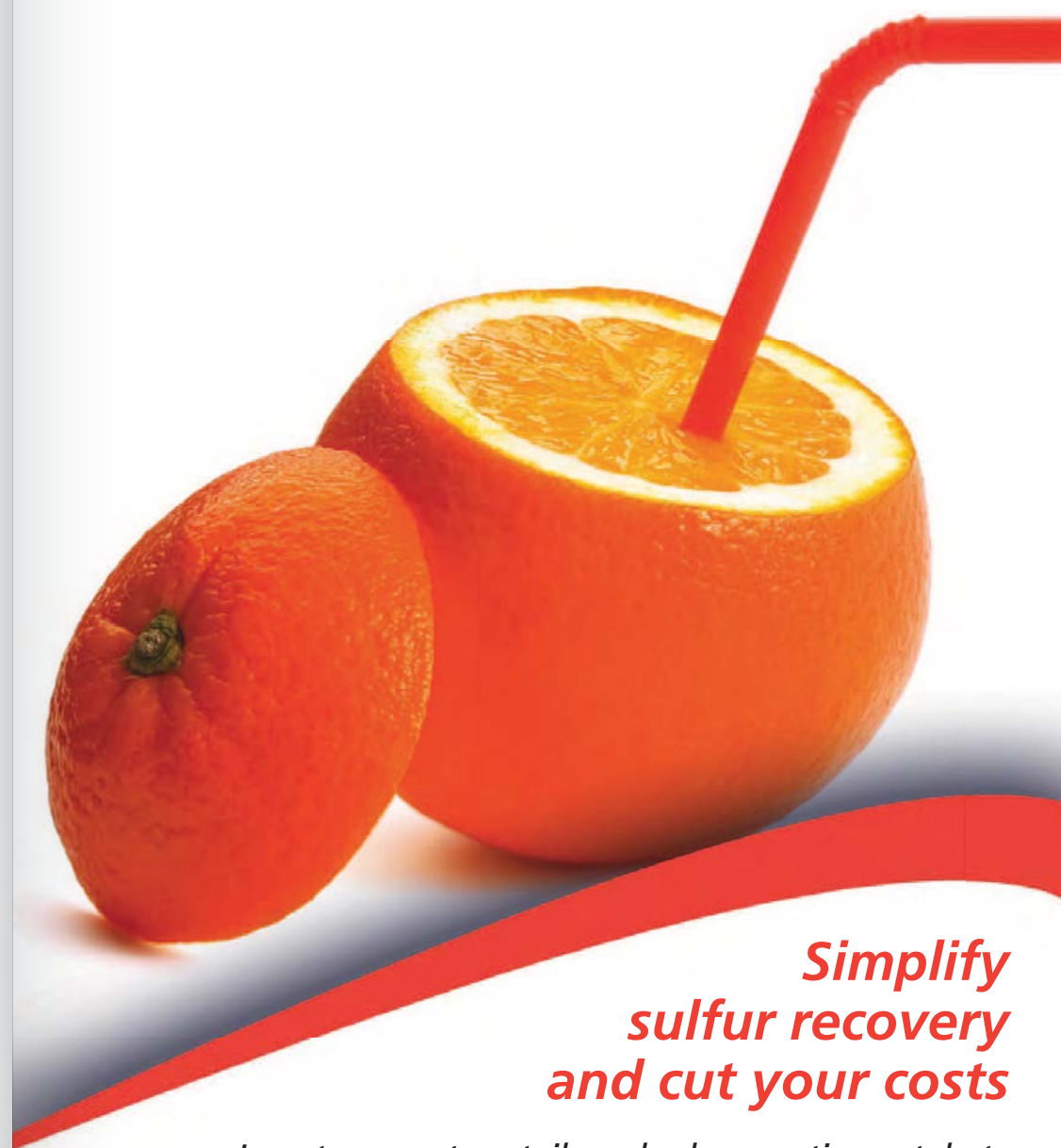


After finishing the corrosion protection, including self supporting dome, the tower was lifted into position by crane.

height of the drying tower including free-standing domed latticework) next to the existing facility (that is still in operation) which is then lifted into its final position in this condition with a heavy crane. It is not until this point in time that the actual downtime of the plant begin. In general, it must be stated that many problems cannot be found until the plant is shut down. Damage to the flange connections, for example, can naturally only be discovered after these have been unscrewed. During such downtimes, it is thus essential that all assembly personnel working on the site react rapidly to and have experience with such downtimes. Other important areas to be protected are the floors, trenches and channels in such a plant. Traditionally, protection of these areas is provided by liquid-tight coatings such as those on an epoxy resin or polyurethane base which are then covered with a ceramic tile bedded and jointed in phenol or furane resin or potassium silica cement. Gutters and channels are protected over the long term using the thermoplastic materials already described.

Summary

For decades now, a wide variety of materials have been used successfully in corrosion protection. The product range encompasses liners, linings using rubber or thermoplastic sheeting and combined systems. The extensive range of materials on offer allows installers to cover all sorts of loads and conditions in plants where sulphuric acid is produced and used. In the event of the failure of a lining after longer operating periods, further developments in application technologies and in the materials themselves make it possible to repair such damage quickly and efficiently. Due to the appropriate norms and quality-assurance steps taken during production, application and finishing of corrosion protection systems, a consistently high quality standard can now be assured. ■



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CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

Sulphur degassing

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Polymers in sulphuric acid service

In this article we report on fluorinated thermoplastic linings for sulphuric acid services, a unique and innovative approach to the design and inspection of FRP for fabricators and end users as well as recent and ongoing research into plastic materials for sulphuric acid services.

Fluorinated thermoplastic linings

The production and handling of sulphuric acid of various concentrations can lead to severe corrosion problems, unless adequate measures are taken to protect the equipment. For this, linings made from fluorinated thermoplastics (fluoropolymers) can be used. Fluoropolymers are very resistant to sulphuric acid, in particular fully fluorinated materials, which are not usually degraded by sulphuric acid at high or low concentrations. Hence, fluoropolymers are very good base materials for long-term resistance against corrosion in sulphuric acid containing environments without any measurable material loss.

Typical ways of installation are liner sheets or liner pipes, reinforced with fibre-reinforced plastics (FRP), structures from mild or stainless steel with bonded fluoro-thermoplastic linings (bonded steel lining) or liners with mechanical fixation. The choice of the lining materials and the

workmanship of the installation both play an important role in the performance of the lined equipment.

Condensing sulphuric acid can lead to severe corrosion problems, in particular if high temperatures and high concentrations of sulphuric acid combine. This can be a major problem for off-gas lines of sulphuric acid production plants, associated with copper, zinc and nickel mining. Here, even materials like titanium and ECTFE (a partially fluorinated thermoplastic) can be attacked in this extremely aggressive environment. Linings made from fully fluorinated melt-extruded thermoplastics such as FEP (tetrafluoroethylene-hexafluoropropylene) and PFA (polyvinylidene fluoride) are a proven option to solve these corrosion problems. They have a much higher temperature and chemical resistance than partially fluorinated thermoplastics like PVDF (tetrafluoroethylene-perfluoroalkylvinylether) and ECTFE (ethylene-chlorotrifluoroethylene), but share their outstanding processing properties, and

usually even exceed the chemical resistance of nickel steels and materials like titanium. They can be installed as sheets in tanks, reactors and other equipment for the general handling of sulphuric acid, but also in pipe dimension for the transport of gases and fumes.

The molecules of fluoropolymers consist of carbon chains, for which the hydrogen atoms in the side chains are partially (partially fluorinated) or fully (fully fluorinated) substituted by fluorine atoms, chemically bound to the carbon chains. The chemical bond between fluorine and carbon is extremely strong, and the fluorine atoms essentially protect the chemically relatively sensitive carbon backbone of the molecules against chemical attack. Chemical resistance means that the fluoro-thermoplastics do not show phenomena like weight increase (swelling by media uptake), weight loss (degradation or dissolution of the polymer) or change of the mechanical properties (for example embrittlement).

Table 1: Fundamental chemical resistance of melt-extruded fluoropolymers

Chemical media	Concentration and remarks	Upper service temperature limit, °C			
		Partially fluorinated		Fully fluorinated	
		PVDF	ECTFE	FEP	PFA
Sulphuric acid (H ₂ SO ₄)	70%	125	125	205	260
	90%	100			
	93%	75			
	96%				
	98%	50			
	100%	-			
Hydrogen sulphide (H ₂ S)	technically pure	100	50		
Oleum (H ₂ SO ₄ + SO ₃)	90 : 10 ratio	-	23		
Sulphur trioxide (SO ₃)	gaseous				
Sulphur dioxide (SO ₂)	gaseous	125	150		

The table does not consider temperature limits posed by the installation methods and only shows confirmed limits; higher temperatures might be possible.
Source: Quadrant EPP



UTComp monitoring of a FRP tank.



FRP is widely used for duct work.

The chemical and temperature resistance of fluoropolymers increases with increasing fluorine content. A real step in the chemical resistance properties can be observed when the system is changed from partially fluorinated polymers to fully fluorinated polymers (Table 1).

Fluoropolymers are technically discriminated into sintered materials like PTFE and modified PTFE versus melt-extruded fluoropolymers like PVDF, ECTFE, FEP and PFA (Fig. 1). Compared to sintered fluoropolymers, melt-extruded fluoroplastics have a number of technical advantages, caused by the fact that they form a liquid melt (in contrast to sintered fluoroplastics).

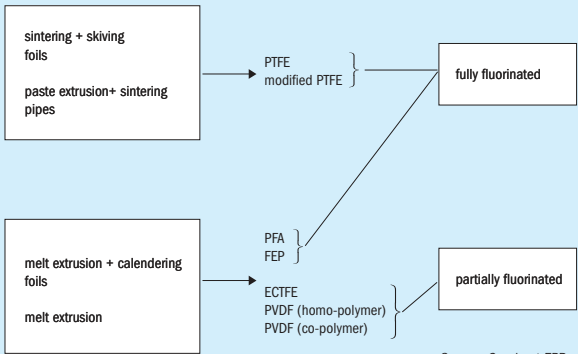
Particularly important are the outstanding weld- and thermoformability of melt-

extruded fluoroplastics. Both are crucial for the fabrication of tailor-made lining solutions and for the process safety of the lined equipment. The latter since the weld seams have to withstand the often extremely aggressive and sometimes even toxic media over a wide range of temperatures and pressures.

Furthermore, knitted fabric backings can be embedded directly into the melt-extruded polymers, which provide high bond strengths for bonded lining applications up to high temperatures.

Good workmanship of the lined equipment as well as a well founded knowledge of the lining materials used and their appropriate way of application are crucial for the performance of the equipment.

Fig 1: Fluoropolymers in the market



CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

Sulphur degassing

SULPHUR
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and skilled inspectors, reliability gains can result. There are limitations of this visual inspection process: confined space entry is almost always required, equipment must usually be evaluated during outages, most pipelines cannot be inspected, limited evaluation can be made of the structural condition of FRP and skilled inspectors are relatively rare.

For years, both end-users and fabricators have been searching for a reliable way of testing the strength and integrity of their fibreglass reinforced plastic (FRP) assets. They require a test that does not involve destructive methods or subjective visual inspections. With a lack of testing, many facilities have no understanding of the current condition of their FRP assets.

In response to repeated requests from end-users needing reliable and valid information about the integrity of FRP equipment and information about life-cycle planning, Canadian inspection and engineering services company UTComp Inc. has examined alternatives to traditional inspection techniques: acoustic emission, visual inspection and destructive testing. Utilising more than 50 years of engineering study, data and testing, UTComp has now developed a fast and innovative assessment process using ultrasound technology that can assess fibreglass assets without shutting down the facility.

The test results can allow maintenance teams to predict maintenance needs and the remaining service life of equipment. The method has been shown to be reliable and valid.

Applications

First consider the case where the thickness of FRP does not change appreciably over time and exposure to contents. This would apply generally for many applications. In this case, the percentage of design strength (PDS) value can be determined periodically, often while the FRP equipment is in operation. The analysis can be used to produce an ongoing history of PDS values (and corrosion barrier condition) for sections of the equipment.

The recommended way to monitor changes is to have a baseline for the FRP in the equipment when it is new, as some variability exists among all new FRP. If this is not available, the value for Normalized

Strength of 100 % has been used successfully. Using this "standard baseline" always assumes that the new FRP was at 100% of its design strength.

It is important to note that each set of readings is independent and the value of the starting point will not affect any data collected for the FRP. At the time of this writing, original baseline data for most FRP in use is not available. The standard baseline value has been found to generally yield conservative predictions for corrective action. As history for particular FRP develops, it is possible for the starting point to be adjusted or modified to match the data.

Remaining service life

The remaining service life is the time until corrective action is recommended. It is reported as the date when corrective action should be expected. In most cases remaining service life is calculated using a straight line model, similar to methods used for metal structures.

Reliable calculation of the remaining service life requires criteria for its calculation. The method used involves obtaining some information about the equipment from nameplates or drawings to determine design safety factors, age and operating conditions. This can usually be done during the first field evaluation. The next step is to determine the PDS where the safety factor is expected to be 2, and identify that as the critical PDS where corrective action is recommended. In addition, the PDS is determined where the equipment is expected to be at ¾ (75%) of its life. At this PDS, an engineering review is recommended to verify the critical PDS and identify potential reliability and lifespan improvements.

If very limited information is available, it is still generally possible to develop the required parameters based on experience and knowledge of FRP.

Condition monitoring

The condition monitoring process starts with some planning for the equipment to be monitored. The plans determine what sections of the FRP are to be tested by considering information available and safe working environment.

Readings are taken from the FRP according to written procedures from equipment that is empty or full and pressurized or evacuated.

After the readings are taken, the data from the ultrasonic testing (UT) equipment is exported to a computer program that prepares a data file. For most equipment, several data files are usually produced at an inspection. These data files are combined

for the asset into an inspection file.

The inspection file is then sent to an experienced engineer who completes the analysis using specialized computer software. Every reading is reviewed and calculations are performed. From each inspection file, a report is generated showing the results from all data files combined to present the FRP asset as a whole.

This will include history and calculation of remaining service life for the equipment as a whole, while recommending corrective actions.

Case studies

This process has been applied to several sulphur dioxide gas cleaning systems. Two cases are presented here.

Duct scheduled for replacement

The subject duct serves as a collector for two smaller ducts at the inlet to a drying tower. This duct is normally inspected internally during normal maintenance outages at 18 month intervals. On several occasions, the inspector identified need for immediate internal repairs. Before this ultrasonic examination, the other inspector recommended replacement of the duct section soon as it was in "poor condition".

The duct has an inside diameter of 2 m and operates at an internal pressure below atmospheric.

The inspection in this case was conducted to determine the urgency of duct replacement.

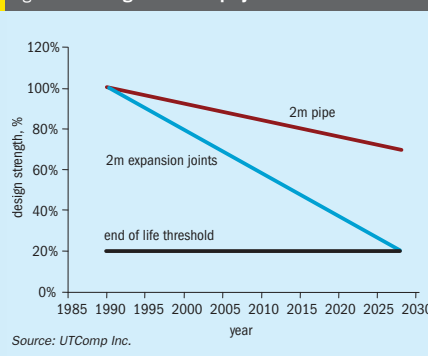
Data was collected from the outer surface of the duct and expansion joints and assessed resulting in the following conclusions:

- The PDS of duct sections averaged 83%.
- The PDS of expansion joints averaged 56%.
- The remaining service life of the duct was determined to be limited by the structural condition of the expansion joints.

The difference in PDS values of the expansion joints compared to the duct can be explained by the varying bending moments that are continuously carried by expansion joints. This will normally cause more rapid bulk modulus reduction than the relatively static external pressure load. Remaining service life projection of the duct is shown in Fig. 2.

It was concluded that immediate duct replacement was not required for the fore-

Fig 2: Remaining service life projection



Source: UTComp Inc.

seeable future. Periodic evaluations have been recommended to verify the rate of strength change.

In this example, there are two important items to note. First, this evaluation was conducted while the smelter and acid plant were operating, with no interruption of production. Second, personnel were exposed to minimal safety risk.

Precipitator outlet duct

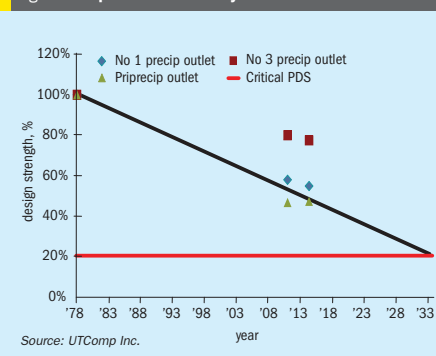
This duct was installed at a smelter in 1978. The owner established an ongoing evaluation of the duct starting in 2011. The chart in Fig. 3 shows the history and remaining service life projections developed to date. Based on the data, no significant action is recommended for some time.

Polymers research for sulphuric acid service

The Polymer R&D Group at Swerea KIMAB AB (former Swedish Corrosion Institute) has been working with polymeric materials in corrosive environment since the early 1980s. One of its focus areas is sulphuric acid services. Over the years it has worked in close co-operation with material and equipment suppliers and end users and has made a number of failure investigations together with systematic studies in the laboratory.

Despite all this work there are still a number of questions concerning the best choice of material and service life of polymers in sulphuric acid services. To tackle this the most important research activities have been identified as PVC materials, with a main focus on welding and welding rods, and fluoroplastics for high concentrations

Fig 3: Precipitator duct history



Source: UTComp Inc.

>93 wt-% and FRP (fibre reinforced plastics) and rubber linings for the concentration range between 72 to 85 wt-%.

Figure 4 gives a rough overview of possible polymer alternatives for different temperature and concentration intervals. For most polymers there is a strong correlation between the maximum concentration and the temperature. It is well known that fully fluorinated polymers such as PTFE, PFA and FEP have excellent chemical resistance to high concentration sulphuric acid. However, there is also industry demand for some less expensive alternatives, especially when the temperature and/or concentration are lower. Sulphuric acid below 72 wt-%, where it is fully dissociated, is generally not a problem for chemically resistant polymeric materials. The range that is therefore of interest to study is therefore between 72 and 100 wt-%.

It is clear that there is still some lack in fundamental understanding of the mechanism behind the reactions limiting the performance of polymers in sulphuric acid. There has been much discussion about the role of SO₃ on the corrosion in highly concentrated sulphuric acid. As can be seen in Fig. 5 there is a dramatic increase in free SO₃ with increasing concentration of sulphuric acid.

The results from some of the research performed by Swerea KIMAB on different polymeric materials in sulphuric acid is discussed below.

FRP

FRP has been investigated as a cost effective material choice for slightly lower concentration sulphuric acid, i.e. below 90 wt-%. Test coupons were exposed to sulphuric

acid of concentrations ranging from 72 to 90 wt-% and temperatures between 60 and 95°C for up to 260 days exposure.

It was found that the concentration had a larger influence on FRP corrosion than temperature.

These initial tests were performed as a first step toward understanding the influence of these two parameters. The next step is to address the chemical mechanisms for the degradation.

Rubber

Different types of butyl rubbers (bromobutyl, chlorobutyl and chlorobutyl-PVC rubber) to be used as lining materials on steel have been investigated. The samples were exposed in a single-sided "cup test" with 70, 80, 85 and 90 wt-% H₂SO₄ at 80°C. It was found that there was a dramatic effect with increasing concentration for the performance of the rubbers.

No significant changes in weight, thickness or hardness occurred until the degradation started. Thereafter all these parameters changed drastically.

HDPE

According to chemical resistant tables polyethylene is not usually recommended for concentrations above 80%. In Swerea KIMAB's experience it is, however, often used at concentrations up to 96 wt-% at low temperatures, i.e. up to about 20°C. Studies of HDPE that has been used for up to 22 years for sulphuric acid at 96 wt-% have shown that there is an oxidised surface layer of about 0.2 to 0.3 mm. As long as the material is free from stress this might not be a problem. However, care should be taken when selecting PE

CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

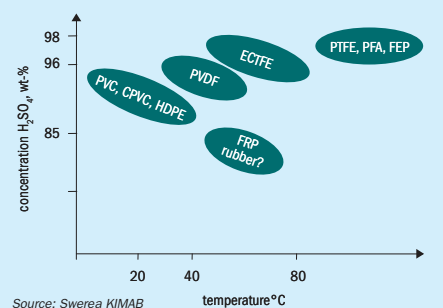
Sulphur degassing

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Fig 4: Concentration temperature performance of polymeric materials for sulphuric acid



Source: Swerea KIMAB

for such application as other grades of PE, possible welds and internal stresses might influence the material suitability.

PVC

Due to a number of failure cases related to stress corrosion cracking of PVC externally reinforced with FRP in high concentration sulphuric acid, a laboratory study on the strain corrosion of PVC exposed to concentrated sulphuric acid was initiated. The investigated parameters were the material grade, the acid concentration and the initial strain level. In addition, calculations were made of the initial strain level in the PVC after external reinforcement with FRP, in dependence of the curing exotherm. The minimum time for crack or craze formation was determined. There was a difference between the materials in the appearance of cracks and/or crazes formed.

In addition to the practical lab study a project is currently running together with the Royal Institute of Technology in Stockholm using a simulation approach with the ultimate goal to predict SCC by computer simulation.

CPVC

There is a fundamental lack of knowledge on simultaneous action of a strong acids and mechanical stress. To be able to investigate this, a test rig has been designed and construction by Swerea KIMAB AB and Scanacon.

Tests have been carried out on CPVC pipes at 40 and 50°C, at 5 bar of internal pressure and with 96 wt-% sulphuric acid. The testing was performed on commercially available pipes with an outer diameter of 32 mm and a rated pressure class

of PN16. It was found that the processing conditions have a major effect on the performance of the pipes. Of two pipes that were made from the same raw material but by two different pipe manufacturers one failed within three weeks at 50°C whilst the other was still intact after eight weeks.

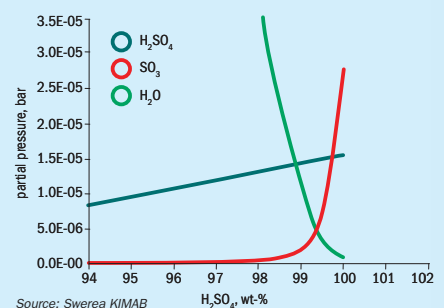
One major concern for CPVC is the possibly negative effect from the phasing out of led from the industrial grade weld rods available. There is at the moment a need for more research and data.

PVDF

There have been a number of failures for PVDF piping for concentrated sulphuric acid service. One reason for this is that many plants are now using higher concentrations of acid than in the past (up to 98 wt-% compared to 93 wt-% previously). It is believed that the failures are a result stress corrosion cracking by SO_3 but the mechanism for this is still not fully understood. There have also been some cases with cracking occurring in socket welds, and another case showed that cracking may also occur at sharp edges in bends and in IR-butt-welds.

ECTFE

ECTFE generally performs better than PVDF at high concentrations H_2SO_4 and is not considered to be as sensitive to stress corrosion cracking as PVDF. However, it has been found that ECTFE with an older type of process stabiliser can be subjected to local path penetration (known as "treeing") of concentrated sulphuric acid. In ECTFE without the old stabiliser the corrosion is very slow. The corroded layer is oxidised but no brittleness can be found.

Fig 5: Partial pressure of H_2SO_4 , H_2O and SO_3 as a function of H_2SO_4 concentration at 90°C

Source: Swerea KIMAB

Other work

In other recent work, several clear casts of resins have been exposed to sulphuric acid in harsher than recommended environments. The results indicated that the pure resins have the capacity to work in these harsher environments.

The findings are a good starting point for finding resin-fibre combinations with better corrosion resistance that could be used for intermediate-high concentrations of sulphuric acid.

Future work will select the most promising resins and continue with fibre-reinforced laminates. Various fibres and sizings will be tested and optimised to minimise the local attacks of sulphuric acid. The work will increase the understanding of the disc cracks/cracking of the resins at 40°C in 85 wt-% H_2SO_4 .

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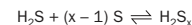
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Making sulphur safer

At best, undegassed Claus sulphur results in nuisance odours, adversely impacts sulphur grinding and increases friability of formed solids. At worst, it results in fatalities and explosions. Although still not mandated in many countries, including the US, degassing to <10 ppmw total H_2S is generally recognised by the industry as a best practice. Recent improvements to sulphur degassing processes are reported, including the first in-situ sulphur degassing technology for refineries and gas plants.

Claus sulphur typically contains 300 ppmw H_2S , nominally ranging from 600 ppmw in the waste heat boiler rundown to 10 ppmw in the final condenser. The liquid sulphur removed from the process gas stream in each condenser will contain dissolved H_2S in the form of hydrogen polysulphides (H_2S_x) and H_2S in equilibrium with the process gas. If this dissolved H_2S is not removed, it will evolve from the sulphur product during storage and/or transport creating potentially hazardous conditions. Degassing the sulphur to reduce the H_2S content considerably reduces the potential hazards.

Contrary to the general laws of nature, apparent solubility increases with temperature, and is reduced less than expected upon equilibration at lower temperatures. This apparent anomaly was eventually explained by the realisation that, above 150°C, "dissolved" sulphur exists predominantly as hydrogen polysulphides – weakly bound polymeric combinations of H_2S and elemental sulphur formed as follows:



Hydrogen polysulphides are insidious for a couple of reasons:

- Natural decay results in the gradual evolution of H_2S , invariably accumulating to dangerous levels. H_2S is toxic at 70 ppmw and lethal at 600 ppmw. Lower explosive limits (LEL) range from 3.5 vol-% in air at 150°C to 4.3 vol-% at 20°C, with a relatively low auto-ignition temperature achievable by, for example, a static electric spark – not unlikely since sulphur is a poor electrical conductor.
- Polysulphide decomposition is accelerated by agitation and exposure to air, such as during pumping and transport.

Truck and railcar vapour space H_2S levels as high as 7000 ppmv have been measured during loading of undegassed sulphur, and are invariably above the LEL at the delivery point. Tests by Elf Aquitaine (SNEA) in the 1960s concluded that 15 ppmw is the upper acceptable limit for total H_2S in liquid sulphur to ensure H_2S levels safely below the 4.3 vol-% LEL in the vapour space of transportation tanks. On that basis, industry has generally adopted a 10 ppmw H_2S degassing target.

While safety is the primary driver for degassing, friability of solid sulphur formed from undegassed sulphur is generally much higher, resulting in more sulphur fines and dust during handling and shipping, and continued evolution of minor H_2S during solid storage generates nuisance odours.

Liquid sulphur degassing

Traditionally, liquid sulphur degassing is carried out in a concrete pit or in a vessel, and is often combined with collection and (temporary) storage of liquid sulphur. A carrier gas readily removes the free H_2S by partial-pressure reduction. Oxidising gases (usually air but also others, eg SO_2 and Claus tail gas) have proven superior to inert gases such as steam or nitrogen, suggesting that polysulphide decomposition is promoted by oxidation of the H_2S component. It arguably follows that a large part of the H_2S is not actually stripped from solution, but oxidised to sulphur, or at least SO_2 , which is readily stripped.

When sweep air is vented to the incinerator (as opposed to the reaction furnace, for example) excessive sweep rates should be avoided to limit the contribution of sulphur vapour losses to emissions.

Steam is generally considered to be a more effective stripping gas than nitrogen, but is also reportedly prone to corrosion. In the case of Claus tail gas, associated H_2S renders the approach to free- H_2S equilibrium particularly important to meet 10 ppmw H_2S in the sulphur.

All major degassing processes employ a combination of agitation and contact with an oxidising sweep gas. Some also utilise a liquid or solid-bed catalyst to reduce the residence time and/or cooling.

Agitation

Agitation promotes intimate gas/liquid contact, and also creates shear forces conducive to the mechanical breakdown of the polysulphide chains. Methods typically include pumped recirculation to sprays or mixers, tank impellers and gas sparging.

Catalyst

Fixed beds of Claus catalyst (activated alumina) are employed to a limited extent. More common, and controversial, are liquid catalysts such as ammonia, ammonium salts (e.g. ammonium thiosulphate), and organic nitrogen compounds (e.g. alkyl amines, urea). In fact, the superiority of steam over nitrogen is attributed to trace levels of boiler water treating chemicals, presumably amines in particular.

Many conclude from experience that small quantities of residual catalyst can result in downstream salt deposition, corrosion and other problems. Examples cited include increased plugging of acid plant sulphur burners, salt build-up in transportation tanks with increased tare weight, fouled heat transfer surfaces and increased friability of formed solid sulphur.

CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

Sulphur degassing

SULPHUR
ISSUE 358
MAY-JUNE 2015

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It is not clear to what extent such problems may be attributable to overdosing.

Cooling

While pre-cooling the sulphur to 130-140°C slightly increases the solubility of free H_2S , the greater benefit is increased O_2 (or SO_2) solubility, since the oxidant must first dissolve in the sulphur in order to be available for reaction with H_2S .

Vent gases

Vent disposition is an important process decision in new designs for efficiency. The vent gases from stripping (which contain H_2S , SO_2 and sulphur vapour) can be treated in several ways. Traditionally the vent gases are routed to the thermal oxidiser, contributing to higher SO_2 emissions. If necessary the SO_2 can be removed by scrubbing, e.g. caustic scrubbing or treated in a Cansolv SO_2 scrubbing system to reduce the emission levels. However, due to increasingly stringent air quality regulations, vents from degassing, rundown pit sweeps, and storage tank sweeps are more commonly being directed to the main burner/reaction furnace. This option requires either a recycle blower or an ejector to pressurise them unless degassing is carried out at elevated pressure.

AMGAS vapour treating process solutions

In response to the increasing industrial awareness towards preventing liquid sulphur off-gas emissions from reaching the atmosphere (i.e. H_2S , SO_2 and S_8 vapour), AMGAS has initiated a programme geared towards improving its chemical scrubbing technologies in molten sulphur applications, e.g. molten sulphur degassing, remelting and storage operations.

AMGAS offers high gas rate (HGR) scrubbers for scrubbing liquid sulphur emissions. These scrubbers were originally designed to scrub gases flowing at high standard gas volumes with minimum back pressure in the scrubbing zone. Although high gas flow rates are not usually encountered when scrubbing liquid sulphur off-gases, limiting back pressure within scrubbing equipment is still critical in liquid sulphur applications. Back pressure build-up during liquid sulphur vapour scrubbing is typically caused by flash freezing of elemental sulphur vapour entering the scrubbing zone, thus forming solids in the system. AMGAS experience is that

the elemental sulphur entering the scrubbing zone typically has a low solubility in the chemical (depending on the choice of chemical and temperature), that is usually exceeded very quickly under typical steady-state operating conditions.

AMGAS HGR scrubbers (HGR 1500 and 5000) feature an ideal design for molten sulphur vent gas treatment. The inlet knock-out achieves liquids separation from wet gas prior to encountering the scrubbing zone. For liquid sulphur scrubbing applications, AMGAS has observed the zone to be effective for condensing and solidifying small amounts of sulphur vapour prior to liquid chemical contact. Field observations have been made of solid elemental sulphur particulate collecting in the knock-out, not impeding operation of the scrubber but requiring removal during periodic cleaning/maintenance of the equipment.

As the gas enters the scrubbing zone, the sulphur-containing gases (H_2S , SO_2 and S_8 vapour escaping the knock-out) are scrubbed by the chemical (e.g. Absorbital™ 320). After the gas is scrubbed free of sulphur species, it enters the outlet vent for release to atmosphere. For lower volume displacement of solution gas from liquid sulphur, the outlet is designed simply with a vent stack. Alternatively, the outlet vent can be configured with a blower designed to draw breakout gases through

the scrubber from the upstream liquid sulphur source. This configuration would be a typical application for a sulphur remelt pit operation.

Higher tonnages of either H_2S and/or SO_2 in the process could in fact warrant installation of two scrubbers in series for gas processing in these systems. This is because maximisation of the absorption capacities for H_2S and SO_2 in two independent chemical volumes would translate into minimised chemical consumptions long-term throughout the project. Thus, payback for the capital costs associated with installing the second scrubber should be quickly recovered by the capital savings in operating the system in this configuration (i.e. reduced consumable chemical costs/disposal costs over time). Liquid sulphur off-gases containing $SO_2 \gg H_2S$, $H_2S \gg SO_2$ or large tonnage $H_2S = SO_2$ could all be predicted to behave the same in a dual stage system (Fig. 1). As the process gas enters the system, the bulk of the elemental sulphur vapour would first be knocked-out. The first scrubber would effectively remove all the SO_2 and elemental sulphur from the gas, the second scrubber in series would remove the H_2S in the process. The dual stage scrubbing scheme will provide a long-term cost benefit to the end-user operating in high tonnage H_2S/SO_2 job scopes.

Fig 1: AMGAS single vs dual stage gas scrubbing

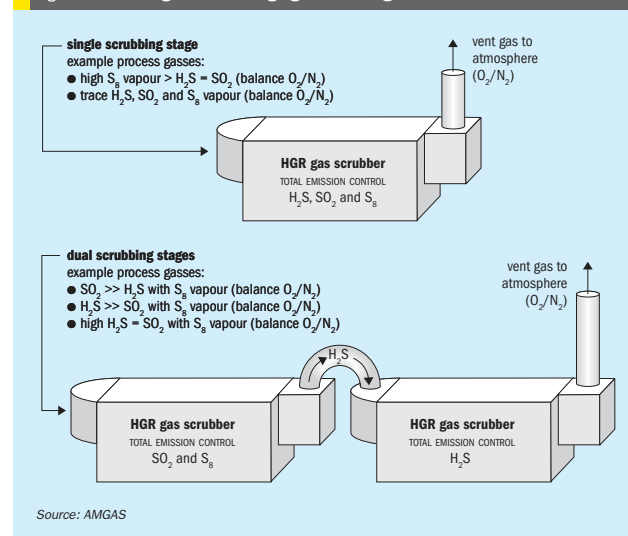
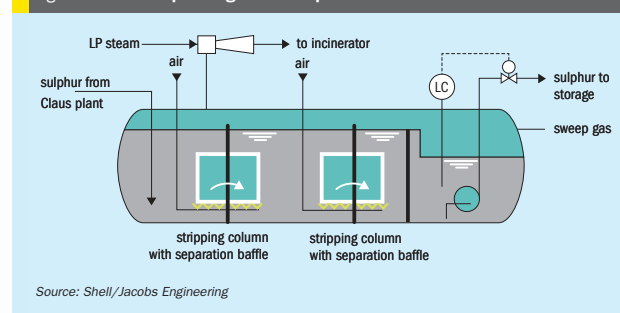


Fig 2: The Shell sulphur degasification process



Shell sulphur degassing process

The Shell sulphur degassing process, licensed by Shell and Jacobs Engineering, is a workhorse in sulphur recovery. This well-established technology, which strips liquid sulphur using air at atmospheric pressure, reduces the hydrogen sulphide (H_2S) and polysulphide levels in liquid sulphur to less than 10 ppmw. With more than 330 units installed worldwide, it has proven its technical and commercial value.

Figure 2 shows the Shell degassing process which uses air as the sweep gas. The stripping air for the process is supplied through spargers located below two or more bubble columns.

Shell degassing at elevated pressure

With emission targets becoming increasingly tougher to meet, capturing the sulphur in the degasser off-gas is an effective way of achieving these targets. Modifications to the existing Shell sulphur degassing technology so that it can operate at a slightly elevated pressure (about 0.9 barg) now enables the off-gas from the degasser to be recycled to the Claus unit. This helps producers to achieve the most stringent emission standards mandated in different jurisdictions.

Increasing the pressure of the stripping air boosts the decomposition rate of polysulphides, which results in a higher degassing rate. Shell has applied this principle in its Shell degassing at elevated pressure

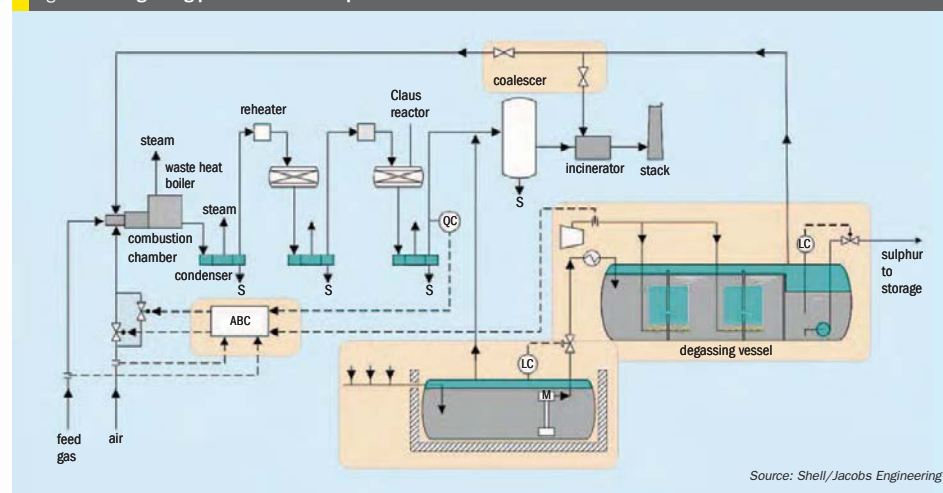
process, which has been on the market for several years.

What drove the development of this pressurised degassing was not increasing the degassing rate, but rather a wish to recycle the vent gases back to a Claus sulphur recovery unit. This eliminates the need for recycle blowers or ejectors, as recycling is done by virtue of the over-pressure in the degassing vessel. It is an elegant way to solve the problem of vent gases that would otherwise be routed to the thermal oxidiser and add to the total emissions of SO_2 .

Degassing at elevated pressure is applied in a vessel and can be retrofitted to an existing sulphur vessel. It cannot be applied in a concrete pit. This change to vessels coincides with a general trend towards using vessels instead of concrete pits for storing and degassing sulphur. This preference is safety and maintenance related. A concrete sulphur pit is not a pressure vessel, so the containment cannot be made intrinsically safe. Sulphur causes concrete to deteriorate and concrete is difficult to repair. A lack of heat insulation also means acid corrosion of the steel reinforcement is a problem, and it is very difficult to make the pit leak tight. A pressure vessel, however, can be designed to be intrinsically safe by normal practices.

A process scheme for a degassing installation that operates at elevated pressure is shown in Fig. 3. Sulphur is collected

Fig 3: Shell degassing process at elevated pressure



CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

Sulphur degassing

SULPHUR
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from the sulphur seals in a collection vessel, which also takes care of ventilating the rundown lines and seals, as gases are vented to the coalescer. The liquid sulphur is then pumped to the degassing vessel via a sulphur cooler, if necessary. The stripping air can come from a reliable Roots blower and its pressure is controlled to ensure there is always a slight overpressure towards the Claus main burner. This ensures positive flow from the degassing vessel to the burner without needing vulnerable check valves. The stripping airflow is measured upstream of the vessel where the air is clean. The flow signal is used in the burner control system to compensate for the quantity of vent gas fed to the main burner. This is done by automatically adjusting the total air demand.

By operating the well-established Shell degassing process at an elevated pressure, recycling of the vent gas to the main burner is easily accomplished and SO₂ emissions can be kept to a minimum. This modified process only requires a limited amount of extra hardware. Several projects utilising pressurised degassing are currently in the design phase.

HySpec™ degassing unit

Enersul Limited Partnership, located in Calgary, Alberta, Canada, developed the HySpec H₂S degassing system (Fig.5) in response to the sulphur industry's need for a compact and efficient sulphur degassing process. This process has been specifically designed to rapidly and economically reduce the H₂S concentration in liquid sulphur by utilising several concepts:

- aeration
- agitation
- introduction of a catalyst
- residence time.

The in-line, continuous flow design of the HySpec process eliminates the need for large molten sulphur pits typically required with traditional batch-type degassing systems. Additionally, the modular configuration of each train significantly minimises onsite construction and preparation work required at the field location.

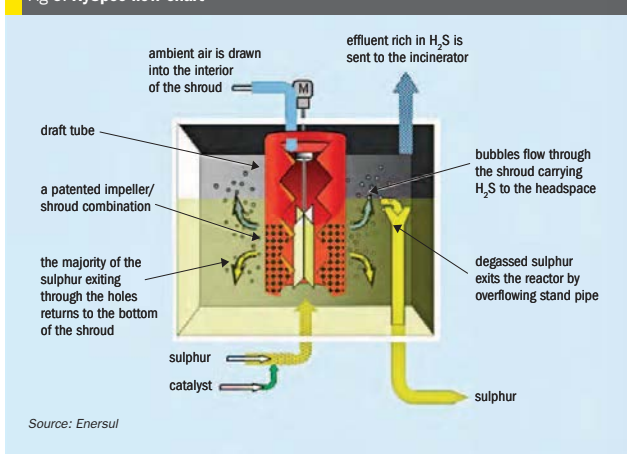
The HySpec process uses gas-liquid contact inside a series of reactor cells and a select catalyst to aid in the rapid decomposition of hydrogen polysulphides (H₂S_x). HySpec reactor cells are fabricated with the processing equipment mounted on top. Each reactor consists of a closed

Fig 4: HySpec plant at night



PHOTO: ENERSUL

Fig 5: HySpec flow chart



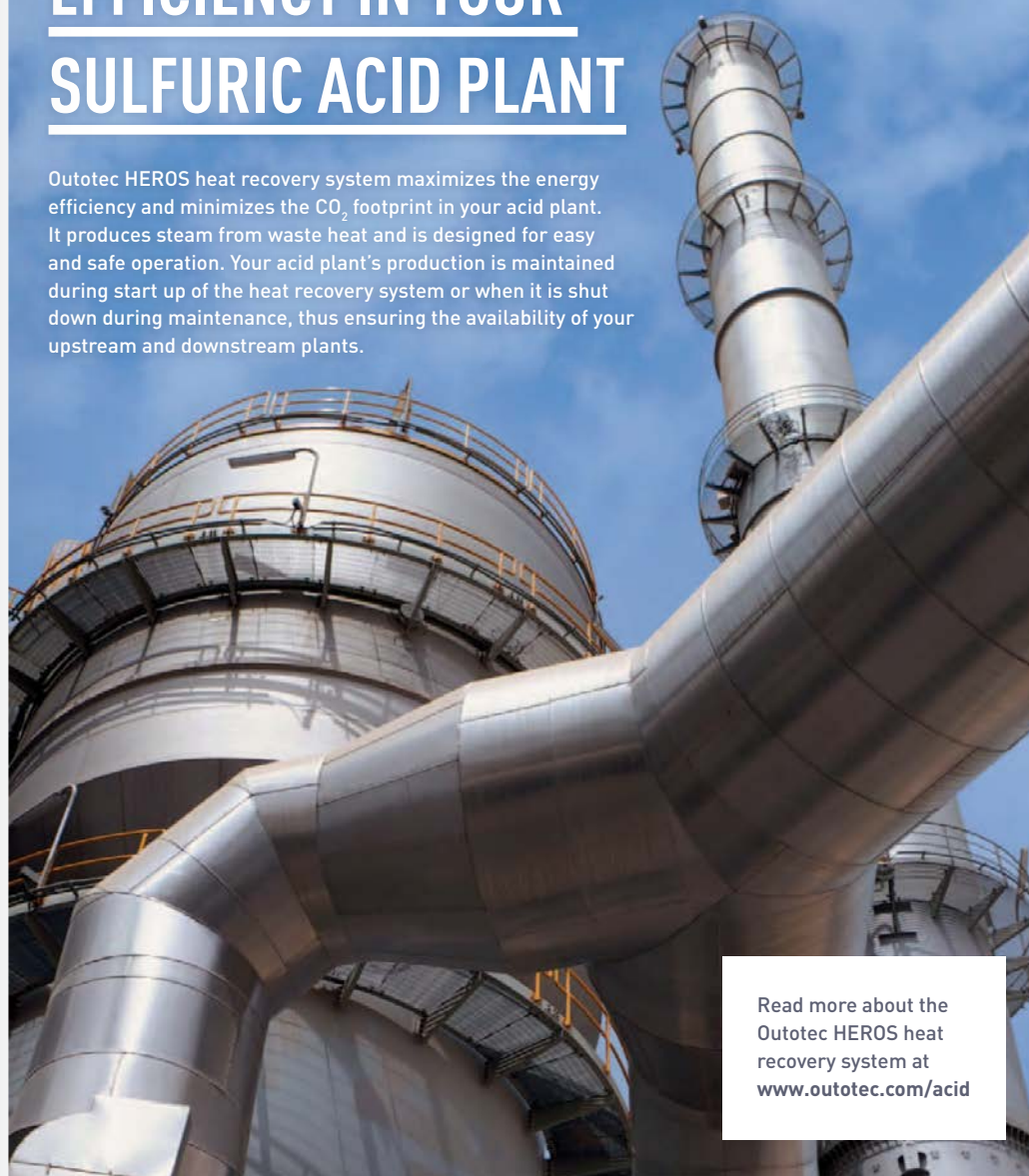
cell with a centrally mounted impeller located inside a shroud. This shroud is a tube, which extends from the roof of the cell into the liquid. It is extensively perforated in the region submerged in the liquid sulphur. The reactor is a very efficient gas/liquid contacting device, yet remains simple in design. The number of reactor cells required depends on the liquid sulphur flow rate and input H₂S concentration.

Incoming molten sulphur, rich in H₂S, is pumped to the bottom of the first reactor cell, and flows over a stand-pipe into a drain leg connected to the inlet of the next reactor cell. Retention time within the cell is only minutes, as gravity flow is continuous through each subsequent cell.

The HySpec process utilises an amine catalyst to enable rapid decomposition of H₂S_x present in the sulphur to H₂S. An important factor in the selection of the catalyst is its volatility, which allows the chemical to evaporate and quickly exit the process along with the stripping air. The catalyst presently used in the HySpec is very active in encouraging H₂S_x decomposition; catalyst concentrations of less than 20 ppmw in the liquid sulphur are sufficient for degassing. A small amount of catalyst is pumped into all but the last reactor in a train to enhance conversion of the hydrogen polysulphides (H₂S_x) to hydrogen sulphide (H₂S). No catalyst is pumped into the last reactor in the train, as it is a

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CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

Sulphur degassing

SULPHUR
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"purge" reactor, dedicated to the removal of the catalyst.

In operation, air is pulled in through a heated intake duct and then into the shroud assembly where it contacts the liquid sulphur, which is being agitated by the impeller. The impeller produces a large number of tiny bubbles by intense mixing and shearing in the impeller zone. The high shear rates generated by the impeller causes intimate contact and thorough mixing of air, sulphur, and catalyst. The catalyst causes the H_2S_x to quickly decompose to H_2S , and the H_2S is rapidly transferred from the liquid phase to the gaseous phase by the agitation and airflow.

The bubbles and sulphur then pass through the perforations in the shroud into a quieter region in the cell. The H_2S rich bubbles rise to the surface of the liquid and reconstitute in the headspace of the reactor cell. The H_2S rich effluent is drawn off by an exhaust fan to be incinerated (or treated in a scrubber). The sulphur is repeatedly drawn back into the shroud for exposure to the incoming ambient air.

Through the use of a blower on the exhaust side of the degassing train, ambient air is drawn into and through each reactor cell and is exhausted into ducting. The H_2S enriched effluent can then be routed to a suitable effluent treatment system such as a thermal oxidation system. This design maintains a negative pressure in each reactor which prevents the fugitive release of H_2S gas.

The liquid sulphur can be pumped or gravity fed into the degasser. Exiting the degasser, the sulphur can be gravity fed to a small pump tank, drained to a holding pit or directly pumped to a degassed sulphur storage tank. Heating coils are installed in the bottom of each reactor to maintain the temperature in the liquid sulphur. All sulphur piping supplied with the HySpec system is steam jacketed.

HySpec has been designed for easy maintenance and safety. A flow-measuring device is used to monitor the airflow through each reactor and will activate an alarm and shut down the process should there be a disruption in airflow. The system is designed such that there will be no release of H_2S into the working area. In addition, all rotating equipment is supplied with safety guards which are removable for servicing.

The HySpec degassing system can be controlled using the existing gas plant DCS system or a standalone PLC. Each degas-

sing train is skid-mounted and is supplied with all the instrumentation and components fully assembled. Field installation is relatively simple and requires hook-up of the sulphur, steam and exhaust lines to the client's interface for these components.

The commercial installations of the HySpec units in Alberta, Canada have been in continuous operation for over 20 years in a high H_2S containing liquid sulphur environment and have met all performance guarantees through this period.

Siirtec Nigi sulphur degassing process

The Siirtec Nigi sulphur degassing process is applied in sulphur plants to reduce the total hydrogen sulphide (H_2S) and polysulphides (H_2S_x) concentration down to less than 10 ppmw.

The process consists of a concrete degassing box equipped with two or more degassing sections. Alternatively the degassing system can take place in a stainless steel degassing column, where sulphur flows upward co-currently with air and then flows by gravity to the receiving vessel.

Each section is equipped with rectangular mass transfer elements. Atmospheric air is co-currently bubbled through the elements with the aim of providing intimate mixing between the gaseous and the liquid phase and promoting mass transfer between the two phases.

The degassing box is designed to properly distribute atmospheric air inside the undegassed liquid sulphur, facilitating the release of H_2S and therefore producing

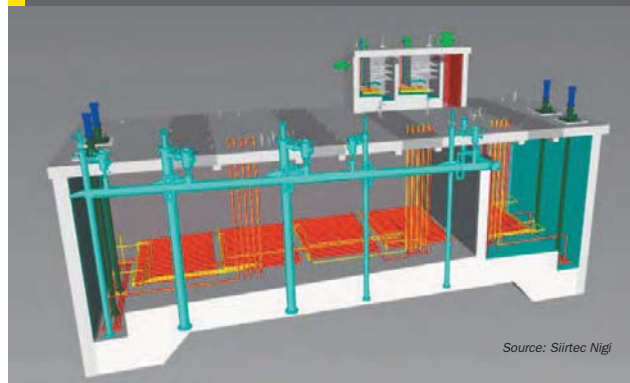
safe degassed liquid sulphur for export/storage.

Most commonly the degassing box is installed above a sulphur storage pit, saving plot space. However the degassing box can also be installed externally from the pit and can be designed in various rectangular forms depending on the layout constraints. An example of a degassing system above the sulphur pit is represented in Fig. 6.

Usually the sulphur pit is divided into two sections separated by a partition wall: the undegassed sulphur section and the degassed sulphur section. The sulphur pit provides the operating storage capacity for the undegassed and degassed liquid sulphur. The elemental liquid sulphur produced in the Claus section condensation steps is discharged by gravity flow to the sulphur pit through fully steam jacketed hydraulic seals. From the undegassed sulphur section, liquid sulphur is sent by flow control to the sulphur degassing box by means of sulphur transfer pumps, in order to carefully control the flow of sulphur entering the contacting sections. Finally the degassed sulphur drips from the degassing box to the degassed section of the underlying sulphur pit equipped with sulphur delivery pumps which drive the on-spec liquid sulphur to the downstream units. The sulphur pit and the sulphur degassing box are connected on the gas side and operate under slight depression by means of ejectors which use saturated steam as carrier medium. Negative pressure leads to a better hydrogen sulphide stripping by means of atmospheric air.

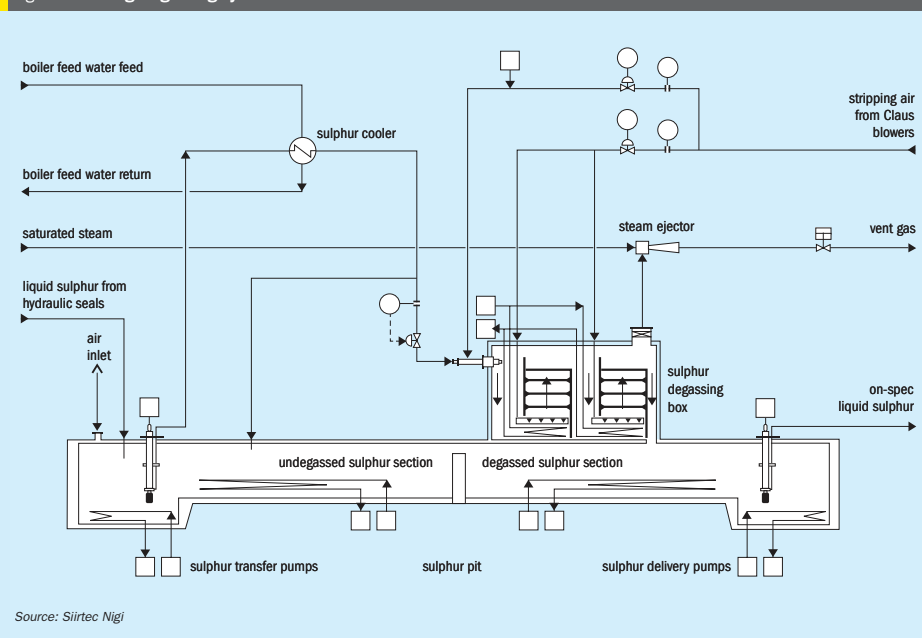
The sulphur pit is made of concrete and its internal surface is covered by a layer of anti-acid bricks assembled with

Fig 6: Degassing system above sulphur pit



Source: Siirtec Nigi

Fig 7: Siirtec Nigi degassing system



Source: Siirtec Nigi

acid resistant mortar. The degassing box is also made of concrete and is internally lined with stainless steel (alternatively an all metal construction can be used). Stainless steel is used for the degassing box internals since all elements are potentially involved in the condensation of sulphur mist entrained in the sweep gas.

The Siirtec Nigi degassing system has the following advantages:

- simple process with a compact layout;
- no use of catalysts with consequent low operating costs and high liquid sulphur quality (no chemical residues are present);
- no additional compressor is required for stripping air.

Figure 7 illustrates a typical process flow diagram of the Siirtec Nigi degassing system consisting of a two stage degassing box installed over the sulphur storage pit.

The liquid sulphur pumped from the undegassed sulphur pit compartment to the degassing box is driven against a vertical steel baffle through a dedicated spray nozzle where sulphur is contacted with air and steam. With such a configuration

a first mechanical separation of hydrogen sulphide from liquid sulphur occurs.

The liquid sulphur which enters the degassing box is collected in the chamber delimited by the first vertical concrete wall, present in the left side, and the first steel plate and subsequently runs via an upward flow in the first degassing stage where atmospheric air is injected in the liquid sulphur through a dedicated sparging device. The degassing air sparger is provided with a suitable number of holes for air distribution through the contacting volume.

The stripping air is usually fed by the Claus combustion air blowers, so no extra blowers are needed. The air bubbled through the sulphur decreases the partial pressure of H_2S and induces a density gradient. Liquid sulphur and combustion air move through the contacting section via a co-current flow and the upward movement of the liquid-gaseous stream.

The atmospheric air has a triple action within the degassing process:

- it acts as a gaseous stripping agent of the hydrogen sulphide dissolved in the liquid;

- it catalyses the degassing process with its oxygen promoting the conversion of polysulphides (the produced hydrogen sulphide is removed from the liquid phase through mechanical stripping);
- it acts as an oxidising agent converting hydrogen sulphide to elemental sulphur (and SO_2) thereby increasing the plant sulphur production rate.

The mixed phase exiting the first degassing stage is separated in the downcomer present in the right side of the first contacting section. The exhaust air containing hydrogen sulphide is removed by means of the steam ejector while the liquid is collected in the space between the two contacting sections from which the second degassing stage is fed. The air involved in the stripping process together with the sweep air present in the sulphur pit free vapour space is sucked by the steam ejector and usually directed to a thermal incinerator or alternatively recycled back to the Claus unit in order to maximise the overall sulphur recovery of the plant.

More degassing stages may be added in series depending on the project needs.

The degassing box is sized considering the equilibrium of the hydrogen sulphide and polysulphides in the liquid sulphur and the kinetic limitations of the relevant involved reactions, thus properly evaluating the residence time and reaction surface inside the degassing box.

The hydrogen sulphide is absorbed in the liquid sulphur as a function of the operating conditions in terms of temperature and partial pressure in the upstream sulphur condensers and leads to the formation of polysulphides which are chemically bound to the sulphur molecules.

Once the hydrogen sulphide absorbed quantity in the liquid sulphur is established as a function of the condensers operating conditions, the equilibrium between hydrogen sulphide and polysulphides is determined by the undegassed liquid sulphur storage temperature.

The decomposition reaction for polysulphides is strongly dependent on the sulphur residence time within the degassing box.

The temperature inside the degassing box and sulphur pit is maintained at a value of 125-140°C by means of internal saturated steam coils in order to maintain liquid sulphur viscosity at the minimum level.

In the case of high degassing capacity and/or low residence time in the sulphur

pit a sulphur cooler is often adopted to compensate for the lack of required heat dispersion and for the consequential high liquid sulphur viscosities which can lead to downstream plugging. The cooler generally cools a slip stream or the entire sulphur flow rate headed to the degassing box.

The reactions kinetics involved in the degassing process are constantly verified and validated through field data collected from sulphur plants constructed and/or designed by Siirtec Nigi in order to always provide a reliable and up to date design.

The concentration of hydrogen sulphide and polysulphides in the liquid sulphur are monitored by Siirtec Nigi using FTIR (Fourier Transform Infra-Red) instrumentation to ensure that sulphur quality meets expectations for any given configuration and design.

Black & Veatch degassing

MAG[®] degassing

The Black & Veatch MAG[®] degassing process provides a simple, cost-effective approach for high performance degassing. It uses a small compressed air source, no chemical additives and is entirely contained within the sulphur pit.

Figure 8 shows a process flow diagram for a typical MAG degassing unit. Sulphur produced in the SRU, containing up to 300 ppmw of hydrogen sulphide, flows from the condensers into the underground concrete sulphur pit. The sulphur pit pumps circulate liquid sulphur through the sulphur cooler for cooling to 138°C prior to routing it to the degassing chambers. Liquid sulphur is circulated through a set of degassing chambers and mechanically agitated by the 1st and 2nd stage degassing eductors, which provide turbulent mixing and extensive surface area exposure of the molten sulphur in the pit to the air in the vapour space. As a result, dissolved H₂S evolves into the vapour phase where it is subsequently swept to the reaction furnace or incinerator by the sulphur pit ejectors. The sulphur pit ejectors induce a sweep air flow through the pit vapour space which keeps H₂S concentrations safely below the LEL.

During degassing and storage of the sulphur in the pit, polymeric H₂S_x compounds will decompose as equilibrium is achieved at the pit operating temperature. This results in the formation of dissolved H₂S in the liquid sulphur, which will physically desorb to the gaseous phase. A small air sparging flow rate is added from the Claus air blowers to

produce a sulphur product containing less than 10 ppmw dissolved H₂S.

Liquid sulphur flows from the degassing chambers to a storage chamber within the sulphur pit. Degassed sulphur is pumped from the product chamber to buffer storage prior to routing the product to its final destination.

MAG advantages and unique features

The MAG process has several key features:

- The residence time available in the sulphur pit is more than ample to reduce the hydrogen sulphide content to less than 10 ppmw. Consequently, a costly additional vessel dedicated to degassing service is not required.
- No degassing chemicals are required. This improves sulphur product quality (there are no chemical residues) and lowers operating costs.
- It is inherently safer than systems using spray nozzles and/or impingement plates because no free fall of sulphur is allowed. Therefore, there is much lower potential for the build-up of a static electric charge.
- The equipment arrangement is simpler, which results in lower costs and improved reliability. The sulphur ejectors require no moving parts or additional equipment other than the sulphur pumps which are larger to accommodate the recirculation flow rate.
- The largest current MAG degassing installation is for the 12 x 570 t/d Sinopec Puguang natural gas treating facility, where the product sulphur is degassed to less than 10 ppmw dissolved H₂S.

BP Amoco process

During the 1970s, Amoco Production Company (USA) developed a process for sulphur degassing, which used an air sweep in conjunction with a Claus activated alumina catalyst.

Since the time of commercial availability of the technology, Black & Veatch (B&V) has been involved in advancing the basic Amoco design parameters and criteria for application to both grassroots and retrofit facilities.

B&V was one of the pioneers of the implementation of sulphur cooling to achieve more precise sulphur temperature control, at a time when most other processes either ignored this issue or employed added sulphur pit residence time to achieve cooling, which is costly. Proper sulphur cooling serves to promote degassing reactions as

well as reduce problems associated with high sulphur viscosity and downstream plugging. Sulphur cooling via the use of a dedicated sulphur cooler/boiler feed water preheater also serves to preheat boiler feed water before it flows to the sulphur plant high and/or low pressure steam generators. Additional steam generation is realised, which partially offsets the capital cost of the cooler.

B&V has designed units operating under pressure where the effluent degassing air/H₂S/SO₂ stream is recycled to the Claus unit thermal reactor burner for additional sulphur recovery. This reduces plant emissions and serves to reduce the air demand provided by the Claus air blowers.

B&V was involved in an advanced Amoco degassing system design which involves placement of a removable modular system into a sulphur pit. Total air sparging and sweep volumes are minimised while total sulphur emissions are significantly reduced. As compared to the above ground design, this option reduces the total equipment count, while also saving plot space.

Fluor/GAA's D'GAASS[™] liquid sulphur degassing technology

The GAA D'GAASS sulphur degasification process (Fig. 9) is one of the leading technologies for the degassing of liquid sulphur with over 100 licensed units and total capacity of over 70,000 t/d. The D'GAASS process accomplishes the removal of H₂S and polysulphides (H₂S_x) from liquid sulphur outside of the sulphur pit in a pressurised vertical vessel. The undegassed sulphur is pumped from the sulphur rundown collection pit/tank to the vessel where it is intimately, counter-currently contacted with pressurised process air across efficient vapor-liquid contacting internals. The sulphur feed to the D'GAASS contactor is normally cooled for optimum degassing efficiency. Cooling is often accomplished by indirect heat exchange with boiler feed water or closed-loop generation of low-pressure steam. The process air requirement can often be met from the plant's instrument or plant air system.

Undegassed sulphur and process air are the only feeds to the degassing contactor; chemical catalysts are not required. The contactor can be located at any convenient location between the rundown pit and storage. For existing SRUs, the sulphur

Fig 9: The D'GAASS unit has a pressurised vertical vessel



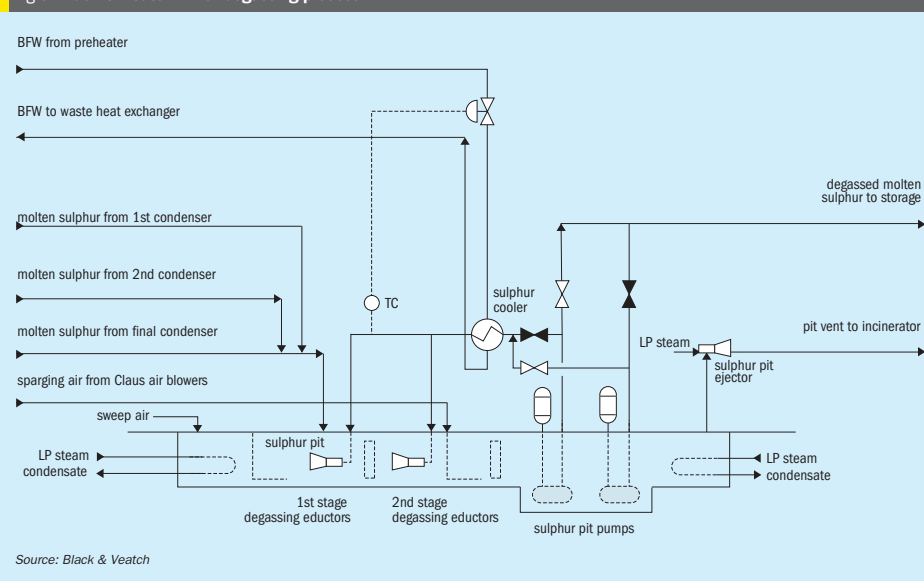
PHOTO: D'GAASS

rundown pit/tank acts as the degassing unit feed tank. No changes other than upgrading the sulphur pumps to higher head feed pumps are required to an existing sulphur pit. For new installations, GAA recommends installing a small sulphur rundown collection vessel or a small concrete pit for collection of the sulphur produced in the SRU. The collection pit only needs to be large enough to permit installation of sulphur feed pumps and required nozzles and to provide a few hours of surge capacity.

The D'GAASS process removes H₂S and H₂S_x through two mechanisms, oxidising most of the H₂S and H₂S_x to sulphur, and stripping the balance of the H₂S from the sulphur. Process air provides oxygen for reaction, agitation of the sulphur, and stripping of H₂S. At the recommended operating conditions, the H₂S content is reduced to less than 10 ppmw without addition of a chemical catalyst to the sulphur feed. Other commercial processes operate at or near atmospheric pressure. Operation at elevated pressure and a controlled temperature accelerates the oxidation of H₂S and H₂S_x to sulphur and SO₂ which can react with H₂S via the Claus reaction to form additional sulphur. Degassed sulphur can be sent to sulphur storage without additional pumping. Guaranteed performance for the D'GAASS Process is 10 ppmw H₂S + H₂S_x (as H₂S) maximum in the degassed sulphur, as determined by FTIR analysis.

The overhead vapour stream from the contactor is pressurised air with ppm

Fig 8: Black & Veatch MAG[®] degassing process



Source: Black & Veatch

concentrations of H_2S , SO_2 , and sulphur vapor; it can be sent to the incinerator. Alternatively, the elevated D'GAASS operating pressure allows sending the overhead vapour stream to the SRU thermal stage, tail gas unit burner, or selective oxidation reactor such as SUPERCLAUS eliminating the degassing unit as an SO_2 emission source.

The major degassing unit controls are:

- temperature control of the feed sulphur
- flow control of the sulphur feed to the D'GAASS unit
- flow control of the process air based on the maximum rated capacity
- level control of the contactor
- unit pressure control.

D'GAASS unit turndown is limited only by the capabilities of the process control instrumentation. If the instrument air system has adequate capacity and pressure, it can supply the process air.

Key D'GAASS process advantages include:

- low capital investment for new and retrofit installations
- easy retrofit to an existing SRU
- simple, reliable operation with low maintenance
- low air requirement and operating cost; no continuous catalyst or chemical use
- pressurised overhead vapour stream can be routed to the SRU thermal stage or other process location for recovery of sulphur components resulting in zero emissions from the degassing operation
- pressurised sulphur product stream permits routing to storage without additional pumping
- higher quality sulphur compared to catalyst-based degassing
- very small footprint; can be installed at any convenient location between the sulphur pit and storage.

Some key improvements to the D'GAASS process since the early installations in the late 1990s include:

- reduction in the D'GAASS process air pressure, permitting the use of single stage compressors, or in many cases, the use of plant or instrument air if adequate pressure and volume is available
- enhancements to the process design to ensure that the temperature of all points in the vapour section of the contactor and the overhead piping are kept above the dew point to eliminate potential corrosion problems.

- using dry process air to minimise water in the process
- modularisation of units up to 800 t/d to maximise more efficient shop fabrication labor and minimise field construction time

Best practices for sulphur vent disposition

Due to increasingly stringent air quality regulations, vents from degassing, rundown pit sweeps, and storage tank sweeps are more commonly being directed to the main burner/reaction furnace. Vent disposition is an important process decision in new designs for efficiency. This differs from past designs where the vents are generally directed to a thermal oxidiser, leading to higher SO_2 emissions.

There is a great advantage in using Fluor's D'GAASS process for liquid sulphur degassing in terms of vent disposition. Since the D'GAASS contactor is operated under elevated pressures, the overhead can be routed to the main burner/reaction furnace; thus eliminating all emissions from the degassing operation. The overhead can alternatively be used as the motive fluid for the rundown pit sweep air, combining both process streams directed to the SRU thermal section.

Regarding the practice of routing the relatively small quantity of the degassing vent to the reaction furnace and implications if any on the SRU control system, there is a great advantage in minimising vent flow rates, including the associated motive fluid.

Recycle flow from sweeps is constant regardless of SRU sulphur throughput. In addition, the motive fluid (air, nitrogen, steam) will affect the SRU thermal section's conversion and temperature. These factors must be taken account of in designing SRU process control.

The impact of the recycle can be particularly significant during turndown operation of the SRU. This is not intuitive, as there should be more volumetric capacity available in the SRU during turndown. However, the relative flow ratio between the feed acid gases and vent additions to the main reaction furnace will change, with the vent being a higher fraction of the overall flow.

For these reasons, the significantly smaller vent flow rate produced using the D'GAASS process, in comparison to in-pit degassing processes, incurs far less impact to the controls of the main burner/reaction furnace, especially during turndown operation.

Process design considerations and precautions

In modern D'GAASS installations, design precautions are taken to avoid corrosion in the vapour area of the D'GAASS contactor and overhead piping system. Causes of corrosion include:

- contactor not being fully insulated. Some common areas based on field failures include lifting lugs, top blind flanges, instrument nozzles, and piping flanges
- water condensation in the process air piping to the contactor, resulting in liquid accumulation and a slug being sent to the contactor.

Precautions to minimise/prevent corrosion include:

- fully jacket all vapour area components of the contactor vessel and overhead piping upstream of the pressure control valve
- where available, heat the upper, vapor section of the contactor vessel including all nozzles using medium pressure (up to 150 psig/10.3 barg) steam
- remove (preferable) or heat any contactor lifting lugs, support clips, and piping supports attached directly to the process
- fully insulate all areas of the contactor vessel including nozzles, flanges, lifting lugs, etc.
- Heat the overhead piping between the contactor outlet nozzle and pressure control valve using medium pressure steam
- fully insulate the overhead piping including all flanges
- use dry instrument/plant air or install dryers on the process air from dedicated process air compressors.

The overall goal is to keep the contactor overhead and associated piping warm enough to avoid water, H_2S , SO_2 , SO_3 dew point conditions, in addition to being above the sulphur freezing temperature.

Issues with level instruments

The most common method of level measurement in the D'GAASS contactor vessel has been with capacitance probes. Earlier unit probes were stainless steel rods inserted into the sulphur. However, some of the mounting nozzles were extended to as much as 18" (450 mm) to reach above an upper platform, and were unheated with un-insulated flanges. The heat loss from the nozzle and probes resulted in corrosion of

the probe in the vapour area and ultimately failure of the probe.

All nozzles are now specified to be steam jacketed, fully insulated, and the level probes are fully Teflon coated.

On larger units there have been problems with the level nozzle location. The preferred capacitance probe location for good signal strength is within 6" (150 mm) of the vessel wall in order to have the required metal ground reference. If the probe is significantly further from the wall, the signal strength will be weaker and the resulting measurement will be inaccurate with constant drift.

Several locations have not followed the GAA specification for capacitance probe level measurement and have installed radar type level detectors. Radar is not a good choice for D'GAASS Process level measurement; all locations with radar installations have experienced very poor level detection performance.

Issues with flow instruments

The liquid sulphur feed rate to the D'GAASS contactor is measured by a Coriolis mass flow meter. The operating principle involves inducing a vibration of the tube through which the liquid sulphur passes. The vibration provides the rotating reference frame which gives rise to the Coriolis effect in which sensors monitor and analyse changes in frequency, phase shift, and amplitude of the vibrating flow tubes. The changes observed represent the mass flow rate and density of the fluid.

If the meter has not been properly braced or the connected piping is vibrating, the Coriolis meter will not function properly. At several locations the meter required proper support and bracing in order to function as per design.

An additional problem has been inadequate steam jacketing of the Coriolis meter. The meter must have a vendor approved and, preferably, supplied steam jacket system.

Near-zero emission configuration

It is now possible to design a near-zero emissions plant, utilising Fluor's patented near-zero emission configuration for collection of sulphur vents. Nitrogen is used instead of air for sweeping the rundown sulphur pit (or vessel) and the sweep vent is routed to the hydrogenation reactor in the tail gas treating unit (TGTU), its upstream heater, and the reducing gas generator (RGG). This configuration avoids routing any vents to the incinerator and

thereby results in essentially no SO_2 emissions to atmosphere.

Use of the D'GAASS process minimises the degassing vent and therefore the impact to the SRU throughput, if any. This decreases both the diluent and cooling effects of the vent in the thermal section of the SRU. The D'GAASS process also minimises the liquid sulphur rundown vessel volume, thereby minimising the sweep air requirement and associated impact to the TGTU design. Naturally, nitrogen must be selected as the sweep medium if the vent is routed here to avoid deactivation of the hydrogenation catalyst with oxygen.

Strict precautions need to be taken with nitrogen use to prevent fires or an explosion due to air ingress. Special care must be taken to passivate the rundown vessel before opening for maintenance or inspections. Because sulphur rundown vessels are typically constructed of steel, and generally contain some steel components (pumps and/or steam coils), there would inevitably be some iron sulphide formed. If an air sweep is used, the oxygen in the air sweep tends to oxidise this pyrite slowly, thereby mitigating the risk of fire.

If however a nitrogen sweep is used, the iron pyrite may have time to accumulate. The accumulated pyrite could rapidly ignite if a sudden gush of air inadvertently enters the rundown vessel for any reason. For sulphur rundown, storage, or handling units employing inert gas blanketing of the equipment, special considerations must be given to opening up these units for maintenance and inspection, that is, when eventually exposing the equipment to oxygen in the air.

Sandvik DG Series sulphur degasser

Sandvik's involvement with the sulphur industry stretches all the way back to 1951 when the company installed its first steel belt cooler for sulphur slating at a refinery in Mexico. Since then, Sandvik has extended its portfolio to encompass every aspect of sulphur processing and handling, from the receipt of molten sulphur from the SRU, through solidification processes that include the market-leading Rotoform and high capacity rotating drum technology, to a complete range of downstream handling processes.

These ranges include the Sandvik DG Series sulphur degasser, a simple, compact, skid-mounted system designed to offer maximum capacity with a small footprint, few moving parts and minimal installation costs and time. The Sandvik

DG is a self-contained system that offers extremely easy operation and reliable, continuous performance (Fig. 10).

A centrifugal fan is used to push atmospheric air into the low-pressure bubbling system located at the bottom of the tank. Sandvik's process produces bubbles to maximise the interface between the sulphur and air that rapidly removes the H_2S . As the bubbles rise up through the liquid sulphur, collecting H_2S , they enter the head space of the tank and are routed to a downstream processing system of the client's choice. It is important to understand that any sulphur degassing process is removing H_2S , and not H_2S_x . This is why the conversion rate of H_2S_x to H_2S within the process is critical to its performance. A catalyst can be used to increase this conversion rate.

Catalysts are sometimes viewed negatively within the degassing industry because of the risk of residual catalyst in the sulphur exiting the system. As long the catalyst is properly removed from the sulphur, there are zero concerns with downstream sulphur quality. The right catalyst allows for degassing efficiencies that are unparalleled by non-catalyst processes. By increasing the conversion rate of H_2S_x to H_2S , the reaction half-life can be greatly reduced, allowing for much smaller degassing equipment. This allows for lower capital and operating costs.

Liquid catalyst injection is available on the DG Series if the capacity requirements dictate the need for it. Catalyst can be injected at various points in the system. Each of these points is independently controlled to provide flexibility in the operation of the unit. If a catalyst is employed in the process, it is not injected near the end, ensuring that no residual catalyst exits with the clean sulphur. In addition, a volatile catalyst will be used to ensure complete removal from the sulphur.

The centrifugal fan and the catalyst injection pumps (if required) are the only pieces of rotating equipment in the process and both are external to the unit; the fact that no moving parts come into direct contact with the molten sulphur means that maintenance is simplified.

The DG Series process is controlled by continuously measuring the following parameters:

- sulphur flow rate
 - sulphur temperature
 - air flow rate
 - catalyst injection rate (if required)
- and intermittent measurement of the following parameters:

CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

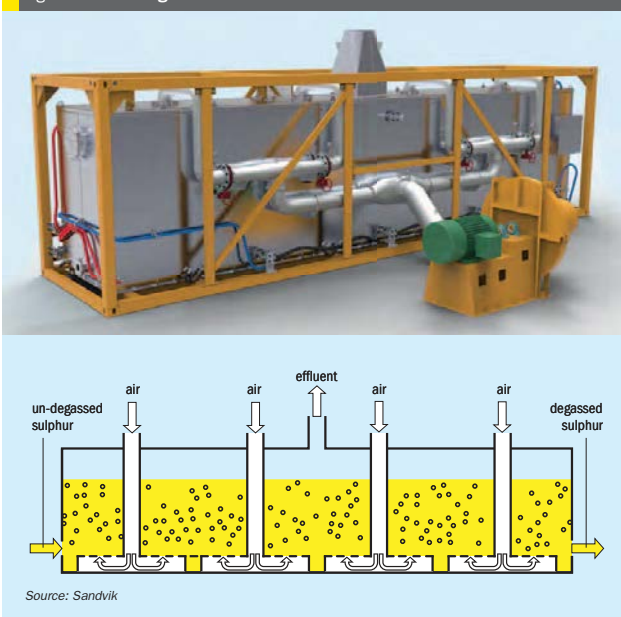
Sulphur degassing

SULPHUR
ISSUE 358
MAY-JUNE 2015

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Fig 10: Sandvik degasser



- incoming level of $H_2S + H_2S_x$ (by FTIR analysis or other means)
- outgoing level of $H_2S + H_2S_x$ (by FTIR analysis or other means).

An operator simply inputs the desired flow rate, and incoming level of $H_2S + H_2S_x$. The output level of $H_2S + H_2S_x$ is 10 ppmw unless the operator specifies otherwise. These parameters allow the programmable logic controller (PLC) to calculate the required levels of air flow and catalyst. The PLC controls the air flow and catalyst injection to use only what is needed. This minimises energy consumption, catalyst consumption and the volume of effluent. The control logic automatically compensates for any variation in sulphur temperature. While the DG has the flexibility to handle any sulphur temperature between 120°C and 160°C, it is recommended to operate at lower temperatures in order to take advantage of an H_2S/H_2S_x equilibrium ratio that favours the removal of H_2S .

The DG tank safely operates at a slight vacuum. Instrumentation is in place to monitor the pressure and activate a shut-down of the equipment if the vacuum cannot be maintained.

The design of the system enables almost complete pre-assembly and pre-wiring prior to delivery at the client's facility, and the low profile allows easy access for operations and maintenance.

Operation is simple with a minimal number of moving parts ensuring low maintenance requirements and high availability, and the PLC delivers optimal use of energy and catalyst, while also minimising emissions. The high capacity, continuous flow-through system allows adjustment on-the-fly and completely steam-jacketed walls enable precise control of sulphur temperature and operation in any ambient environment.

RATE internal degassing with catalyst

Current sulphur degassing technologies take place either inside or outside the sulphur pit.

External degassing takes place in a column using Claus catalyst or packing to reduce the residence time significantly but it increases the operating and capital costs and there have been corrosion issues in some existing degassing units.

Inside pit degassing requires at least 24 hours residence time and requires larger pit. Internal sulphur degassing technology employs proprietary air sparging nozzles which pull the liquid sulphur through the nozzles, mixing the sulphur with very small air bubbles and providing a high bubble surface area to volume ratio, effectively increasing the mass transfer of H_2S while providing liquid agitation in the liquid inventory. The nozzles are strategically placed at the bottom of the sulphur pit. Air for the spargers is provided from the plant air system. A steam eductor is provided to evacuate the evolved H_2S from the vapour space in the pit such that the H_2S concentration remains well below the low explosion limit (LEL) of 3.5%.

Morpholine can be used as the sulphur degassing catalyst to reduce the residence time. This liquid catalyst is an amine type which will reduce the residence time to less than one hour. It does not have an impact on the sulphur quality, it is environmentally friendly, and most importantly most of the residual catalyst is removed by the stripping air. The catalyst is a common amine readily available from most chemical suppliers. Residual catalyst in the product sulphur is typically < 0.5 ppmw.

Operating test data shows that morpholine degasses the liquid sulphur 30 times faster than quinoline with sparging air and has 7 hours residence time.

The best form of sulphur is polymeric sulphur, where sulphur is in a stable condition. Operating test data shows that in the second compartment of the sulphur pit, where there is a seven hour residence time, the catalyst will be evaporated within one hour and the sulphur will be in the stable polymeric form. Morpholine will have been removed from the sulphur and will therefore not have any impact on the quality of the sulphur.

Sulphur degassing in the concrete pit is the most common is most widely practiced but many facilities are having problems with cracking and other issues. A carbon steel vessel can be located in the sulphur pit to eliminate the problems with the concrete pit. The degassing can take place in the carbon steel vessel and a catalyst can be used to reduce the high residence time.

In a recent expansion project designed by RATE for increasing the capacity in a revamp, the customer insisted that the existing pit should be used while still maintaining 10 ppmw of H_2S . Since the residence time for degassing would be insufficient if the existing sulphur pit were used at the increased

capacity, morpholine was added to maintain 10 ppmw of H_2S plus a new sulphur cooler.

RATE equips the sulphur pit vessel with at least two temperature indicators – one below the low-low sulphur level to indicate sulphur temperature, and one in the vapour space near the sweep air outlet to detect a sulphur fire. In addition, a vapour-space H_2S monitor is also provided. While the primary function is to alert the operator to high H_2S levels resulting from reduced sweep rate, it can also serve as a basis for reducing the sweep rate if necessary to reduce incinerator emissions resulting from excessive sulphur vapour losses.

Problems with conventional sulphur pit

For 60 years, the standard approach to collection of sulphur rundown streams from Claus condensers has been gravity drainage to a below-grade concrete pit. Pit excavation is often expensive due to factors such as high water tables, frost or contaminated soil.

In some cases, the soil has to be evaluated before any construction takes in place, in other cases, like in Canada, rocks under ground have created a lot of trouble when digging and constructing underground pits. Rocks push the concrete walls and create cracking which may require regular maintenance. Another common problem is sulphur pit fires as a result of using carbon steel coils and corrosion after a period of time.

Pit concrete walls invariably develop cracks, particularly in the case of substandard design or construction, which is not uncommon. Sulphur will migrate into the crack up to the point that the temperature has dropped below the freeze point. The cooler section of the crack will contain moisture and air. Once changes in the temperature gradient across the wall, for whatever reason, result in < 40°C at the sulphur interface, bacteria (thiobacillus oxidans) become established. Thiobacilli gain energy by oxidation of sulphur to sulphuric acid and require O_2 , H_2O and micro-nutrients for ideal growth. Some of the energy arising from sulphur oxidation is used to fix CO_2 for carbon metabolism. The bacteria grow optimally in the 25-30°C range but are inactive below 5°C and, although they are killed above 40°C, they will lie dormant below 0°C for considerable periods. Subsequent temperature fluctuations marginally > 40°C will kill some of the bugs, whose corpses become nutrients for the survivors.

The bottom line is that rather than simply sealing the crack as might be assumed, sulphur migration invariably invites acid attack from within the concrete wall.

Fig 11: Sulphur pit cracks before start-up



Groundwater incursion is another very common problem. Water migrating inward through cracks ultimately flashes at some point, causing severe erosion. And that is only half the problem. Resultant steam in the sweep air (from coil leaks as well as groundwater) causes rapid sulphurous acid corrosion of any carbon steel surface sufficiently cool for moisture to condense. Unless ambient sweep air is preheated, which is not normally the practice, condensation invariably occurs at some areas of not only pit/tank roofs, but downstream piping.

In some cases, the entire Claus train has been elevated to avoid below-grade collection – hardly a cost effective solution. RATE suggests that to date, arguably the best solution has been a horizontal carbon steel collection vessel in a concrete vault. Cracks in the concrete are not enlarged by sulphuric acid from bacterial metabolism of sulphur, groundwater seepage is more easily arrested in the absence of sulphur and heat, and the risk of product contamination is greatly reduced.

Air sweep is inherently more effective in a horizontal cylindrical steel vessel, whose geometry results in a closer approach to plug flow. Explosions in rectangular concrete pits have resulted from localised H_2S accumulation in relatively static zones despite apparently ample air flow.

The obvious downside of a steel vessel within a vault is the significantly greater cost, which is potentially prohibitive on larger units.

Figures 11 and 12 show cracking in a sulphur pit after the construction has been completed and before the unit was started up. The project is located in Canada and demonstrates that in many areas digging the ground to build a pit can be very difficult and costly and may require repairs on a regular basis. In addition, after start-up of the unit, the crack expanded. Following a comprehensive evaluation, it was found that underground water was leaking into the pit through the rocks that were pushing the concrete.

Fig 12: Sulphur pit cracks after start-up



Carbon steel vessel versus concrete pit

Sulphur pit coils have historically been made of carbon steel. In the past it was taken for granted that substantial iron sulphide sludge deposits would accumulate over time, and operators were admonished not to expose the coils to avoid ignition of the sulphur by pyrophoric oxidation heat. In recent years RATE, as well as others, have upgraded to 316 SS to reduce this concern, as well as to generally extend coil life. RATE also specifies that pit roof nozzles, including jackets, be 316 SS, and that nozzle jackets extend below the roof to avoid solid sulphur.

With small-to-moderate size Claus units, there has been a general industry trend toward horizontal steel collection vessels, whether above grade or in a concrete vault, thus eliminating the maintenance issues inherent with concrete sulphur pits. Another advantage of such vessels is that they can be externally steam traced, typically with Controls Southeast ControTrace elements or panel coils. This eliminates the need for SS, minimises internal iron sulphide accumulation, eliminates risk of steam leaks to the process and permits coil repair during operation. The entire vessel circumference (not just below the sulphur level) should be heat traced as necessary to maintain all internal skin temperatures greater than 120°C to avoid solid sulphur deposition conducive to under-deposit acid corrosion.

Collection pit/vessel vapour spaces are commonly swept by ambient air flow induced by a steam jet eductor. In most cases the inlet air is not preheated, in which case the effluent sweep air will likely still be <80-100°C and it thus becomes particularly important that the eductor suction line be fully steam-jacketed and flanges, which act as cooling fins, be insulated to maintain all internal metal temperatures above 120°C in order to avoid localised buildup of solid sulphur which will restrict flow. If such buildup does occur, the sulphur can often be remelted by temporarily interrupting the flow,

CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

Sulphur degassing

SULPHUR
ISSUE 358
MAY-JUNE 2015

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thus allowing conduction from adjoining jackets to heat up the flange joint which is most likely to be the location of the restriction.

ICOn™ – a new approach to sulphur degassing

Controls Southeast, Incorporated (CSI) recently announced the launch of its new ICOn™ degassing system for refineries and gas plants. “ICOn is a major step forward for our organisation and the industry in treating hydrogen sulphide (H₂S) within the Claus process and upstream of the sulphur pit,” says Jackson Roper, Executive Vice President at CSI/AMETEK. “Operators struggling with the maintenance and cost limitations of existing technologies will find ICOn very beneficial for both retrofit and green-field applications.”

The ICOn degassing process works within the SRU to optimise the Claus process without the need of additional air, pressure, ejector or rotating equipment. ICOn is the first in-situ degassing process to remove the residual H₂S from the elemental sulphur before storage, greatly reducing the risk to onsite workers and environmental exposure.

“With its in-situ operation characteristics, small footprint, improved reliability features, and overall reduction in sulphur storage emissions, the ICOn process represents a breakthrough for sulphur degassing technology and an evolutionary leap for sulphur degassing,” says Al Keller, Sulphur Processing Lead at Phillips66.

Phillips 66 partnered with CSI in mid 2013 to develop a novel new degassing apparatus at a refinery in the United States based on latest research and knowledge of liquid sulphur degassing. The new process enables sulphur degassing to be an external, easy to operate device that is compact and operates within the pressure envelope of the SRU. The key features of the process are:

- a compact contact zone that should fit in the plot area surrounding a typical condenser-pit or other gravity driven sulphur rundown
- supply of agitation/carrier gas from the higher pressure section of the plant moving toward the lower pressure section of the plant
- degassing only the sulphur requiring it
- removing scale, catalyst, and other trash in the sulphur from the condenser prior to the contact zone
- use of SxSeal™ 2000 sulphur seals from CSI-Ametek to prevent excessive head losses in the contact zone while controlling the flow of sulphur out to storage.

A properly chosen catalyst can expedite H₂S_x decomposition, without the presence of oxygen or increased pressures. This allows for novel gases to be utilised for sparging, including the readily available Claus process vapour itself, despite its high H₂S content.

Degassing occurs much more rapidly with a catalyst and it can occur at near atmospheric pressures in a very compact contact zone. Furthermore, non-consumed catalyst structures provide suitable catalytic decomposition sites, eliminating the need for consumed catalyst to be added to the system.

Apparatus and process description

Sulphur feed to the apparatus is limited to those higher flow rate sulphur streams with higher dissolved H₂S content. Table 1 shows measurements of dissolved H₂S and H₂S_x taken from operating sulphur plants. It can be seen from Table 1 that there is minimal impact of sulphur from the last two condensers on total H₂S content.

Sulphur comes out of each condenser into an SxSeal™ 2000 to remove scale, corrosion products, catalyst, and other trash, and also to maintain liquid head as high as possible into the contact zone. A small slipstream of process gas from either the first or second condensing stage is routed to the apparatus and enters the contact zone. Undegassed sulphur and the process gas meet in the contact zone containing the degassing catalyst.

The contact zone is designed to keep pressure drop as low as possible and to maintain gravity flow to sulphur storage. Process vapour pressure drop must be conserved to be able to return the spent sparging gas into the Claus process without external motive force. Process gas taken from a first condenser is returned to the inlet of the last converter bed to give higher concentration H₂S and SO₂ a last chance to convert to sulphur to minimise impact on the TGU. Simulations show the bypass impact on overall sulphur yield for a typical 3 bed Claus unit is less than 0.5%. This should have a negligible impact on overall SRU + TGU sulphur recovery.

The catalyst uses a sturdy support and retention system to prevent the catalyst from leaving with the sulphur product. Sulphur leaving the contact zone proceeds to sulphur storage via another SxSeal 2000 sulphur seal. The seal holds backpressure on the degasser to keep the process gas in the Claus SRU pressure envelope while minimising head losses to maintain gravity flow.

Table 1: Measured Claus sulphur quality

	Actual ppmw		
	H ₂ S	H ₂ S _x	Total
WHB	434	192	626
Cond. 1	263	353	616
Cond. 2	54	50	104
Cond. 3	12	10	22
Cond. 4	2	1	3

Source: CSI

Pre-pit: location improved reliability

The apparatus is designed to operate in close conjunction with the SRU, but at the same time being modular and minimally invasive. No pit modifications are required, as the apparatus operates between the condenser and the pit. Since the sulphur is processed in real time, without any motive force, there is no need for separate undegassed sulphur storage pits, partitions or vessels. No modifications are needed for the existing sulphur pit – no baffles, sparging boxes or weirs.

Having degassed sulphur in the pit decreases the rate of corrosion, as there is no longer any water vapour forming in the pit. When the pit holds undegassed sulphur, this water vapour mixes with sulphur to create sulphuric acid, which can rapidly eat away at the pit liner¹⁰.

Furthermore, the apparatus has a small footprint, allowing tie-in next to condensers and existing liquid sulphur rundown piping. These short runs eliminate a great deal of piping, valves, and the steam heating system needed to support them.

No air, no pressure, no rotating equipment

The apparatus operates without any external motive forces, utilising only the intrinsic pressures within the unit. There is no need for air compressors, air driers, or blowers. The apparatus simply takes a slip stream off the first or second condenser and returns it to the last reheater or fourth condenser respectively. This eliminates the operation and maintenance expenses associated with conventional degassing systems.

Furthermore, no external motive forces are required for the sulphur itself. The sulphur naturally passes from the condenser, through the SxSeal 2000s, through the contactor, through a final SxSeal 2000 and into the pit. The only motive for this action is gravity and the inherent pressure of the condensers. The apparatus is free draining, space permitting. No sulphur pumps

are required to supply the skid, or to drive the sulphur through the skid.

No waste stream

The degassing apparatus does not have a waste stream that needs to be processed. The off gas is routed back into the SRU (without blowers or external motive forces). No waste stream is sent to the thermal oxidiser, significantly reducing the overall SRU SO₂ emissions. Degassing operations have been quantified as contributing up to 50% of overall stack emissions for some refineries.

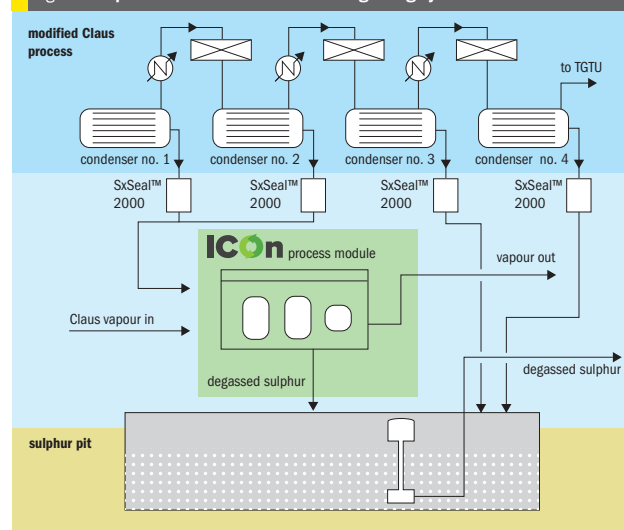
Since the pit only receives degassed sulphur, the sweep air system can be operated at reduced flow rates with increased reliability. This reduces pit SO₂ formation, and minimises vapour sulphur in the pit vent gases.

In retrofit applications, a common problem in pit sweep systems is plugging where non-engineered heat tracing is used. With tube tracing, it is difficult to ensure proper contact with the pipe wall, and local cold spots are inevitable. Furthermore, steam distribution issues such as steam trap failures and elevated condensate return pressures can prevent proper heat transfer to the pipe. Inadequate insulation, or interruptions in insulation, provides locations where ambient conditions can rapidly cool down the pipe wall to below the freezing point of sulphur. Accumulations of solid sulphur on the pipe wall compound by leading to even cooler wall temperatures. When the lines plug, dangerous build-up of vapours can accumulate above LEL levels.

With this process, the necessary sweep air flow rates are no longer governed by explosion concerns (sulphur degassed to less than 10 ppmw is widely accepted to be sufficient to not exceed the LEL in the vapour space). The existing sweep air lines can be run at lower flow rates, decreasing entrained sulphur vapour and reducing the strain on the heat tracing. Plugging and corrosion concerns are significantly reduced.

Furthermore, it may be possible to eliminate the forced sweep air system all together, as commonly done for sulphur tanks, environmental agencies permitting. Natural convection (utilising the chimney effect) is a robust way to sweep the vapour space to atmosphere. Proper heat tracing or jacketing of the pit vents would prevent corrosion and plugging, and natural convection sweep systems have very high reliability. Removing the sweep air sent to the thermal oxidiser further reduces the overall SO₂ emissions of the unit.

Fig 13: Simplified schematic of the ICOn™ degassing system



No exotic metals

Since the apparatus operates at the same conditions as the Claus unit, no specialised metallurgy is required. This allows for use of carbon steel in the reaction vessel and for all piping.

Lower operational and maintenance costs

The compact, modular design of the apparatus also lends itself to lower operational and maintenance costs. Since the apparatus operates without any motive forces, there is no additional strain on existing utilities, nor is there any need for compressors, pumps or blowers.

There is no rotating equipment to service, or instrumentation control loops to maintain. There are no level indicators to fail, or control systems that can malfunction. The apparatus is inherently more reliable, as there are no moving parts, elevated pressures, control loops or external motive forces to monitor for expected performance.

Furthermore, the pit itself requires less maintenance. Meta-stable polysulphanes in the pit naturally decompose, forming water and eventual sulphuric acid. This acid leads to rapid corrosion of the pit liner or vessel wall, requiring significant expense during turnarounds to maintain. A pit or vessel containing degassed sulphur is inherently less corrosive than a pit containing undegassed sulphur.

CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming project listing

COVER FEATURE 3

Sulphuric acid materials

COVER FEATURE 4

Sulphur degassing

SULPHUR
ISSUE 358
MAY-JUNE 2015

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Subscription rates:
GBP 440; USD 880; EUR 680

Subscription claims:
Claims for non receipt of issues
must be made within 3 months of
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ISSN: 0039-4890

Design and production:
JOHN CREEK, DANI HART



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

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BCInsight

Published by: BCInsight Ltd
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London SE1 7SJ, England
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CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming
project listing

COVER FEATURE 3

Sulphuric acid
materials

COVER FEATURE 4

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CONTENTS

What's in issue 358

COVER FEATURE 1

Oil sands update

COVER FEATURE 2

Sulphur forming
project listing

COVER FEATURE 3

Sulphuric acid
materials

COVER FEATURE 4

Sulphur degassing

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