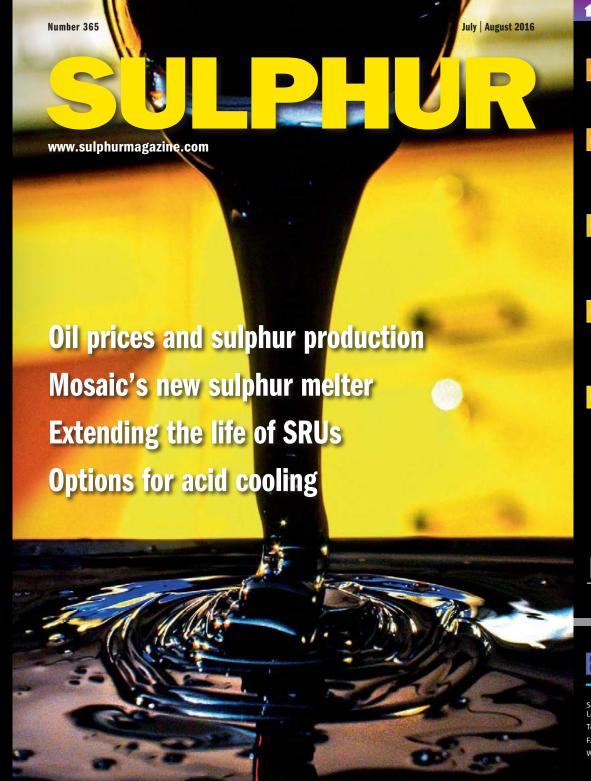
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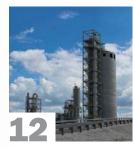
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Changing US sulphur

Mosaic's new melter is transforming the US market.



Acid cooling

Silicon alloy vs anodically protected steel.

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However, the

syncrude still

needs to find

a market.

Fire and **brimstone**

he terrible wildfires that have ravaged the area around Fort McMurray in northern Alberta for the past two months have been the costliest disaster in Canadian history. While evacuation was timely and fortunately no lives were lost to the fires themselves, up to 10-15% of Fort McMurray itself was destroyed, with some surrounding townships far worse affected, 580,000 hectares was eventually burned and 100,000 people forced to evacuate at the height of the blazes. Sulphur can only add our sympathies to those who have lost homes and property to this dreadful event.

The insurance estimates, which are in the region of C\$3.6 billion according to the most recent evaluation, do not include lost production from oil sands facilities, which could add another \$1-2 billion to the national bill. Several of the major sites were shut down so that staff could be safely evacuated. It is estimated that up to 1 million barrels per day of production was lost for a few weeks - about one quarter of Canadian production - contributing to the recent uptick in oil prices worldwide.

But the disaster has also obscured a remarkable fact, which is that, aside from the weeks when fires made it impossible, the oil sands were by and large still producing in spite of the run of low oil prices, and indeed, against industry expectations, the outlook for new production still seems reasonably bright - at least for now. While several oil sands projects have seen delays and cancellations in the past year, eleven projects currently have expansions plans and six new ones are also still under development. Research and consulting firm GlobalData has calculated that total planned capital expenditure in the oil sands patch from 2016-2025 still totals \$40.6 billion, adding another 715.000 bbl/d of incremental supply to 2023, Cenovus is expected to generate new production from five projects, at Narrows Lake, Foster Creek G and H, and Christina Lake Phases F and G., and there are also expansion projects for Husky, Suncor and Pengrowth, but the largest new development will be the Canadian Natural Resources Ltd (CNRL) Horizon project, which will add 140,000 bbl/d of new production. And in spite of delays. Kearl Phase 3 with a capacity of 80,000 bbl/d and the Kearl Phase 4 debottleneck which will add another 45,000 bbl/d are expected to start operation in 2016 and 2017 respectively.

At the same time, operating costs are continuing to be cut as operators move away from big mining projects towards smaller in situ SAGD operations, and if opex of \$20-25/bbl can be achieved,



GlobalData calculates internal rate of return at 10-15% for new projects even at current oil prices. Break-even oil prices for new green field projects are around \$40-50/bbl, but for expansion projects where some capital expenditure has already been committed can be as low as \$25/bbl, and with US Gulf refineries set up to handle heavy crude and declining supply from Mexico and Venezuela, there is market opportunity for Canadian suppliers.

However, while the cost no longer seems to be the barrier to new expansion that it was once assumed to be, the syncrude still needs to find a market. Until the end of June, the approval of the Enbridge Northern Gateway pipeline seemed to have finally laid that particular issue to rest, but the Federal Court of Appeal's overturning of that approval seems to herald more years of wrangling with Canadian First Nations groups along the route, as happened with the Energy East pipeline. With the US blocking of Keystone XL and cross-border rail lines running close to capacity, where Canadian syncrude will actually go has become an open question once more.

Likewise the more optimistic forecasts for oil sands development have been rapidly scaled back in the wake of lower oil prices. In 2013, the Canadian Association of Petroleum Producers (CAPP) estimated that by 2030 production would reach 5.2 million bbl/d. In 2014 they revised that down to 4.8 million bbl/d and last year to 4 million bbl/d. The most recent forecast was for 3.77 million bbl/d.

And then there is the question of what will happen to sulphur from the operations. Some of this has already boosted US refinery output as more syncrude and bitumen makes its way to the US Gulf Coast, but with upgrader projects bearing the brunt of cuts it seems not much of the sulphur will be extracted in Canada. Meanwhile, Mosaic's new sulphur melter, which we discuss in this issue, may mean Canadian liquid sulphur increasingly finds itself shut out of US markets. Sulphur stockpiles in northern Alberta already total several million tonnes, but may find themselves growing higher still.

Richard Hands, Editor



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What's in issue 365



MARKET INSIGHT

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

SULPHUR

Uncertain outlook (same as last time)

Global sulphur prices started to recover in May, showing signs of stability as tight supply in the spot market provided support. The devastating wildfires in Alberta, Canada disrupted sulphur production from oil sands facilities, at a time when spot availability for tonnes from the Middle East was also limited. The stabilisation was driven by supply-side factors rather than an untick in demand as the downstream processed phosphates market still failed to show promising signs of improvement. Through June, sulphur prices began to ease again, as buvers in key markets retreated to the sidelines, awaiting lower offers.

Middle East producers have been focussing on contract commitments, with spot tenders few and far between. Supply from the UAE's Shah gas project continues to be exported under contracts, despite the project being heard to be running at full capacity so far through 2016. Following the more stable spot market through May. prices for June contracts were announced at slight increases. In Qatar, Tasweeg increased its prices by \$4/tonne to \$83/

Fig 1: China sulphur imports

Chinese imports remained relatively high in the

first five months of 2016 with the UAE, Saudi Arabia & Canada remaining the largest suppliers

Kazakhsta

Oatar

Iran South KoreaUAE

Turkmenistan

Saudi Arabia

Jan-May 2016

million tonnes

rest of world

Source: Integer/GTIS

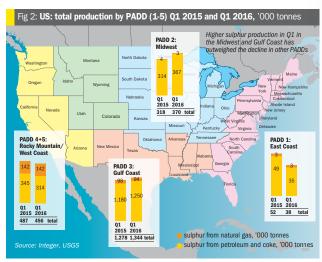
Canada

tonne f.o.b. Ras Laffan. Adnoc announced a \$1/tonne increase to \$86/tonne f.o.b. Ruwais for shipments to India. Aramco Trading posted its price at \$82/tonne f.o.b. Jubail, a \$2 increase on May, The trading arm of Saudi Aramco has also changed the timing of its monthly price announcement. from the 10th of each month to the end of the month, which is likely to lead to a smaller gap between the three producer prices. While Al Hosn's Shah project continues to runat capacity, significant delays have been heard for Qatar's Barzan project. The two phase project was expected online in 02/03 2016. However, due to technical reasons this has been delayed. Estimates suggest start up will take place in 2017. This provides more stability to the Middle East supply balance for 2016 as sulphur recovery from Barzan is expected to be over

800,000 t/a in total at capacity. Sulphur imports in China remained strong in the first five months of the year to May, up by 19% to 5.2 million tonnes compared with the same period in 2015. Saudi Arabia remains the top ranking supplier for China, although the UAE has overtaken South Korea as the second leading supplier. The changing trade dynamics continue to erode Kazakhstan and Qatar

tonnage to China - down by 60% and 33% respectively on 2015 so far. Meanwhile. as imports have climbed, so have sulphur stocks at the nine major ports, rising to 1.7 million tonnes in recent weeks. This is a turnaround on the strategy adopted throughout 2015, when ~1 million tonnes became the new normal. The higher stocks are a bearish tone for the short-term outlook in China unless there is a significant change in the phosphates market. Spot prices continue to come under pressure. with numbers talked in the low-\$80s/tonne c.fr at the end of June. Major domestic sulphur producer Sinopec held a maintenance turnaround, stabilising local pricing, but the planned restart at the end of June adds to the bearish sentiment.

Vancouver spot prices strengthened in May and 1H June on the back of the devastating wildfires in Alberta, Western Canada. The mass evacuation and proximity to oil sands operations led to the shutdown of operations for safety. No plants were heard damaged as a result of the fire but the stoppages led to an immediate tightening of availability from the port of Vancouver and prices ticked up to \$90/ tonne f.o.b. in some deals. As the situation became more stable, some operations have started a ramp up of operations, with sources indicating sulphur availability from end July/early August is a possibility. Price ideas also eased, down to the low/mid \$80/tonne f.o.b.. Any further disruption to supply out of the region could lend support



to export prices, at a time when prices are likely to soften elsewhere.

Quarterly contract discussions will also be underway across all regions soon, with price indications uncertain. Some suppliers have indicated decreases will be unlikely. but the lacklustre phosphates market continues to take its toll on sulphur. In Brazil, Q3 price discussions were heard around the high \$70/low \$80s/tonne c.fr range on the buyer side while suppliers had not dropped below \$80/tonne CFR. Demand in Brazil has been challenged by squeezed margins for fertilizer producers and an uncertain economy. Sulphur imports in January-May 2016 have dropped by over 9% year on year, reflecting the weaker tone in the market. Supply from the US continues to rise, up by 25% on 2015, also signalling the more stable production levels in the US Gulf coast.

Over in India, FACT issued a tender for 25,000 tonnes of sulphur for arrival at Cochin at the end of July. An award was made in the low-\$90s/tonne CFR, in line with spot prices in the region. High finished fertilizer stock levels in India have slowed the market considerably in 2016.

Phosphates producer Philphos was heard resuming its operations at its Isabel plant at the end of May with raw materials procurement under discussion. The sulphur demand outlook remains unclear however due to the neighbouring smelter PASAR and potential availability of sulphuric acid. Acid may be preferred instead of elemental sulphur due to the gap in prices between acid and sulphur.

SULPHURIC ACID

Stable outlook

Despite the weak tone in the sulphur market, sulphuric acid prices have become more stable and even firmed in Northwest Europe for exports with the price range up by \$5/tonne on a month ago at \$0-10/tonne f.o.b. The higher range has been supported by tighter availability and a more balanced position of smelter acid producers. Renewed buving interest in Latin America from Brazil is expected to encourage prices to remain in the double digits on the high end of the range. A three month long planned turnaround at KGHM's smelter is also expected to provide some support, as reduced volumes will be available to the export market from the producer during this period. The local market will be the main priority.

The latest tender from Brazil from Timac for 15-18.000 tonnes of acid for July arrival was awarded in the low-\$40s/tonne c.fr, with supply pegged from Europe. Freight rates were heard below \$30/tonne.

OCP/Morocco remains a key outlet for acid producers in Europe, with trade continuing its upward trajectory in 2016. Imports in 2015 overall were already at a high rate, at close to 900,000 tonnes as consumption rose to meet the demands of the Jorf Lasfar processed phosphates hub. For January-April 2016, acid imports to Morocco were up by over 50% to 408,000 tonnes. This trade shift is a key supporting factor for the out-

look in Europe, particularly as other markets have been weaker in 2016 so far. The main exporter to Morocco is Spain, with tonnes from Germany sky rocketing to over 70,000 tonnes, compared to just 5,000 tonnes in the same period in 2015.

The main weak spot in the global acid market has been northeast Asia. A turnaround at the Taganito nickel leaching project led to surplus acid becoming available from Japan, putting downward pressure on export pricing. Double digit negative netbacks down to -25 to -30/tonne f.o.b. were a feature of the market through May and into June. By mid June prices firmed slightly, up to -15 to -5/tonne f.o.b.. Latest prices have reflected spot business to India and Argentina. The restart of Philphos' phosphates facilities in the Philippines may increase sulphuric acid demand from PASAR, with an acid pipeline heard being tested at the end of June.

sumption low due to cut backs at leaching operating in light of the low metal prices. Imports in the period Jan-Apr 2016 were 124,665 tonnes, down from 176,184 tonnes in the same period in 2015 with large reductions from Japan and Mexico. The Chile acid deficit is estimated to be lower than in 2015, in the region of 1.5 million tonnes according to some sources, as producers announce they are operating below capacity. In the longer term, the outlook is brighter with more buying anticipated in 2017 as the commodity markets improve and underlying demand fundamentals prevail.

Chile has remained quiet, with acid con-

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Price indications

| Cash equivalent | January | February | March | April | May |
|------------------------|---------|----------|-------|-------|-----|
| Sulphur, bulk (\$/t) | | | | | |
| Vancouver f.o.b. spot | 113 | 95 | 80 | 75 | 80 |
| Adnoc monthly contract | 122 | 105 | 88 | 185 | 86 |
| China c.fr spot | 108 | 100 | 86 | 85 | 85 |
| Liquid sulphur (\$/t) | | | | | |
| Tampa f.o.b. contract | 95 | 95 | 95 | 70 | 70 |
| NW Europe c.fr | 148 | 148 | 143 | 143 | 116 |
| Sulphuric acid (\$/t) | | | | | |
| US Gulf spot | 45 | 45 | 45 | 45 | 35 |

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SULPHUR

- Outlook: Sulphur prices are likely to erode in the coming weeks as traders in China looks to liquidate high stocks into the local market. Middle East producers may have to drop prices further in upcoming monthly contracts to encourage spot activity.
- Third quarter contract price negotiations will test the outlook for the market, with softening expected compared to the second guarter across the main markets; North Africa, Latin America and Asia.
- New demand from Sheritt's sulphuric acid plant in Moa, Cuba will likely be an outlet for further trade from Vancouver, lending further support to Western Canadian sulphur pricing. The full extent of the impact of the wildfires in Alberta may also vet to be felt and it remains to be seen if availability will normalise at the end of July/early August as scheduled.
- The delay to Qatar's Barzan project has led to a more stable outlook for Middle

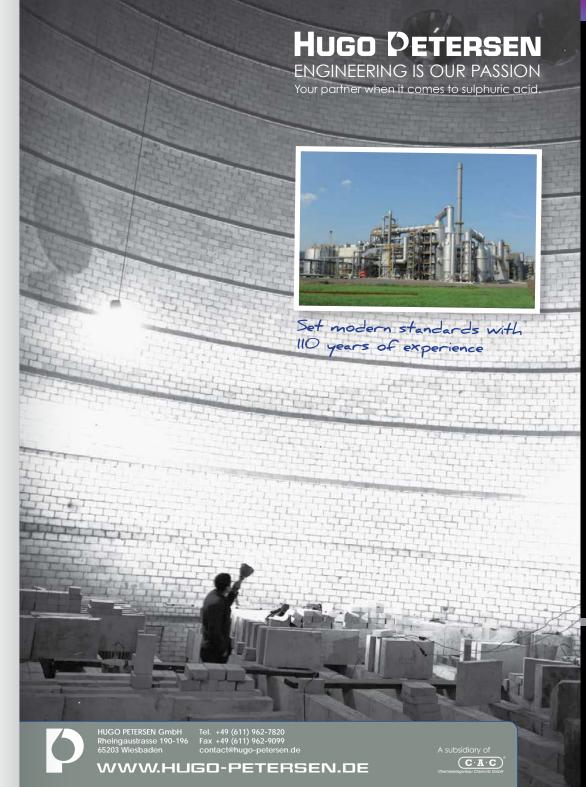
East pricing in 2H 2016, although there is still considerable downward pressure for 2017 as new projects come online

- India is a market to watch in 2H 2016 as to how fertilizer imports develop to potentially support sulphur consumption. The market has been stagnant through much of the year so far and remains a bearish factor for sulphur pricing.
- Developments in the oil and gas sector in China will add significant sulphur production in the domestic market.
- Outlook: The short term market outlook remains uncertain with a more bearish sentiment likely to emerge. Should phosphates demand materialise in the latter part of the year, this would help sulphur prices reach a floor in pricing, with potential to recover during Q3/Q4.

SULPHURIC ACID

 The start up of Sherrit's new sulphuric acid plant in Moa, Cuba will be a key determining factor for the acid market in the outlook as European acid usually exported to Cuba will need to be displaced.

- Acid trade into Morocco has become a significant outlet for European acid, and could pose an alternative market for some of the acid tonnes usually destined for Cuba. However, the long term sustainability of acid imports in Morocco remain uncertain due to the potential to also import sulphur for the production of sulphuric acid domestically.
- Demand in Asia is expected to improve with the restart of the Taganito nickel project in the Philippines and could lend further support to more stable prices from North East Asian smelters.
- · Latin America is likely to remain a weak spot for the outlook, owing to a bearish Chile market as the commodity slump continues to weigh on the copper market and leaching projects.
- Outlook: Acid prices are likely to remain or firm in Europe in the short term outlook, with producers in a comfortable position. The price gap between North East Asia and North West Europe may narrow as surplus acid in Asia is absorbed into end user markets.



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Fires shut down oil sands production

The terrible wildfires raging around Fort McMurray in northern Alberta have forced the evacuation of tends of thousands of residents and shut down production at most of the major oil sands facilities in the region. The US Energy Information Administration (EIA) estimates that disruptions to oil production averaged about 800,000 bbl/d in May, with a daily peak of more than 1.1 million bbl/d. Although projects are restarting as the fires subside, it could take weeks for production to return to previous levels, and the EIA has predicted that output will be down by an average of 1.8 million t/a.

400,000 bbl/d over the whole of June. The major oil sands facilities at Suncor and Syncrude were evacuated when winds pushed fires close to them, and production at Syncrude was completely shut down for the first time since 1978, according to the company. Local pipeline capacity was also shut down in response to the fire, reducing crude oil offtake capacity, as well as the supply of diluent required to process the oil sands into syncrude.

Sulphur production in the Fort McMurray area totals close to

Trans Mountain pipeline given go-ahead

The Canadian National Energy Board has given its go-ahead for Kinder Morgan's Trans Mountain Expansion Project, paving the way for a final approval by the Canadian government by the end of the year. The Trans Mountain project aims to add 980 km of new pipeline to its already existing infrastructure at a cost put at C\$6.8 billion. It will add 590,000 bbl/d of syncrude carrying capacity to the existing 300,000 bbl/d, taking it from the south of the oil

sands patch at Edmonton, Alberta to the coast at Burnaby in British Columbia. The decision is an important milestone in the development of Canada's oil sands. especially following the failure of the US government to approve the Keystone XL

CNRL fined for H₂S releases

Alberta's Environment Department has fined Canadian Natural Resources Ltd. C\$500,000 for two incidents at its Horizon oil sands facility, 70 km north of Fort McMurray. The fines relate to two histori-

cal releases. In the first, in May 2010, the plant's sulphur recovery unit failed and hydrogen sulphide escaped both at ground level and via a flare stack. The fine was for failing to report the incident until June 3rd, six days after the release, contravening a requirement under the Environmental Protection and Enhancement Act and resulting in a C\$350,000 penalty. The second, unrelated incident in August 2012 was again a failure of the sulphur recovery unit and release of an unknown quantity of hydrogen sulphide gas via the flare stack as it failed to fully combust the gas, which was deemed to be a contravention of the plant's approval. The company was fined C\$150,000 for that occasion, Other charges were dismissed or withdrawn. Of the total penalty, C\$425,000 will be donated by the Environmental Dept to researchers from the University of Calgary. who will use the funds to research the toxicological effects of chemicals measured in the air in and around Fort Mackay.



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GERMANY

Conference urges phased sulphur restrictions

The Motorship's 38th Propulsion & Emissions Conference, which took place in Hamburg on 11-12th May, heard David St Amand of Navigistics Consulting argue that the International Maritime Organisation (IMO) should consider phasing in the global 0.5% fuel sulphur cap set to be introduced in either 2020 or 2025. St Armand. the author of a report supplementary to the IMO's own marine fuel availability study, indicated that the study's sponsors will likely put its conclusions to the IMO's Marine Environment Protection Committee in October, St Amand modelled demand for compliant fuel based on the likelihood of slow steaming becoming less common,

the potential uptake of scrubbers, alternative fuel uptake and changes to the design efficiency of vessels. With no speeding up of vessels, the study predicted that added demand for 0.5% sulphur fuel in 2020 would be 3.6 million barrels per day, rising to 4.4 million barrels a day if scrubber uptake is lower than the IMO anticipates. Given that the International Energy Agency anticipates that a demand increase of 2 million barrels a day would put refiners under enormous pressure, he proposed a staggered introduction for the global cap. which is currently the subject of another, official study being conducted by CE Delft for the IMO. It is due to be completed by MEPC 70 in October - after which a decision on the date of entry into force will be

UNITED STATES

IHS predicts return of risk premium to oil market

Shifting power relationships in the Middle East are reordering regional geopolitics, entrenching a stalemate of conflict that threatens to further destabilize the region. Wars in Syria and Yemen and against the Islamic State, combined with the balancing of supply and demand in oil markets later this year, will likely return a risk premium to oil prices in 2017, according to a new report by IHS. The reports says that global oversupply of 1.0-1.5 million bbl/d during 2015 negated the market impact of political risk, meaning that oil prices did not rise despite Islamic State attacks in Paris, Egypt, Turkey, the United States and Belgium. However, with global oil demand growth expected to catch up with or outstrip supply, especially if disruptions continue, over the next six to 12 months, a risk premium could well return as a factor on the price of oil. The degree by which the new risk premium impacts price will depend on developments in the Middle East as well as other key producing areas displaying potential for supply disruption. such as Venezuela and Nigeria.

ing employs a novel reactor system that

uses hydrogen and catalyst more efficiently, leading to lower capital and operating costs while significantly reducing sulphur content in motor fuels, according

The hydrotreater will being Allied's production into line with new lower sulphur standards for diesel fuel which had prevented the company selling its products into the diesel market and instead having to ship them to Mobile to be sold as marine fuel or to Tuscaloosa to be processed. Allied anticipates that the new hydroprocessor will give the company an additional 1.5-2.5 million gallons per year of ultra-low sulphur diesel.

Sulphur recovery market to reach \$2.1 billion

A new report by Future Market Insights puts the market for sulphur recovery technology at \$2.1 billion by 2026, with an annual growth rate of 11.5% over the 10 year forecast period - 11.7% for tail gas treatment technology. The report considers sulphur recovery in three sectors - oil, gas, and others (e.g. coal gasification). The gas segment - the largest - is expected to register a CAGR of 11.0% in terms of value over the forecast period, due to the increasing demand for gas and increasing number of sour gas processing plants in Middle East and Central Asia, Regionally, the Middle Fast and Africa area dominates with over 50% of the market share for sulphur recovery technology in 2015, and this dominance is expected to continue to 2026, although the Americas will see the highest CAGR, followed by the Asia-Pacific region.

Honeywell spins-off ammonium sulphate business

Honeywell is divesting its ammonium fertilizer business as part of a spin-off of its resins and chemicals operations. The spin-off will form a separate, standalone company named AdvanSix Inc. Dave Cote, Honeywell's chairman and CEO said: "our \$1.3 billion Resins and Chemicals business enjoys a leading position in the industries it serves adn a global cost advantage. It is favourably positioned to continue to achieve global growth as a standalone enterprise, with added flexibility to make capital investments that enhance its offerings and service to customers."

AdvanSix is set to become a leading manufacturer of nylon, Sulf-N ammonium sulphate fertilizers and a range of chemical intermediates on completion of the

spin-off. AdvanSix will asloo be the world's largest single-site producer of caprolactam due to its ownership of the Hopewell, Virginia plant. Erin Kane will become president and CEO of AdvanSix when it is up and running. She is currently vice president and general manager of Honeywell Resins and Chemicals, a position she has held since October 2014. Honeywell hopes ot complete the spin-off by early next year.

ExxonMobil expands Rotterdam hvdrocracker

ExxonMobil is expanding the hydrocracker unit at its Rotterdam refinery to upgrade heavier by-products into cleaner, highervalue finished products, including EHC Group II base stocks and ultra-low sulphur diesel, to meet growing global market demand. The refinery, operated by Esso Nederland BV, will use ExxonMobil's proprietary hydrocracking technology, Pending receipt of permits, construction is scheduled to begin in 2016 and unit start-up is targeted for 2018. ExxonMobil's Rotterdam refinery has a daily throughput of 190,000 barrels.

Drilling to begin at Pars Phase 14

The Iranian Offshore Engineering and Construction Company (IOEC) says that it will begin offshore drilling operations at Phase 14 of the South Pars gas field by mid-July 2016. The company intends to drill 22 wells in its part of Phase 14, with operations being conducted over two and a half years Drilling operations at platforms A and C of the phase are being carried out by the national Iranian Drilling Company. and platforms B and D are being drilled by IOEC. Phase 14 will produce 56.5 million cubic metres per day of sour gas, 75,000 bbl/d of gas condensate, 1 million t/a of liquefied gas, 1 million t/a of ethane and 400 t/d of sulphur.

Lukoil starts up refinery upgrade

www.sulphurmagazine.com

Russia's second largest oil producer, Lukoil, has started up opened the country's largest vacuum gasoil (VGO) hydrocracking facility at its Volgograd refinery, built as part of a sweeping modernisation of the country's refineries. The \$2.2 billion VGO complex, which also includes hydroCONTENTS

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JULY-AUGUST 2016

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August start-up for new hvdroprocessor Allied Energy's new hydrotreater at its Birmingham. Alabama refinery will be complete by August according to contractor DuPont, which is supplying its IsoTherming® hydroprocessing technology for the ultra-low diesel (ULSD) project. IsoTherm-

Sulphur 365 | July-August 2016 Sulphur 365 | July-August 2016 gen and sulphur production, can process up to 3.5 million t/a of VGO. It will help Lukoil improve overall fuel quality and increase output of ultra-low sulphur diesel by 1.8 million t/a, from its current level of nearly 4 million t/a. Last year Lukoil commissioned a new crude distillation unit at

Sulphur production at the refinery will increase by 44,000 t/a once the new VGO facility is at full capacity.

the refinery, raising throughput from 11

million t/a of oil to 15.7 million t/a. The

government agreed plans to modernise

Russia's refineries in 2011 after gasoline

supplies almost ran dry due to a lack of

KA7AKHSTAN

Kazakhstan looks for decision on Tengiz expansion

The Kazakh government is pushing the Chevron-led TengizChevrOil (TCO) joint venture to make a final investment decision soon on the huge Future Growth Project (FGP) expansion of the Tengiz oil field. The FGP is set to increase oil and gas production at TCO by 30% by 2022, but a decision on whether to proceed with the project, which could cost tens of billions of dollars, has been postponed due to the oil price slump. Tengiz produces about 600,000 bbl/d of crude oil as well as 15 bcm of natural gas - around one third of Kazakhstan's output of the latter. Much of the gas is reinjected, in order to maintain well pressure, although more is being produced as production rises, and most of the gas production from the new phase would be reinjected, so sulphur output would probably not be affected/ Chevron has a 50% stake in TCO, alongside ExxonMobil (with a 25% share), Kazmunaigas (20%) and Lukoil (5%).

Processing plant, TCO.

SAUDI ARABIA

Rabigh sulphur plant on-stream later this year Rabigh Refining & Petrochemical Co.

(Petro Rabigh), a 75%-25% joint venture between Saudi Aramco and Sumitomo Chemical Co., says that it has completed mechanical work on its ethylene cracker expansion project at the port of Rabigh. The Rabigh Phase 2 expansion increases ethylene gas processing capacity from 30 million cfd to 125 million cfd and raises ethylene production from 1.3 million t/a to 1.6 million t/a. Other parts of the Phase 2 expansion, which include a 220,000 t/a polyether polyol production unit, a naphtha processing unit, and a sulphur recovery unit, are scheduled for start-up during 40 2016, the company said. The sulphur recovery section has a capacity of

Maire Tecnimont subisdiary Kinetics Technology was awarded the EPC contract for the Clean Fuel Project section of the plant at a value of \$148 million. KT's scope consists in the execution of a 17,000 bbl/d Naphtha Hydrotreater and the 290 t/d sulphur recovery unit.

INDIA

Chennai Petroleum upgrade complete by November

The Chennai Petroleum Corporation Ltd says that it will complete work in November on a new sulphur recovery unit which forms part of a major \$465 million upgrade programme. The expansion includes a residue upgrader with a delayed coker to help convert 'bottom of the barrel' fractions to value added products such as LPG, diesel and other distillates, and a new crude oil

pipeline from Chennai port to the Manali Refinery at an estimated cost of \$40 million. CPCL is also setting up a fluid catalytic cracker gasoline treatment unit at an estimated cost of \$75 million with the objective of reducing sulphur content in its output to less than 10 ppm (Euro-VI). Capacity at the sulphur recovery unit will be 200 t/d.

UNITED KINGDOM

Sour gas processing plant cancelled

BP has confirmed it has scrapped plans for a new gas sweetening plant at Shetland's Sullom Voe terminal. The company announced that the project had been put on hold "due to the current business climate", and said that it now intends to focus on enhancing the gas sweetening capability of its existing plant at Sullom Voe. The project would have flared H₂S-rich gas via a 55-metre high incineration stack and a 70 m main flare stack. A company statement said: "given the current business climate and as a result of revised west of Shetland sour gas production modelling work, the Sullom Voe Gas Sweetening (SVGS) partners have concluded that a more cost-effective solution to meeting future gas sweetening needs for the region is possible. Consequently the revised SVGS project will focus on enhancing (and potentially expanding) the gas sweetening capability of the existing plant at SVT and maintaining the existing offshore sour gas 'scavenging' capability on Clair and Schiehallion

CHINA

Start-up for new hydrotreater

Sinopec ahs started up a new diesel hydrotreater at its Quanzhou refinery. The 78,000 bbl/d hydrotreater was licensed from DuPont's IsoTherming technology, has successfully completed performance testing and met performance guarangees. IsoTherming technology employs a novel reactor system which DuPont claims uses the hydrogen and catalyst more efficiently, lowering capital and operating costs. The hydrotreater is designed to process a variety of cracked feedstocks to produce diesel with less than 10 ppm sulphur (Euro-V standard).

The \$4.9 billion grassroots Quanzhou refinery has a capacity of 240,000 bbl/d, and started up at the end of 2013, and achieved full capacity in 2015. Sulphur recovery prior to the start-up of the new hydrotreater was 800-900 t/d.

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Sulphur 365 | July-August 2016

New copper smelter for Gujarat

Adani Enterprises is in the process of setting up a 1 million t/a copper smelter at an investment of \$1.5 billion at the Adani Port Special Economic Zone in Guiarat. The project includes a copper smelter, sulphuric acid plant, copper refinery, continuous cast copper wire rod plant, precious metal recovery plant, phosphoric acid plant, and an aluminium fluoride plant among others, according to an environmental impact statement filed by the Indian Ministry of Environment and Forests (MoEF). The copper concentrate and rock phosphate required for the project will be sourced by a mixture of imports and domestic production. Sulphuric acid output will be 3.000,000 t/a, some of which will be used to produce 500,000 t/a of phosphoric acid. The company estimates that the smelter could be on-stream by 2019 assuming all permits are granted.

Food grade phosphoric acid plant

Guiarat Alkalies and Chemicals Ltd savs it is considering developing a hydrazine hydrate plant and food grade phosphoric acid plant at Dahei. The funding for both the projects would be spread over 2-3 years with costs being met from internal revenue streams, according to a company filing, Project costs are estimated at \$24 million for the hydrate project and \$45 million for the phosphoric acid plant. The company already has an existing 26,400 t/a industrial grade phosphoric acid plant at the site.

EGYPT

Outotec to supply two acid plants to El Nasr

Outotec has agreed with Spanish engineering company Intecsa Industrial, part of ACS Group, on the design and delivery of process technology and proprietary equipment for two sulphuric acid plants. The plants are to be built for the El Nasr Co. for Intermediate Chemicals (NCIC) fertilizer plant in Egypt. The order is valued at over €30 million and has been booked in Outotec's 2016 second quarter order intake

The two new sulphuric acid plants designed by Outotec, each with a capacity of 1,900 tonnes per day, will produce high grade sulphuric acid from elemental sulphur for fertilizer production and steam for energy generation. The plants will meet all the current and planned Egyptian environmental requirements. In order to recover as much energy as possible, the heat recovery system uses the surplus heat of the waste heat boiler and absorption section and turns it into low- and high-pressure

The sulphuric acid plants are expected to be operational in 2018.

"We are pleased to be involved in the NCIC fertilizer project through our partner Intecsa Industrial, Outotec's advanced sulphuric acid plant solution will be the key

part of the fertilizer production complex

and enable efficient use of resources with

minimal environmental impact," says Pertti

Korhonen, President and CEO of Outotec.

Belgian-based EcoPhos has contracted

Veolia to supply concentrator to phosphate plant

Veolia Water Technologies to supply two HPD® evaporation and crystallisation systems as part of a new fertiliser production facility in Egypt. The HPD systems will be installed as two senarate units and will include a calcium chloride preconcentration and concentration plant as well as a phosphoric acid concentration system. The facility is being developed by Evergrow, a private fertilizer and chemical company based at Giza, which is developing a new production complex at the El Sadat Industrial Zone in Menofia Governorate. The new facility will include the production of 60,000 t/a of di-calcium phosphate, 33,600 t/a of purified phosphoric acid (PPA), and 90,000 t/a of granular, anhydrous calcium chloride. The phosphate end product will be sold into the agricultural and animal feed markets following the start-up of the plant at the

Laurent Palierne, business development manager at EcoPhos, said: "Veolia's equipment will concentrate phosphoric acid to 85% HaPO, and 160,000 t/a of calcium chloride of which, 90,000 t/a will be granulated to 96% CaCl2. Purified calcium chloride is a co-product of our eco-friendly. proprietary EcoPhos process and results from the reaction of hydrochloric acid with low-grade rock to produce DCP and PPA."

EcoPhos is providing the technology licence, basic and detailed engineering services, and supplying proprietary and general equipment to Evergrow, and will off-take all of the di-calcium phosphate for its animal feed phosphate business Aliphos. The process uses hydrochloric acid from SOP furnaces and low grade rock phosphate as feed stock.

FINLAND

New acid plant for paper mill

Metsä Group is building a sulphuric acid plant at the bioproduct mill in Äänekoski, Finland. The plant will be constructed by Valmet. The €20 million investment will be the first large-scale sulphuric acid plant to be integrated into the pulp manufacturing process, according to the company. It will process sulphur-containing off- gases from the mill into 35 t/d of sulphuric acid, which the bioproduct mill needs in the manufacturing of, among other things, tall oil. This will reduce the mill's sulphate load on natural water courses as compared to the current mill at Äänekoski, even though production capacity will nearly triple. The internal recycling of chemicals will also reduce chemical transportation by about 360 truckloads a year.

The plant will begin production at the same time as the bioproduct mill, in 30 2017.

"A plant that makes a process chemical out of the sulphuric compounds in odorous gases is a significant step towards a closed chemical circulation, which will improve the bioproduct mill's environmental performance even further," commented Merikallio, project director of the bioproduct mill.

Electrochemical waste water treatment system

Outotec has developed a new electrochemical water treatment process (EWT) for treatment of industrial waste water from the mining and mineral processing industry. Outotec has combined its experience in water treatment, process design, electrolysis and hydrometallurgy into a cost-effective modular product - Outotec EWT-40. The process is highly automated, minimising the personnel requirement while ensuring high quality performance, and can be purchased as a standalone process island with full maintenance, spare parts and operational support services. Potential

sources of water contamination from the mining industry include drainage from surface and underground mines, wastewaters from beneficiation, surface run-off and acid mine drainage.

SOUTH AMERICA

Acid plant revamp

Outotec says that it has been awarded a €33 million contract by a customer at an undisclosed location in South America to revamp a copper smelter and sulphuric acid plant. Outotec will deliver engineering, process technology and equipment for improved gas handling and reduced sulphur dioxide emissions, improved heat recovery and water management, as well as technical assistance during the construction, commissioning and start-up of the smelter and acid plant.

"We are pleased to provide specialized technical services to our customer and help them to comply with the new environmental regulations. In this project we have combined our efforts with our customer to extend the life cycle of their facilities, secure business sustainability and care of environment in a mutually beneficial way", said Jyrki Makkonen, head of Outotec's Metals. Energy & Water business area.

UNITED STATES

Veolia buys Chemours' Sulphur **Products division**

Veolia's North American business is

buying the Sulphur Products division of Chemours for \$325 million. The division specialises in the recovery of sulphuric acid and gases from the refining process, which are recycled into clean acid and steam used in a wide range of industrial activities. Veolia, whose traditional European municipal water business is stagnating, is seeking growth in industrial waste recycling and focusing on waste that is toxic or hard to treat. Veolia said the takeover will bring growth opportunities in the refinery services sector, and help Veolia capture future demand for clean gasoline related products. The new unit had 2015 revenue of \$262 million and employs 250 employees at seven sites across North America. The transaction is expected to close in the second half of 2016, subject to regulatory approval. Chemours, which has a market capitalisation of \$1.52 billion was spun off from DuPont last year.

Another attempt to save La Orova

zvnski has told residents of La Orova that he will make his "strongest effort" to reopen the polymetallic smelter at the town. The smelter was closed down in 2009 when US-based operator Doe Run Peru went bankrupt, re-started in 2012 running just the zinc and lead lines, but closed again in 2014 when the operator was unable to buy concentrates or fund environmental upgrades to allow operation of the copper smelter. The plant, now in the hands of its creditors, faces liquidation in August this year unless a new buyer can be found. Kuczynski takes office on July 28, but he has asked La Oroya residents to march to Lima to help him press the incoming opposition-controlled Congress to extend the liquidation deadline. However, Kuczynski's party will have just 18 seats in the 130-member Congress. while his defeated presidential rival. Keiko Fujimori, will have 73 seats. Kuczynski says that he wants to Peru to become a refining and smelting hub to boost its copper, zinc, tin, gold and silver exports

La Oroya had about 180,000 t/a of acid production from its zinc and lead circuits at the time of last operation. An acid plant which would have handled emissions from copper production, and which would have generated 330,000 t/a of acid remains uncompleted

Start-up at copper smelter

China Minmetals has started production of copper cathodes at its 100,000 t/a Shuikoushan smelter in Hunan province. The smelter will consume roughly 270,000 t/a of copper concentrates at full capacity, using a smelting technology developed jointly by Minmetals and Shuikoushan. Although Minmetals, owns the Las Bambas copper mine in Peru, is not expected to divert tonnages from there, but will instead bring in material from the wider market.

Mosaic interested in Vale fertilizers?

Mosaic is understood to be in talks to buy Vale's fertilizer unit, potentially valued at as much as \$3 billion. Mosaic is reportedly on the lookout for undervalued phosphate and potash assets worldwide which can be purchased relatively cheaply in a



The La Orova smelter Peru

weak commodity market. Vale has fertilizer assets in Canada, Peru, Argentina and Mozambique, as well as its major presence in Brazil, the world's fourth largest consumer of fertilizers after China, India and the US, and a country where demand is expected to outpace global growth in fertilizer demand over the next decade.

Also in the frame is Norwegian fertilizer major Yara, which confirmed in May that it is considering purchasing part of Vale's fertilizer business in Brazil. Vale is reportedly looking to sell a 40% stake in its Brazilian fertilizer assets for around \$1.2 billion as part of a plan to raise \$10 billion, after posting its largest quarterly loss in decade. although if it were to sell its entire fertilizer business it could be worth \$3 billion. The company's fertilizer assets include Fosfertil - Yara's share of which Vale bought out in 2010. Yara subsequently bought Bunge Fertilizers from Vale in December 2012. Vale posted a record annual loss last year of \$12.1 billion

Liofsa looks towards food grade phosphoric acid Lithuania's phosphate fertilizer manufac-

turer Lifosa, 100% owned by Russian chemical and fertilizer giant EuroChem, says that it plans to invest approximately €75 million in a new food grade phosphoric acid plant. Lifosa currently primarily produces DAP. with around 900,000 t/a of capacity, but the company reportedly considers that the prospects for industrial phosphates are more "robust" and the addition of this production line would boost competitiveness. To expand production, Lifosa also says that it plans to build new production premises at Kedainiai, in central Lithuania. The company says that it will disclose more details later in the year, once the final investment project is ready

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Harold H. Weber, Jr., P.E., vice president, Regulatory Affairs and Special Projects for The Sulphur Institute (TSI), will retire on June 30th, 2016. Mr. Weber departs TSI after 32 years of advocating responsible and beneficial resolution of issues associated with international sulphur transportation and logistics. His accomplishments include working with regulatory agencies to adopt appropriate requirements for sulphur transportation. Most notably, he fostered adoption of a special provision for formed. solid sulphur in the United Nations Recommendations on the Transport of Dangerous Goods, a new chapter in the International Maritime Solid Bulk Cargoes Code, and regional adoption of this special provision around the world.

Prior to joining TSI in 1984, Mr. Weber managed road construction programs, including sulphur asphalt paving, for six years with the US Federal Highway Administration and an additional six years with the Pennsylvania Department of Transportation, managing road and bridge construction. He served as TSI's representative on the Association of American Railroads Tank Car Executive Committee.

For 38 years of his professional career, Mr. Weber has been involved with

the sulphur industry. His efforts to bring together industry members to improve availability of safety information and leading practices will continue to have positive impacts on industry long after his retirement. "While I am sad to leave TSI behind, my wife and I are eagerly anticipating more family time and travel," said Mr. Weber. "Harold is a valued member of The Sulphur Institute's team and its legacy as an industry-wide advocate for sulphur," commented Robert McBride, TSI President and CEO.

Morocco's Office Cherifien des Phosphates (OCP) has opened a subsidiary in Geneva under the name Saftco. Saftco will be involved in trading commodities, including phosphates, fertilizers and chemicals. The new president of Saftco will be **Choho Tarik**, one of the four co-directors of OCP, and the former director of downstream subsidiary Areva. OCP recently announced the creation of a network of subsidiaries in 15 African countries under the auspices of OCP Africa, with the aim of expanding the continent's underdeveloped fertilizer market.

Anglo American has announced the appointment of **Ruben Fernandes** as CEO of Anglo American in Brazil. In addition to

his current role as CEO of Anglo American's Nickel and Niobium & Phosphates businesses, Ruben Fernandes will also lead the Iron Ore Brazil business (Minas-Rio), with effect from 20th June 2016. Ruben Fernandes will continue to report to Duncan Wanblad (CEO of Base Metals & Minerals) in respect of the Nickel and Niobium & Phosphates businesses, whose divestment processes are progressing, and to Seamus French (CEO of Bulk Commodities) in relation to Iron Ore Brazil. Pedro Borrego, who has served as interim CEO of Iron Ore Brazil since November 2015 and who was integral to the development and commissioning of the Minas-Rio operation over many years, will assist Fernandes with the transition over the coming months, prior to taking up a new role based at Anglo American's London head-

Duncan Wanblad, CEO of Base Metals & Minerals, said: "We congratulate Ruben Fernandes on his appointment to lead our Brazilian businesses. While we are currently progressing divestment processes for our Nickel and Niobium & Phosphates businesses, Ruben is well placed to provide leadership across Anglo American's interests in Brazili."

Calendar 2016

JUNI

27-2

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

Email: conferences@crugroup.com

ASRL Chalk Talks, CALGARY, Alberta, Canada

Contact: Patricia Alegre, Alberta Sulphur Research Ltd Tel: +1 403 220 5346

Fax: +1 403 284 2054 E-mail: asrinfo@ucalgary.ca

SEPTEMBER

12-1

Brimstone Sulphur Symposium, VAIL, Colorado, USA Contact: Brimstone STS Ltd, 6547 South Racine Circle, Suite 1600, Centennial, Colorado 80111, USA. Tel: +1 909 597 3249 Fax: +1 909 597 4839

Email: mike.anderson@brimstone-sts.com Web: http://brimstone-sts.com/symposia/ vail/vail-registration-page/

OCTOBER

9-11

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

Web: www.universulphur.com/mespon

NOVEMBER

7-10

CRU Sulphur 2016 Conference and Exhibition, LONDON, UK Contact: CRU Events Chancery House, 53-64 Chancery Lane, London WC2A 1QS, UK.

Tel: +44 20 7903 2167 Email: conferences@crugroup.com

1116

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

2017

FEBRUARY

26 - 1 March

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

MARCH

Phosphates 2017, TAMPA, Florida, USA Contact: CRU Events Chancery House, 53-64 Chancery Lane, London WC2A 1QS, UK. Tel: +44 20 7903 2167

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SULPHUR PRODUCTION SULPHUR PRODUCTION



Do oil prices affect sulphur production?

While the precipitous drop in oil prices in 2014-15 has led to many project postponements and delays on upgrading and processing plants in the heavy oil/oil sands sector, will there actually be a significant effect on overall sulphur production?

he slowdown in the Chinese economy has had a huge knock-on effect on oil prices, coming as it did at the same time as a surge in oil supply from a number of different sources, but most particularly from US tight oil production, extending the fracking techniques developed in gas extraction into oil-bearing shales. However, what has really kept oil prices at their current relatively low level for the past year (see Figure 1) has been Saudi Arabia's decision to continue to keep pumping oil in order to maintain or gain market share. So, given that 48% of sulphur production comes from refining of crude, does the crude price have any impact on sulphur production?

Oil output

The most likely consequence of such a large drop in oil prices would be, one would expect, a fall in oil production and concomitant drop in sulphur output. However, while a great deal of new investment has been postponed in the current oil price environment, actual cuts in oil output have been few and far between. In particular, Saudi Arabia, with the lowest oil production costs and greatest spare production capacity, has refused to play its traditional role of swing producer, and continued to pump oil in spite of protests from other OPEC members such as Iran, Venezuela, Ecuador and Algeria, some of whom are

suffering from the low oil price environment in terms of budgets and public spending.

Saudi Arabia's initial hope seemed to be to force higher cost competitors out of the market, including Brazilian deep water production and US shale/tight oil producers, but this seems to have been slow in coming. In the meantime, OPEC has not been able to agree on production cuts, and the best that could be agreed at its most recent meeting was a production freeze at current levels among some members, including Saudi Arabia, Kuwait and Venezuela. In February, Russia also agreed to an oil production freeze at its January level – admittedly a record for post-Soviet oil production.

The worry from OPEC's point of view is that cuts in production would simply open the way for new US tight oil production. Another fly in the ointment is Iran, which is just emerging from many years of international sanctions, and which is keen to sell oil to improve the country's financial position. Iran has been busy trying to ramp up production from its previous production

level of 2.6-2.8 million bbl/d to its pre-sanctions level of 4.0-4.3 million bbl/d, as we discussed in the March/April issue (pp22-24). Like Saudi Arabia. Iran has low costs of production, and can make a profit even at such low oil prices, and Iran has so far refused to join the OPEC production freeze. Another snag for OPEC is Iraq, whose production has risen to its highest level since the US-led invasion in 2003, and whose hard pressed and cash-strapped government is reluctant to let production fall back again. Iraq has nevertheless said that it will freeze production if others do, but the lack of agreement with Iran has been Iraq's excuse to keep pumping.

The consequence has been that actual cuts in oil production have so far taken a long time to materialise, only finally starting to appear in the past couple of months. US output has fallen the most. with Canada and Venezuela also cutting production. US output is reckoned to be down by 800,000 bbl/d since mid-2015, and the Energy Information Administration (EIA) says that it expects another 800.000 bbl/d of cuts over the next few months. Latin American production is down 440,000 bbl/d on a year ago, with Venezuela representing almost half of that fall, as the country faces economic crisis and unrest. China is expected to

Fig 2: Oil price impact on US tight oil production

140
120
0il production index (Jan 2104 = 100)
88
60
WITI monthly average price, \$
20
0
Note that has a purple of the production index (Jan 2104 = 100)
88
Source: IEA

see a 6% fall in production over 2016 due to ageing fields and poor economics. Signs of tighter supply have helped lift oil prices slightly in recent months, as Figure

US tight oil

The ostensible reason that Saudi Arabia has kept pumping oil is to put US tight oil production out of business. However, as Figure 2 shows, while the decline in oil price has had a rapid effect on the rig count, with only a few months' delay between price falls and falls in rig count, the amount of oil actually coming from US tight oil production has barely slowed. While some of this may be down to more efficient drilling techniques and technology, the main explanation appears to be that it has been the wells that are in declining production which have been preferentially shut in, while more recent wells with increasing production have been left running. With tight oil wells having a relatively short lifespan, on the order of a couple of years, this appears to mean that there will be a lag of 1-2 years between falling rig count and falling production. However, we now appear to have entered that period. In its medium-term oil outlook issued on Monday, the IEA forecast that US light, tight oil production from shale would fall by 600,000b/d this year and another

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Options for acid cooling

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BCInsight

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200,000b/d in 2017 before prices recover and stoke additional output.

However, the IEA has also cautioned that the responsiveness of the US market could also mean that in the event of a sustained improvement in world oil prices, these rigs could equally be back in use again and production could recover rapidly. Fatih Birol, executive director of the IEA, has said that if oil prices rally, the rise would be capped quickly by a corresponding rise in US tight oil production. He has said the oil price could recover to \$80/bbl by 2020, but a price above \$60 would be enough for US production to grow again.

Conventional wisdom is that one of

the higher cost oil producing sectors is

Oil sands production

Canada's oil sands patch, and so it was expected that this would be an area that might see reductions in output. However, in fact - in spite of a spate of proiect deferrals and postponements for new capacity, especially more expensive upgrading capacity - output has continued to increase, with overall Canadian production (including both conventional and oil sands production) rising 3.5% during 2015 to 3.89 million bbl/d, and oil sands production could rise 6% in 2016. with the extra coming from existing expansions which were already well advanced and where money had already been spent. There have been some cancellations, like Shell's 80.000 bbl/d Cameron Creek in situ project, and producers have laid off staff and made efforts to cut costs, but this appears to have borne fruit; the Bank of Montreal estimates that during 2015 break-even production costs fell 18% and ranged between \$25/bbl for producers who use steam and \$40/bbl for the mining operations, ExxonMobil claims to have cut costs by 40% to \$19.20/bbl.

This effect has been masked somewhat by the disruption to Canadian oil sands production caused by the wildfires which have raged around Fort McMurray, forcing the temporary shutdown of more than 690,000 bbl/d, much of which is only now returning to production. Nevertheless, Suncor savs that it should still produce 430-460,000 bbl/d during 2016, as compared with 463.000 bbl/d in 2015, and that it still plans to start up the 180,000 bbl/d Fort Hills project in 2017, on budget and on schedule. Suncor has also moved to consolidate by purchasing rival Canadian

Table 1: US refinery sulphur output. million tonnes

| Production area | Q1 2015 | Q1 2016 |
|-----------------|---------|---------|
| PADD1 | 0.049 | 0.035 |
| PADD2 | 0.314 | 0.367 |
| PADD3 | 1.18 | 1.25 |
| PADD4+5 | 0.345 | 0.314 |
| Total | 1.888 | 1.966 |
| Source: US EIA | | |

Oil Sands through a successful tender that closed in February. With the caveat that it can take years for a new oil sands operation to ramp up to full production, a paper total of 423,000 bbl/d of new capacity is under construction and scheduled to be in operation this year, up from 116,000 bbl/d added last year.

While industry experts estimate that US light, sweet oil prices need to be \$60-80/ bbl to warrant any significant new investment in oil sands mines, current production appears able to weather the present low oil price environment.

US refinery output

One potential effect of lower oil prices is that more expensive, light sweet crudes become more affordable, and so refiners who have to meet stringent sulphur specifications may switch to processing lighter feeds. There is some evidence that this has happened in parts of the US, as it helps to build up credits for the forthcoming switch to so-called 'Tier 3' regulations on sulphur content of gasoline. Many US refineries are in the middle of a significant capital investment programme to meet the new regulations, which come into force on January 1st next year and which will cut permitted sulphur content of gasoline to 10 ppm from the current 30 ppm. However, there have been some guestions as to how many refiners will be able to meet the new standards, and the price of credits for producing low sulphur fuels issued by the US Environmental Protection Agency (EPA) - which can be offset against higher sulphur production, have skyrocketed from \$25 to \$400. The EPA estimates that up to 40 of the 108 refineries which will have to meet the new standards will be forced to use credits to comply.

Even so, as Table 1 shows, overall US refinery sulphur output is also actually up this year as compared to last, especially in the PADD2 (Mid-West) and PADD3 (US Gulf Coast) regions, as the impact of the new investment in sulphur processing capacity makes itself felt.

Future supply growth

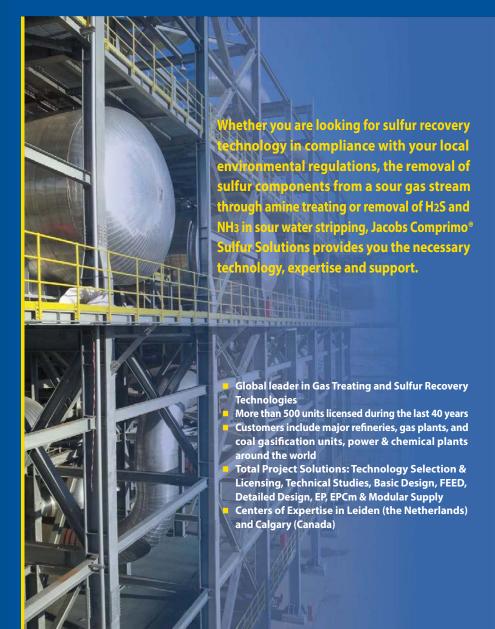
While cancelling an investment where there may already be significant sunk costs can be a difficult decision, postponing spend on new developments is a much easier decision to take, and so the main effect of a drop in oil prices is to push back new capacity into the future. There are now signs that production is beginning to fall in some places because of the drop in exploration investments. RBC Capital Markets has calculated that projects capable of producing more than 500,000 bbl/d of oil were cancelled, delayed or shelved by OPEC countries in 2015, and this year promises more of the same. The effect on US tight oil production has, as we have seen, been even more marked.

Sulphur supply

The question for the sulphur industry is what effect this has on sulphur production - sulphur from oil processing is responsible for almost half of all sulphur production, after all. As far as current oil cutbacks go. US tight oil production is for the most part light, sweet crude. The EIA calculates that roughly 90% of the more than 3 million bbl/d growth in production from 2011 to 2015 consisted of light sweet grades with an API gravity of 40 or above and a sulphur content of 0.3% or less. The impact of this tight oil on sulphur production has thus been relatively modest. Canadian oil sands syncrude of course, by contrast, is heavy and sour, but as we have seen. there has been no real cutback in output except for the temporary outages provided by the wildfires in Alberta. Venezuelan production is down, representing a significant slice of sour crude, but OPEC has so far only been able to agree production freezes, while Iran and Iraq continue to pump more oil. Next vear will see more Canadian oil sands production and the anticipated restart of the Kashagan project in Kazakhstan. Investments in desulphurisation capacity in refineries are made on the basis of regulations and have to look at much longer time frames than a couple of years of low prices. So the answer to the question at the start of the article - do oil prices affect sulphur production – appears to be 'not much'.

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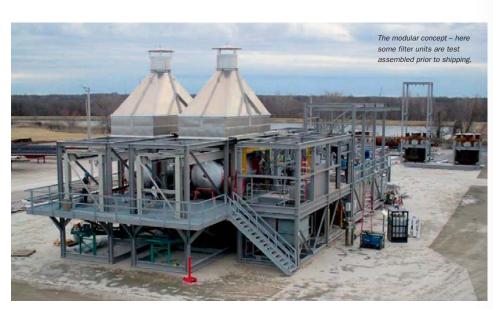
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US taps into new sulphur sources

Mosaic's new million tonne sulphur melter at New Wales in Florida has the potential to radically change the US sulphur market by allowing access to large tonnages of solid sulphur from overseas.

ormed from the merger of Cargill and IMC Global, and supplemented by its 2014 purchase of the phosphate assets of CF Industries. Mosaic is the world's largest producer of finished phosphates, with an annual operational capacity of 11.7 million t/a of processed phosphates (including DAP, MAP, animal feed, and its MicroEssentials speciality nutrient). It also has the capacity to mine 16 million t/a of phosphate rock in Florida, second only to Morocco's OCP in size. The company is also North America's largest single buyer and consumer of sulphur. At the start of 2016 it completed work on a new 1 million t/a sulphur melter at its New Wales site near Mulberry, Florida, which means that the company can now take solid sulphur as well as the liquid cargoes it has been used to.

Market drivers

At the SOGAT 2016 Sulphur Workshop. Herman Wittje of Mosaic explained the market rationale behind his company's decision. Mosaic manufactures on average around 4.5 million t/a of phosphoric acid, and in so doing consumes 4.5 million t/a of sulphur. Historically this has been brought in as liquid sulphur from Canada or other parts of North America (including some vessels from Mexico), but falling production, especially from Canada, was beginning to potentially threaten Mosaic's security of supply. Canadian sulphur production fell from 8 million t/a in 2004 to just over 5 million t/a in 2015. Over the same period, US sulphur production from sour gas dropped form 1.4 million t/a to

500,000 t/a. However, at the same time, sulphur production in other regions, especially the Middle East, has been rising rapidly, from about 12 million t/a in 2014 to 22 million t/a in 2018. Large new sulphur producing capacity in Abu Dhabi, at Habshan and Shah, is putting huge new volumes of sulphur onto the world market. The problem for Mosaic is that all of this new sulphur is in granulated form, while the North American market has always traditionally been a liquid sulphur market.

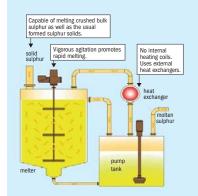
The construction of the melter, then, allows Mosaic access to the large cargoes of granulated sulphur emerging from the Middle East and elsewhere. But over and above security of supply, Mosaic also hope that the melter may allow them to improve their competitive position in terms

of cost of sulphur. Typical freight rates for molten sulphur from Alberta to Florida can be more than \$100/t, as it must be carried by rail the entire distance. Seaborne freight rates from Russia or the Middle East, conversely, can be as low as \$15-25/t, especially in the current oversupplied bulk freight market. Mosaic hope that the flexibility offered by the melter will also give them an advantage in negotiating with existing suppliers. If Mosaic could shave even \$20/t off their delivered sulphur price, the \$20 million melter would pay for itself in a few months.

Location

Having decided on the concept of the sulphur melter, the next questions for Mosaic were the facility's size and location. The capacity chosen for the melter was 1 million metric tonnes per year, just under 25% of Mosaic's annual consumption, giving them a comfortable margin in the event of any potential supply shortfall from North America – although of course, the option remains open to them to build a second train if need be.

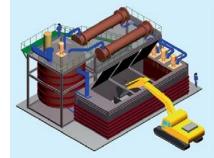
While Mosaic initially considered siting the melter directly on Tampa Bay, the choice of the New Wales site for the melter minimises the distance that liquid sulphur needs to be transported, allowing it to be released directly into Mosaic's Florida operations, which consume over 80% of the company's sulphur requirements. New Wales itself is the largest of Mosaic's Florida sites, with steam and on-site utilities already present, reducing operating costs. Access is provided by two ports on Tampa Bay where the dry sulphur can be unloaded. Port Red Wing is almost due west of the New Wales site at a distance of 26 miles (41km), while Port Manatee. slightly further south, is 46 miles (73km) away. Red Wing can handle vessels of a draft of 9.9 metres, and Manatee 12.2 metres, allowing it to handle Panamax vessels. There are 80,000 tonnes of bulk storage capacity at Red Wing and 55,000 tonnes at Port Manatee. Both ports have unloaders capable of handling 8,000 t/d. and allowing Mosaic to bring to bear its own existing logistical operations which include vessels, barges, rail and truck transportation and both solid and liquid bulk storage, allowing them to guarantee offtake to any potential supplier. It also allows Mosaic to potentially back haul finished products back to Red Wing and Manatee in the same trucks and trains Fig 1: Key components of the New Wales high capacity sulphur melter system, based on CTI consulting technology



- High volume sulphur melting units with capacities up to 4.000 t/d.
- External heat exchanger (HEX) gives high heat transfer coefficient, allowing high melting rates.
- High circulation rate through HEX for efficient heating and melting.
- All vessels and equipment are above ground.
- Vertical "in-tank" pumps.
- All molten sulphur is contained during unplanned shutdown.
- Customisable to meet specific customer requirements.

Source: Devco

Fig 2: New Wales melter schematic. Rectangular pump tank, cylindrical melter mixing tank and tube-shaped heat exchangers



- Modular construction for easy shipment and onsite assembly.
- High availability due to ease of removing non-meltables.
- Sulphur system designed to drain into pump tank.
- Access hatches allow easy cleanout.
- Designed for efficient maintenance of equipment.

Source: Devco

that the sulphur is delivered, for onward transport by sea or by barge up the Mississippi River.

The technology

The design and construction of the melter was handled by Tulsa-based Devco, working in partnership with sister companies Crescent Technology Inc (CTI), who provided the sulphur melt technology, and materials handling exports River Consulting. Other key partners included Lewis Pumps, MECS and Lightning Mixers. The innovative design, by CTI, does not use internal heating coils in the melter. Instead there is a continuous flow of molten sulphur into which the dry sulphur

between the dry sulphur and molten sulphur makes for more efficient heat transfer and melting, with the processes also speeded up by the rapid agitation provided via the rotating impellers. Molten sulphur then circulates to the pump tank and some is then pumped back into the melter after pasing through the heat exchangers, where heat is added to the process externally via three large 20m low pressure heat exchangers which use process steam from elsewhere at the site on the outside of the exchanger, heating molten sulphur as it passes through on the internal side. Using external heat exchangers allows the molten sulphur to be circulated at a higher velocity, according to Devco.

is mixed (see Figure 1). Intimate contact

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relatively modest 7 metres across, helping keep within the limited footprint - space for the melter was extremely restricted at the site. The rate of circulation of molten sulphur can then be used relatively easily to control the rate of heat transfer and the working rate of the melter. This means that turn-down can be to effectively almost zero, as the system continues to circulate even without the addition of new sulphur. The whole structure is raised above

All of this allows the melter vessel to be a

a pit, allowing the entire system to be drained if access to the pump tank is required. Likewise the melter is raised above the pump tank, and non-meltables collect at the conical base of the melter tank and drain into the pump tank, settling at the bottom. This means that the solids at the base of the pump tank can be cleaned out even during operation, as shown in Figure 2, without having to disturb the melter vessel itself and trigger a major shutdown. The triple heat exchanger system is also likewise designed with redundancy, so that one can be off-line at any given time for maintenance without stopping operation.

The system is completed with a 6,000 tonne storage hopper for the dry sulphur and a filtration system which cleans sulphur coming from the melter before it travels to the acid plant. The melter is fairly tolerant of a wide range of composition for the input sulphur, and is designed to handle moisture content of up to 5%.

Construction

Mosaic had what Devco describe as an "aggressive" schedule for implementation of the project. The project only received board approval in May 2014, but was hoped to be operational during late 2015. Construction eventually took 14 months from ground breaking in November 2014 to mechanical completion. The rapid timescale was achieved, Devco says, through using modular construction, allowing equipment packages to be assembled at Devco's facility in Tulsa and transported as a 14'x14'x40' container block. This allowed more control over the materials and construction environment and reduced the risk of schedule slippages, as well as reducing exposure to labour costs as compared to field construction.

The main candidates for modularisation and off-site assembly were the control units, process equipment, utilities and pipe racks,



The finished New Wales melter

which could be supplied skid-mounted and pre-wired/tubed. The pump tank was also fabricated in Tulsa, as were the filtration units. Only the larger melter mixer tank had to be fabricated locally in Florida, at a site only 20 miles from New Wales.

Devco's Mark Gilbreath, who was closely involved in the project from start to finish, advises that this approach does demand good communication between the engineer/constructor and the customer to explain where all the material is. However, unusually high rainfall during the summer of 2015 demonstrated the advantages of pre-assembly in an off-site fabrication shop, allowing the project to keep to schedule. During the main construction phase at the site there were 253 people working a total of 135,000 engineering hours, 100,000 fabrication hours, and over 300,000 construction hours. Mosaic subsequently presented Devco with a Bronze safety award during their annual contractor safety meeting and presentation in April this year, recognising a high level of safe practice achievement working on Mosaic sites. Bronze was the highest award a contractor is eligible for during their first year of major work.

Material-wise, stainless steel was used for the bucket elevators and screw convevors, while the sulphur pump tank and heat exchangers are carbon steel, as are the piping, valves and filters in contact with molten sulphur. The melter vessel is also carbon steel, with ceramic brick for the splash zone at the top. The silos are enoxy lined acid resistant concrete, with the silo cones in stainless steel-lined carbon steel.

Start-up and commissioning happened early in 2016, with handover in April. Design capacity for the melter is 155 st/ hour (140 tonnes/h), or 4,600 st/d (4,200 t/d), but Devco says that it has operated

as high as 200 st/h (180 t/h) with no issues. Operating at an existing site with steam and electricity available from the sulphuric acid plants means that one of the project's key features is the carbon neutral nature of its operation - as steam was already available on-site, there was no need to add any additional energy for the production of sulphur.

Market impact

The US has traditionally been largely a liquid sulphur market. Prior to the start-up of the New Wales melter, the only sulphur remelter in the US was at Galveston, operated by Savage Services and co-owned by Savage and Mosaic under the auspices of Gulf Sulphur Services. However, the start-up of the melter offers the possibility of Mosaic tapping into new sources of sulphur and the emergence of new trade routes to the North American market. During commissioning Mosaic bought sulphur from Abu Dhabi and Kazakhstan for test runs. Changes in Mosaic's sulphur procurement could also force US Gulf sulphur producers to make and export more solid sulphur to Brazil or other markets such as Morocco Mexico which has exported 300-400.000 t/a of liquid sulphur to the US in recent years has simultaneously built 360,000 t/a of solid sulphur forming capacity, presumably anticipating the loss of custom from Mosaic and looking to supply Brazil or Cuba. Most likely is the displacement of Canadian sulphur imports, which are one of the highest cost suppliers

However, the impact of the melter has so far been masked by Mosaic's own cutbacks in phosphate production, which was reduced by 400,000 t/a in February 2016. USGS sulphur statistics for 10 2016 show sulphur imports were actually down slightly at 504,000 tonnes, as compared with 533,000 tonnes for 10 2015. Imports from Mexico in 10 2016 were fairly constant, at 59,000 tonnes - the same as for the same quarter in the previous year. while imports from Canada were down by 30,000 tonnes on the quarter. US sulphur exports were up by 170,000 tonnes at 529,000 tonnes for Q1 2016.

1. Wittie, H. & Gilbreath, M., 2016, Mosaic New Wales Sulphur Melter, TSI Sulphur World Symposium 2016, 11-13 April 2016, Vancouver Canada

Copper and sulphuric acid

The copper industry has a major influence on sulphuric acid markets on both the demand side, for leaching, and on the supply side, for smelting. With the copper industry in the doldrums, Sulphur looks at the impact on sulphuric acid markets.

round one third of all sulphuric acid production comes as a by-product from smelting of primary metals. especially copper. With regulations on emissions of SO₂ from smelters continuing to tighten around the world, this means that almost any new smelting capacity will generate more acid. On the debit side, the share of acid for metal leaching as a component of overall sulphuric acid demand is not as great - around 10% of all acid demand. of which around two thirds goes to copper extraction. Although copper production via leaching has grown faster than smelting over the past couple of decades, it still only accounts for around 20% of copper production. This means that increased demand for copper tends to mean increased output of sulphuric acid. There is also a disproportionate impact on supply in acid markets, as while some acid leaching plants use a sulphur-burning acid plant rather than buying sulphuric acid wholesale, on the copper side (unlike, say, nickel leaching, where most plants have a sulphur burning acid plant)

many do not, and instead buy acid. According to CRU, 25% of demand in the merchant sulphuric acid market is accounted for by copper leaching operations. Likewise, acid produced from smelting is non-discretionary production and must find a market somewhere, and most of the traded acid supply on the market is from copper smelters. The health of the copper market, then, has a major impact on the international market for

Copper markets

Copper demand is irresistibly linked to industrial markets. It is used extensively in: transportation - cars, railway locomotives. buses, subway carriages etc.; construction particularly wiring and piping; power and telecommunications infrastructure; industrial machinery; and electronics and consumer products. As such, it is a key index of industrial production and industrialisation, and it is no surprise that over the past few decades copper use has shifted from mature

industrial regions like North America and Europe to the fast-industrialising countries of Asia. China in particular has driven new copper demand, coming to represent over 45% of all copper demand. This it will also be no great surprise that copper demand has mirrored the Chinese economy - rising rapidly through the first two decades of the millennium, in spite of a brief dip following the global economic crash of 2008, but recently slowing precipitately.

the major countries involved in its mining are Chile, China, Peru, the United States, Australia, Russia, Canada and central African states along the so-called 'copper belt' like Zambia and the Democratic Republic of Congo (DRC). New copper mining capacity is capital intensive and takes some time to bring on-stream, and supply had a hard time keeping up with demand, leading to copper's run of high prices.

Copper has however faced a growing kets remain relatively depressed.

Copper supply is fairly widespread, but

SULPHURIC ACID

crunch over the past couple of years as Chinese demand has slowed rapidly, from 10% growth year on year to 3.8% in 2015 and an estimated 0.6% this year. In particular, sectors that buy copper, such as construction and manufacturing, have been hit hard. At the same time, copper mining capacity which was being developed in the expectation of more Chinese demand has continued to come on-stream. Table 1 shows the effect on production consumption and stocks of these changes - consumption was continuing to increase rapidly up to 2014. but since then has stagnated, while new production has continued to appear and stocks have built. More recently, cutbacks in copper production which were announced in 2H 2015 and Chinese stock building have led to a rally in copper prices - around 10% since January, Nevertheless, copper mar-

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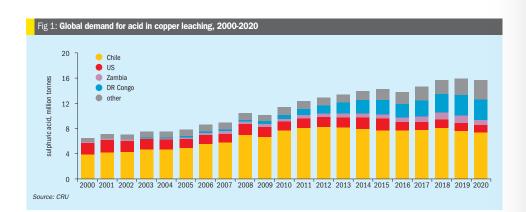
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Copper leaching

Acid demand for copper leaching amounted to just over 14 million t/a in 2015, according to CRU figures. Around 3 million t/a of this was supplied by sulphur-burning acid plants, the rest being sourced from merchant sulphuric acid. Chile was and is the major consumer of acid for copper leaching, its consumption peaking at over 8 million t/a in 2012, but falling ore grades and production cutbacks have reduced this figure in the past few years, and Chile's share of that consumption is steadily falling. Other major users of leaching for copper extraction include the USA, Peru, Zambia and the DRC.

The mines that supply the solvent extraction/electrowinning plants that leach the copper tend to be at the higher end of the cost curve, and so have preferentially been targeted for cutbacks by the major producers. At the end of last year, as the slowdown in the copper market began to bite, there were a number of cutbacks at copper operations, and this disproportionately affected SX/EW capacity. In August. Asarco said that it would shut down a concentrator plant at Hayden, Arizona and slow production at its nearby Ray mine, which had already had two rounds of lavoffs in 2015. At the same time Freeport-McMoRan Inc. said that it would cut its mining expenditure by 25% (\$700 million) in 2016 and announced that it was suspending mining operations at its Miami mine in Arizona (which produced 26,000 tonnes of copper in 2014), a 50% reduction in mining rates at the Tyrone mine (which produced 43,000 tonnes) and adjustments to mining rates at other US mines. It also said it was looking to sell its stake in the El Abra mine in Chile – Chile's Codelco says that it may be interested in purchasing this. In September Glencore elected to suspend operations at Katanga Mining Ltd in the DRC and Mopani Copper Mines in Zambia for 18 months, removing an estimated 400,000 tonnes of copper cathode from the market. Glencore also postponed expansion plants at Collahuasi in Chile, which it co-owns with Anglo-American, and cut production by 30,000 t/a.

The overall effect of these cutbacks can be seen in Figure 1. Acid demand for copper leaching is forecast to drop this year before returning in 2017-18 as new plants start up and temporarily shuttered capacity is able to return to production with the resumption of copper demand, but a lack of new capacity and falling use in Chile we will see demand plateau to 2020.

Copper smelting

Mature industrial regions continue to be the major exporters of smelter acid, with South Korea and Japan the largest exporters, at 2.7 and 3.0 million t/a respectively. Canada also exports 2 million t/a, mostly to the US, and Europe another s 5.4 million t/a, mainly from Spain, Germany and Bulgaria. Some smelter shutdowns have occurred in Europe and especially North America, but the fastest growth in new smelter capacity has been in China. The Chinese acid market has stayed relatively balanced, generally running a small deficit (this rose to 1.2 million t/a in 2015. according to Integer Research). However, it remains to be seen what effect the current glut in the copper market will have on

In spite of an agreement by the ten largest copper refiners at the end of 2015 to cut output by 350,000 t/a (around 5% of output), and government intervention to buy surplus copper. Chinese stockpiles of copper - especially those held by large smelters - have been growing, and there are increasing signs that China may turn to exporting it. Some industry analysts believe China may hold up to 1 million tonnes of refined copper stocks, including bonded stocks, exchange stocks and metal held by traders and smelters, equivalent to 11% of 2015 consumption. At least eight large Chinese smelters are allowed to export refined copper cathode under a tolling scheme, allowing them to import concentrate without a 17% tax provided that they export the refined metal, simultaneously avoiding a 10% export tax. In the meantime, capacity continues to increase. China Minmetals started production of copper cathodes at its 100,000 t/a Shuikoushan smelter in Hunan province in May. for example. China is also continuing to invest in copper mine capacity overseas. in Chile, Africa and elsewhere, to keep up the supply of concentrates. CRU says that recently commissioned smelter projects in China have achieved good operating rates. and that copper smelting is still profitable in China, and hence attracting investment. while finance is readily available for new projects. The only possible fly in the ointment is a shortage of concentrates looking to 2017-18 due to postponements in new mine capacity. Nevertheless, with demand from domestic phosphate production plateauing, most analysts foresee China being in surplus in acid over the next few years and becoming a net exporter.

Sulphur-assisted carbon capture and utilisation

Gary Albarelli and **Mike Lloyd** of the Florida Industrial and Phosphate Research Institute describe work conducted with researcher **Bogdan Wojak** which has opened up the possibility of recovering CO₂ for carbon capture and utilisation via sulphur intermediates.

he unrelenting rise in coal use without deployment of carbon capture and storage (CCS) is fundamentally incompatible with climate change objectives. The world faces an unabated global demand for energy, both for livelihood and for pure economic growth, as well as an existing, sizeable, carbon-intense infrastructure. There is no rational nearterm energy future that does not involve continued use of fossil fuel. Maintaining coal-fired power generation would make practical sense if control of carbon dioxide could be made affordable. Current CCS technologies do not only increase capital costs but also impose significant performance penalties, challenging the competitiveness of coal-fired power generation. Furthermore, many locations worldwide lack the suitable geology for CO2 storage, one of several factors expected to constrain CCS deployment.

Our technology¹ attempts to solve this predicament via a hybrid energy system (HES), in which CO₂ is recirculated by way of conversion to an intermediate sulphur compound; carbonyl sulphide (COS). The conversion enables utilisation of the enormous latent chemical combustion energy value of sulphur to generate complementary electric energy for the various energy-consuming steps in the CCS processes.

Carbonyl sulphide, when reacted with sulphur dioxide, reduces back to sulphur and CO₂. Thus, the sulphur as a fuel feed-stock is recycled, producing neither any detrimental environmental impact of sulphur oxides nor any solid waste. The application of this concept for power generation is virtually universal and a wide variety of arrangements or modifications to the proposed system are possible.

Capabilities and shortcomings

The recirculation of carbon, which constitutes the underlying concept of carbon capture and utilisation (CCU), aims to improve the economic viability of carbon capture. This may well result in accelerating intermediary measures to drive CCS deployment. However, CCU can contribute to alleviating global CO₂ emissions only if the recirculated CO₂ has come from power plants or industry – not from natural geologic sources as is common with, for example, conventional enhanced oil recovery (EOR). In addition, the energy required by the carbon capture and utilisation process should come from carbon neutral sources.

The specific prerequisite for the utilisation of sulphur as a fuel is that the CO₂ already captured from power plants and/or industrial facilities be converted to an intermediate sulphur compound by an industrially proven process of catalytic oxygen/sulphur exchange reaction with a common industrial solvent carbon disulphide (CS₂). However, the necessity of adding the CO₂ conversion system to the post-combustion CO₂ capture system increases the complexity and raises the capital and operating costs of the power plant.

Moreover, to convert substantial quantities of carbon dioxide cost-effectively requires massive scale CS_2 manufacture. Fortunately, carbon disulphide can be synthesised from the plentiful waste materials that are found around chemical, petroleum and other industries. For example, in the Canadian oil sands, carbon disulphide can be rapidly and satisfactorily produced by the use of waste products such as petroleum coke and large stockpiles of sulphur. It can also be alternatively formed by utilisation of $\mathrm{H}_2\mathrm{S}$ from a gas stream containing

the processing of tar sands. However, the drawback of employing carbon disulphide for CO_2 conversion is that the carbon from CS_2 production substantially increases the quantities of CO_2 – equivalent to the volume being converted.

lower molecular weight alkanes derived in

To avoid increasing the volume of CO₂. the conversion can be performed by the reaction of CO2 with hydrogen sulphide (H2S). Typically, this reaction can be carried out by contacting gaseous carbon dioxide and gaseous hydrogen sulphide with a catalyst, in the presence of a sorbent. This specific method of CO2 conversion to COS was commercially employed by Shell at the North Sea Gas Terminal Emden, Germany as a conditioning method prior to distribution of natural gas contaminated with a lean volume of H2S. However, a more efficient catalyst system must be developed before this method can be applied for the purpose of CO2 conversion.

Hydrogen and renewable energy sources

The largest potential for the utilisation of considerable quantities of CO_2 is in the process of making hydrocarbons which require a large scale supply of hydrogen. How to obtain the hydrogen still remains an enduring challenge. The main obstacle for abundant production of H_2 by electrolysis is the high cost of electricity compared to petrochemical methods such as steam reforming of methane, a source that is cheap but hardly green. The high cost of hydrogen production using electrolysis led to the search for a less expensive technology, one of which is the thermochemical cycle.

Thermochemical cycles are processes in which water is decomposed into hydrogen

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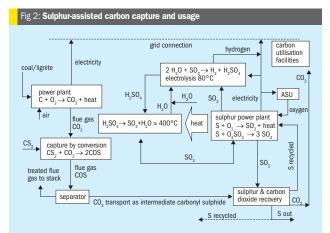
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Fig 1: Sulphur-assisted carbon capture and storage grid connection electricit ASU ASU coal/lignite grid oxygen connection oxvge sulpur power plant oxy-fuel power plant $S + O_2 \rightarrow SO_2 + heat$ $C + O_2 \rightarrow CO_2 + heat$ compressor CO. SO, grid connection CO. transport converter carbon dioxide recovery $CS_2 + CO_2 \rightarrow 2COS$ carbonyl sulphide CO. sequestration S recycle S out



and oxygen via chemical reactions using intermediate elements which are recycled. The leading thermochemical processes, all of which have in common the high temperature reaction thermal decomposition of sulphuric acid, are three sulphur water-splitting cycles: the Sulphur-lodine (SI) process, the Hybrid Sulphur (HyS) or Westinghouse process, and the Ca-Br process. The water-splitting cycles consist of a series of linked chemical reactions which result in the dissociation of water molecules into hydrogen and oxygen. All of the intermediate chemicals are regenerated and the only consumable is water.

Among these, the two-step Hybrid Sulphur (HvS) cycle is the simplest. It was patented by Brecher and Wuin in 1975 and extensively developed by Westinghouse in the late

1970s and early 1980s. The key component of the HvS process is the electrolyser, also called a SO₂-depolarised electrolyser (SDE). where hydrogen (H2) and sulphuric acid (H₂SO₄) are produced as products of the reaction between water and dissolved SO₂:

$$SO_2 + 2 H_2O \rightarrow H_2SO_4 + H_2$$

electrolysis (25-100°C) (1)

The sulphuric acid is then decomposed at high temperature into sulphur dioxide, oxygen and water:

$$H_2SO_4 \rightarrow SO_2 + \frac{1}{2} 02 + H_2O$$

thermochemical (800-1000°C) (2)

The presence of sulphur dioxide along with water in the electrolysis reduces the required electrode potential to well below

that required for the electrolysis of pure water, thus reducing the total energy consumed by the electrolysis. In practice, SO₂ electrolysis may require no more than 25 % of the electricity needed in alkaline water electrolysis, although at the expense of the need to decompose H2SO4 at high temperatures in order to recycle the SO2. The decomposition of SO2 to SO2 is thermodynamically unfavourable at lower temperatures, so it is carried out at temperatures above 800°C in order to produce a sensible equilibrium conversion. To be feasible. the process was designed to be coupled with a very high temperature nuclear power plant, which would supply both the heat needed for the sulphuric acid concentration and decomposition steps and the electricity required for the electrochemical part. A very high temperature reactor belongs to the group of "Generation IV" nuclear power plants, which have yet to be constructed. Additionally, the cycle needs

an expensive chemical plant.

The coupling of the HyS cycle with a solar heat source has also been studied in an attempt to achieve sufficiently high temperatures for sulphuric acid decomposition. Water electrolysis powered by renewable energy resources would produce only hydrogen and oxygen, avoiding the emission of CO2; however, renewable energy resources alone are inadequate. Producing electricity from direct solar radiation or wind is limited by the unpredictability and variability of these sources. Currently, wind power is the fastest growing renewable energy source, especially in Europe. For example, in Denmark, over 20% of the demand for electricity is generated by wind power. However, at an optimum location, generally offshore, a windmill-driven generator will only run at its nominal power during 30% of the time, while at most landbased locations wind generators typically operate at nominal power 20% of the time. Compensating for the rapid fluctuations in output of large-scale wind and solar-based generators is difficult for conventional steam-based power plants and lowers the utilisation factor of the other power plants. which increase the capital costs per kWh. Running conventional fuel-based power plants at a low load drastically increases their fuel consumption, increases their CO. emission, and drastically increases their maintenance costs per kWh. Technologies which provide these capabilities are in place, e.g., gas engines, which are low in emissions, quick and flexible and also

allow heat recovery and energy storage integration. Yet, with coal still being the cheapest fuel in most parts of the world, natural gas has a hard time to compete.

Furthermore, the CCS concept assumes that the station is running at a constant level of power generation and carbon emissions. As such, there is yet no method to alleviate the effect of changes in demand on the CCS.

Switching from fossil fuels to bioenergy does not necessarily reduce CO2 emissions overall. Depending on how the biomass is produced and used, the resulting emissions and climate impact can be better or worse when compared to fossil fuels. The JRC. the European Commission's in-house science service, states that "the assumption of biogenic carbon neutrality is not valid under policy relevant time horizons". In addition, the US Environmental Protection Agency recognises that "carbon neutrality cannot be assumed for all biomass energy a priori (Framework for Assessing Biogenic CO2 Emissions from Stationary Sources, 2014). The main environmental drawback of large-scale electricity generation from geothermal energy (specifically in volcanic areas such as Iceland) is that the wells contain high amounts

of CO2, derived from metamorphism of carbonate, which produces worldwide average emissions of 122 g CO₂ per generated kWhe.

For a short- to medium-term application, a new alternative Outotec open cycle process (OOC) has been proposed for hydrogen production. This process involves only one stage (SDE) and does not require sulphuric acid decomposition. The SO2 used in the process can be obtained from flash smelting, sulphides roasting, sulphur combustion or any other similar operation, and because sulphuric acid is a commercial product, the cycle may be left open.

Although various systems and methods for carbon neutral energy and hydrogen production have been discussed, all or almost all of them suffer from one or more disadvantages. Thus, there is still a need to provide methods and systems that provide an improvement.

In general, this system exploits a sulphur thermochemical water-splitting process to efficiently generate hydrogen. This sulphur thermochemical water-splitting process (HTS)

is able to operate at significantly lower temperatures with reduced complexity by employing a sulphur depolarised electrolyser (SDE) that receives its thermal and electric power from a sulphur-combusting power plant. More specifically, method uses the sulphur depolarised electrolyser (SDE) for receiving electricity, H₂O and SO₂ and for electrolysing the H₂O and SO₂ to produce hydrogen and sulphuric acid, a decomposition reactor for receiving and decomposing the H2SO4 into SO₃ and H₂O, wherein the H₂O is recycled to the SDE. The system also includes a sulphur submerged combustor for converting the SO₂ to SO2 and producing Sn vapour. The system further includes a sulphur power plant for combusting Sn vapour to produce SO2 electricity and heat and for supplying the SO₂ and the electricity to the SDE and for supplying the heat to the decomposition reactor. The hydrogen is delivered to a carbon capture and utilisation facility where it can be reacted with carbon dioxide to form fuels or chemicals.

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Refinery SRUs – an Indian perspective

Prajwal Adiga and **Nilesh Mangukia**, Linde Engineering India Pvt Ltd, look at the impact of tightening sulphur fuel regulations and increased fuel demand on Indian refiners.

ndia's rapid growth and urbanisation has also put a number of its cities on the World Health Organisation's list of highly polluted cities. The government has therefore mandated a jump in fuel sulphur standards from Bharat Stage IV to VI (equivalent to Euro 6 fuel specifications) by April 2020. This will require a cut in sulphur content of fuel from 50 ppmw to 10 ppmw. This deeper sulphur removal challenges the capacity of currently operating sulphur recovery units (SRUs) across Indian refineries. This article is a theoretical case study of one such refinery SRU requiring a revamp to enhance sulphur handling capacity.

Background

As vehicle fuel consumption rises governments have been active in legislating in order to curb SOx emissions. Refiners have had to adapt to these standards, failing which imposes the threat of penalties. Refiners in India are facing similar challenges in order to realign their existing processes for the expected leap from the Bharat Stage (BS) IV to BS VI standards as well as satisfying increasing demand for fuels for commercial and logistic purposes. The vision of these refiners in terms of capacity enhancement and quality upgrades will determine whether existing systems and processes are suited for this change or whether they require modification to the existing system or construction of complete new associated units.

In the theoretical case under discussion, the existing system is assumed to have shortcomings in terms of processing capacity. In particular its sulphur recovery unit will require either modification or an additional train to cater to these additional processing requirements. The existing

SRU is assumed to be a two train Claus configuration with tail gas treatment with an effective sulphur recovery efficiency of 99.9 wt%, dealing with an H₂S load generated from a diesel hydrotreater (DHT) and diesel hydrodesulphuriser (DHDS) unit with the following characteristics:

Existing DHT capacity: 2 million t/a
On-stream time: 8,000 hrs
Sulphur content: 1.5 wt%

 $\begin{array}{lll} \text{Existing DHDS capacity:} & 2.5 \text{ million t/a} \\ \text{On-stream time:} & 8,000 \text{ hrs} \\ \text{H}_2 \text{S content:} & 1.6 \text{ wt\%} \end{array}$

The effective sulphur recovery unit (SRU) capacity for processing the DHT unit at a permissible limit of 50 ppm (by weight) set by BS IV in the final product stream is approximately 98.7 t/d, while for the DHDS unit, with similar permissible limit, the SRU capacity has to be approximately 112.6 t/d. Hence a combined processing capacity of 230 t/d via two SRUs is required, with normal operation understood to be 2x115 t/d. However, each train is capable to of processing at full load in case the other train is under shutdown.

With diesel demand up by 7.7% this year and an effective increase in demand worth 6.4% over the past 10 years, the processing capacities of the DHT and DHDS have to be upgraded according to a 10 year plan. It is assumed that demand is set to show a similar trend and hence a capacity upgrade of 6.4% is considered for further evaluation.

Upgraded DHT capacity: 4.1 million t/a
On-stream time: 8,000 hrs
Sulphur content: 1.5 wt%

Upgraded DHDS capacity: 4.65 million t/a
On-stream time: 8,000 hrs
H₂S content: 1.6 wt%

Further to this, with the product quality enhancement criteria set by potential roll out in BS VI norms, SOx emissions have to be brought down to 10 ppm (by weight) in the finished fuel. The combined impact of both factors result in an increased overall SRU processing capacity of approximately 400 t/d. Hence, existing processing capacity has to be enhanced by about 74% to absorb this additional load.

)ptions

The following are the options available to address this increase in processing capacity:

- Option A: Add an additional SRU train with a processing capacity of around 169 t/d.
- Option B: Modify the existing units to process higher gas loads.

Let us evaluate both the scenarios in their entirety and understand the pros and cons of both these approaches.

Option A

An additional SRU train with the extra processing capacity seems to be a simple approach, as the only thing to worry about is building a grass-root unit. Existing production remains unhampered, as none of the existing sulphur recovery units need to be tweaked. Modifications in the units feeding the SRUs can be sequentially upgraded, thus ensuring continued production, even though at a lower than design rate. An identical unit design can also help in maintaining identical operating practices and operator awareness about risks. Having three trains running in parallel helps in covering the total gas load via two units in case if one of the three unit trips. This approach also reduces the risk of dependency on a single spare train during a one train trip scenario, as the total gas flow has

to be flared if the second unit also trips.

However, there is major capex, as an entire train has to be built, and additional capacity available in the other trains cannot be better utilised. Additional staff are required to keep this train in operation. Further, with all three units running, it becomes important to operate at lower turndowns, resulting in low-key plant performance. This also results in higher utility consumption (specifically fuel gas and electricity).

Altering the existing units to cover the higher

Option B

loads can be an economically viable solution as capex comes down drastically. The way to alter the existing system is to introduce the concept of oxygen enrichment. The primary bottleneck for the existing system is hydraulic limitation of the system. Oxygen is sourced in the form of air which contains approximately 79% nitrogen, an inert which will travel all the way from burner to incinerator without adding any value to the process. To quantify the above statement, for a 230 t/d sulphur-producing unit, 15,982 Nm3/h of air is required which will include 12,626 Nm3 of hydraulic system volume every hour in terms of nitrogen. If this is reduced by way of adding pure oxygen, the air flow can be reduced, thus, the same system can now cater to higher gas loads. The effective volume increment of oxygen for a 400 t/d SRU unit will be 2,481 Nm3/h, with a total oxygen demand of 5.837 Nm3/h. In order to accommodate this 2,481 Nm3/h of additional oxygen, the same volume of nitrogen has to be reduced which would mean reducing air flow by 3,140 Nm3/h. Hence, effectively, an additional 3,140 Nm3/h of oxygen has to be sourced (i.e. 2,481 Nm3/h of additional oxygen and 659 Nm3/h of oxygen shortfall as a result of reducing air by 3,140 Nm3/h). The estimated level of enrichment in this case will be 36 33%

It should be noted that this only considers single train operation. For two trains operating in parallel, the system should be able to perform in air-only mode, as each train is designed to operate with air-only mode up to its rated capacity of 230 t/d, and for the revised capacity of 400 t/d, each unit operating in parallel has to process about 200 t/d. Table 1 summarizes the theoretical estimates. These estimates are subject to variation when compared with simulation results.

The model retains the hydraulic volume of the system intact without necessitating addition of a new SRU train, but

| Table 1: Estimates for oxygen enrichment case | | | | |
|---|----------------------------|---------------------------|--|--|
| Parameter | Existing | Revamp | | |
| Unit capacity | 230 t/d | 400 t/d | | |
| Sulphur produced | 299.5 kmol/h | 520.8 kmol/h | | |
| Equivalent O ₂ | 149.7 kmol/h | 260.4 kmol/h | | |
| | 3356.3 Nm ³ /h | 5837.0 Nm ³ /h | | |
| Total Air | 15982.2 Nm ³ /h | - | | |
| Surplus N ₂ | 12625.9 Nm ³ /h | | | |
| Additional O ₂ | | 2480.7 Nm ³ /h | | |
| Equivalent N ₂ volume to reduce | | 2480.7 Nm ³ /h | | |
| Air flow reduced to meet load | - | 3140.2 Nm ³ /h | | |
| O ₂ reduced due to air reduction | | 659.4 Nm ³ /h | | |
| Total pure O ₂ to be supplied | - | 3140.2 Nm ³ /h | | |
| Net air flow | 15982.2 Nm³/h | 12842.1 Nm³/h | | |
| % enrichment | - | 36.33% | | |

some modifications in the existing unit are required for the revised mode of operation. Additional pipelines for oxygen have to be laid, requiring detailed study of the existing unit's layout and routing these lines as per space availability. As the enrichment level is categorised as medium-level oxygen enrichment (28 mol% < 02 enrichment < 45 mol%), combustion air piping also has to be upgraded as O2 will be injected into the air line. In case of enrichment levels less than 28 mol%, no equipment modifications are anticipated beyond providing a tie-in point for oxygen into the combustion air line. Further, for the evaluated system. a new specially designed oxygen burner must be installed. Other associated modifications may be related to instrumentation as installed flame scanners have to be suitable to differentiate flame intensity between air only and enrichment mode of operation. If not, a new set of flame scanners have to be added. Further, the control system has to be upgraded to admit O2 into the furnace. Modifications in sulphur rundown lines and storage facility are expected because of the increase in sulphur production. Operating practices have to be aligned to the modified system for efficient and safe operation. While the above guidelines are well suited for typical H₂S-rich refinery gas feeds, they do not necessarily hold true for facilities processing acid gas feeds that are relatively low in H₂S and high in carbon dioxide (CO₂).

Tampering with a proven system seems a bit daunting, but the advantages that this revamp can offer in terms of overall cost are significant. However, such modifications will have a short window and have to be accomplished during a complex shutdown in order

to avoid flaring of high H2S-bearing feed gases. The utmost care should be taken in order to avoid revamp errors, as the availability of these units is critical once the complex resumes production. Pure O₂ handling has to be properly ensured, also adapting to stringent cleaning requirements for lines handling pure O2. Further, the instrumentation system for handling O2 should be state of the art, ensuring the safety of plant and personnel. The operating cost of the unit will rise whenever single unit operation is planned as O₂ is priced significantly high in the market. A PSA unit providing low purity levels of oxygen can be set up to cater to these needs, the viability of which is dependent on the frequency of utilisation of oxygen enrichment mode

Conclusion

With a strong desire to increase sulphur processing capacity in many gas plants and refineries driven by the shift towards heavier feedstocks, stringent environmental policies and meeting increasing demands, refiners either have to build new facilities or expand the processing capacity of existing facilities. Utility pricing and equipment cost are major drivers in deciding which to opt for. In most of the cases, oxygen enrichment as a method to expand an existing facility's capacity can turn out to be the most economical solution.

Linde Engineering is well placed to support customers with either of the options (i.e. new plants as well as revamp with oxygen enrichment). Linde's strong EPC capabilities supported by proven SRU licensors can bring benefits to customers over the life cycle cost of these projects.

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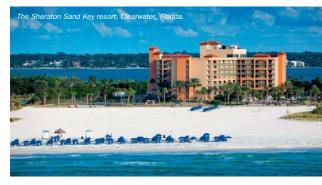
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40th Annual Clearwater Convention

Simon Inglethorpe reports on this year's 40th AIChE Annual Clearwater Convention, held at its usual venue, the Sheraton Sand Kev resort, on Florida's Gulf coast on 10-11 June.

or four decades now, industry engineers have gathered at Florida's idyllic Clearwater Beach for the AIChE's two-day annual convention on sulphuric acid and phosphoric acid technology. The convention, which is always run on a Friday and Saturday, is renowned for its relaxed atmosphere and ability to combine business with friendship, food and family. An impressive 370 international and US delegates attended the 2016 convention.

Rick Davis of Davis & Associates and Crystal Alonso of The Mosaic Company opened proceedings by chairing the longstanding sulphuric acid workshop on Friday afternoon. The theme of this year's workshop was advances in process control. This workshop aimed to cover the collection and interpretation of process data and the very latest in analyser technology.

"What we try to do with these workshops is have an open forum to talk about

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one aspect of the sulphuric acid process, hit it from different points and hope it all comes together," explained Davis. "Today we're going to be talking about advances in process control. I believe one of the areas that have made the most significant changes is the control systems for the sulphuric acid process."

Digitalisation: the Holy Grail?

Digitalisation is about using digital technology to generate new revenue streams. create opportunities to add value and transform business models, a definition that Outotec's Hannes Storch described as "all or nothing".

Storch was positive but pragmatic in his assessment of the potential for digitalisation at sulphuric acid plants: "Digitalisation is some sort of Holy Grail right now in the industry, one which never fails. But I can

tell you, from my experience, it can fail. Although everybody's quite positive about it. if you don't do it the right way, analogue systems sometimes have an advantage."

Digitalisation has two main areas of application at sulphuric acid plants; static or dynamic process simulators and expert systems. In practice, digitalisation can mean the adoption of distributed control systems (DCS), acid-specific instrumentation and enhanced process controls.

One example of an expert system is the Plant Operability, Reliability and Safety System (PORS) used in heat recovery systems such as Outotec's HEROS technology. This "black box solution", by incorporating operational data and process know-how. improves awareness of key operational trends. PORS can be used in acid coolers to check pH trends and calculate heat and mass (acid and water) balances, for example.

Storch summed up the case for digitalisation: "Plants are getting more complex. Plant equipment can fail and certainly does fail. Sometimes you have operators without sufficient experience, or sufficient documentation at the plant to gain that experience. Here, there is certainly an advantage to using digitalisation, in whatever form, Digitalisation can support operational maintenance. But no system can make up for good operating and maintenance practice, that's for sure,"

On the prospects for fully-automated sulphuric acid plants, Storch concluded that "there are many hurdles to be overcome, be it on instruments, be it on plant layout, but digitalisation can certainly sup-

Building on things we know about

Brian Lamb of MECS elaborated on a particularly valuable example of digitalisation in the sulphuric acid industry - dynamic process simulation. The MECS operator training simulator (OTS) was an example of an innovation that "builds on things we already know", said Lamb, This was because OTS combines three existing technologies - the sulphuric acid process, the PC platform and DuPont's TMODS dynamic simulator software.

A key strength of the OTS is its ability to create a virtual plant environment that "works and feels" like a sulphuric acid plant. Training using this type of simulator is also very rapid with one operator commenting "we can do 10 years of experience in eight

hours". Lamb emphasised how valuable skilled operators are for the industry, particularly the importance of equipping them with "the right skills to prevent emergencies". OTS is able to meet this need, said Lamb: "It solves the training paradox by simulating emergencies so that when operators see that event in the future they're ready for it."

"By combining sulphuric acid process know-how with existing PC hardware and the dynamic simulation software that DuPont invented back in 1988." summedup Lamb "We've combined these tools in an interesting way to make operator training simulators that marry dynamic simulation capabilities to real knowledge about the sulphuric acid process. By doing that we can help operators to train faster and help sulphuric acid plants run better."

Early moisture leak detection

Breen Energy Solutions originally developed its AbSensor measurement device in 2005 as an ammonium bisulphate detector in the energy sector. The dew point-based device can, however, also be applied to sulphuric acid measurement. The company was bought by US company HBM Holdings last year. "In 2016, our goal is to expand our international coverage and start working with sulphuric acid manufacturing facilities with our technology," commented Breen's Chetan Chotani.

He explained more about the AbSensor and its applications: "It offers in-situ, real time measurement of condensable dew point. We can measure sulphuric acid in coal-fired power plants anywhere from 1-100 ppm roughly. We were asked to make extremely low-level sulphuric acid measurements in combined cycle gas turbine applications, we're talking about 0.001 ppm measurements, and we were successful in those measurements as well

The company has developed a new AbSensor-ADM-SA design for sulphuric acid plants. This completely sealed unit can measure acid dew point "pretty much across the entire range", according to Chotani. The sensor is able to withstand 20 psi. resist high H2SO4 concentrations and operate over a 32-800 fahrenheit temperature range. Chotani listed its potential sulphuric acid plant applications: "In reality, sulphuric acid dew point measurement is essentially about early moisture leak detection. Various failure points exist in the sulphuric acid plants where moisture can come into the process. The moisture can come from drying tower malfunctions, waste heat boiler tube leaks, cleaning system malfunctions. and other things potentially.

Measuring H₂SO₄ at high concentration

Current sensor technology for detecting sulphuric acid concentration is typically based on measurement of conductivity, density or refractive index. But all three approaches have limitations at the upper H2SO4 concentration range, as Sebastian Vreemann of German-based SensoTech explained.

Sonic velocity based measurement, in contrast, is sensitive between 80-100% H₂SO₄, as sound speed changes dramatically over this concentration range. Senso-Tech has developed an immersion sensor using a piezoelectric transmitter and receiver to measure sonic velocity at frequencies >1 Mhz. Sonic velocity measurements are extremely accurate at high H2SO4 concentrations compared to conventional technology. according to Vreemann, with a typical accuracy of +/- 0.05 wt.% H₂SO₄ being typical.

Sonic velocity sensors provide in-line measurement, do not drift, are insensitive to colour or transparency, are easy to mount, virtually maintenance-free as they have no moving parts, are corrosion resistant, able to withstand both vibration and pressure shocks, and can operate over a -90-200 centigrade range. Absorption towers in sulphuric acid plants generally make an ideal site for these types of sensors

Ultrasound vs refractive index measurement

Another German company, Berlin-headquartered Flexim, offers two types of HoSO. sensor technologies: PIOX R. a refractive index based detector, and PIOX S, a nonintrusive ultrasound device. Brian Revnolds explained how the two types of sensor complemented one another and their distinct sulphuric acid industry applications.

PIOX S. a clamp-on process analyser. uses two transducers to measure average speed of sound within a pipe and exploits differences in the sonic velocity of water and HoSO.. As with SensoTech's technology, Flexim's PIOX S device is suitable for sulphuric acid measurement at concentrations above 80%. More than 20 PIOX S sensors have been installed at a major Central Florida phosphate fertilizer plant for concentration monitoring and hot acid mass flow measurement. PIOX S is also

well-suited to heat recovery systems and ultrapure sulphuric acid measurement.

Flexim's PIOX R device measures the refractive index of sulphuric acid and is suitable for H₂SO₄ mass flow metering over a concentration range of 0-85%. "No one else has it" commented Reynolds, as its design is based on patented transmitted light technology. The device is pre-programmed and calibrated, can be mounted on a flange and has the advantage that it doesn't drift with fouling or scale build-up.

The big data challenge

The sulphuric acid industry is already gathering a lot of data, pointed out Chris Davis of lon247, as its process sensors are digital and monitored. The industry's problem is not the data itself, in his view, but what to do with it and how to turn it into action-In future, it should be possible to share

data across the industry, submit data anonymously to bigger databases, and eventually make strategic decisions based on real time, historical and outside sources of data. However, a number of hurdles and industry knowledge gaps are preventing this currently, such as data integration costs and question marks over compliance with cyber security guidelines. The development of open standards is another unresolved issue. Enabling systems to null data from sources such sulphuric acid plants also requires a type of standard interface called an application programming interface (API). The sharing, exchanging and understanding of data also requires the adoption of data standards.

There are clear rewards for businesses in accessing big data, though, suggested Davis. Those enterprises able to turn big data into actionable information in future will both save money, by reducing waste and improving efficiency, and have a competitive advantage in his view.

An industry data standards committee is being formed to hep meet the big data challenge. Having the ability to talk to systems and gather information was the next priority, "We need to look at documenting what is a standard API," urged Davis. Better IT help and more advice on identifying suitable control systems was also necessary, "What that means is discussing with your vendors what control systems would be best to start with. And, of course, reaching out to IT application specialists to connect these systems together - IT should be your friend," concluded Davis.

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Chemical composition

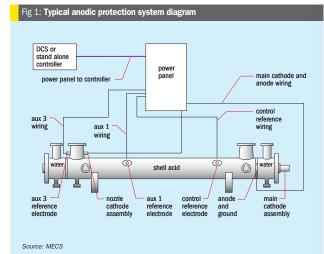
Weighing up the options for acid cooling

For decades, anodically proctected (AP) stainless steel, shell-and-tube coolers have been the traditional, reliable and economic choice for acid cooling applications in the sulphuric acid industry. Over the past ten years non-AP, high silicon (Si) alloy acid coolers have been gaining acceptance in the industry due to their ease of operation and reduced maintenance, but which is the better option?

cid cooling in a sulphuric acid plant is primarily accomplished with one of three heat exchanger options: anodically protected (AP) stainless steel heat exchangers, high silicon (Si) alloy heat exchangers, or plate and frame heat exchangers. There are pros and cons to each choice depending on the size of the cooler and site specific requirements. Each sulphuric acid cooler application is unique and requires careful consideration of all the variables. This article explores the benefits and potential pitfalls of the two most popular options, AP acid coolers and high Si alloy acid coolers.

Sulphuric acid coolers are a critical piece of process equipment in any sulphuric acid plant. The primary function of acid coolers is to remove excess heat generated from the heat of absorption in the absorption tower and heat of dilution in the drying tower. Sometimes the heat is recovered for hot water or even low pressure steam generation. Conventional acid coolers are a shell-and-tube heat exchanger with water on the tube side and sulphuric acid on the shell side. These two liquids when mixed create a highly exothermic reaction and locally create weak sulphuric acid. Both the higher temperature and the weaker acid will result in rapid corrosion of stainless steel, Si SS alloy or any acid cooler material. As such failure or leaks in the acid cooler normally result in immediate stoppage of the plant and repair of the acid cooler: a robust and reliable acid cooler is therefore imperative

Since inception, anodically protected (AP) stainless steel shell-and-tube acid coolers developed in the 1960s have



been the best available technology for this application. Usually AP coolers are reliable, robust, low maintenance, long lasting and economic. Many AP acid coolers have been in service for decades (some for 40 vears) and it is widely considered industry standard practice to use AP coolers for

In the 1980s high silicon austenitic stainless steel alloys were introduced into the sulphuric acid industry and alloy acid coolers followed thereafter. This equipment has some differences versus AP acid coolers. In specific cases alloy acid coolers are preferable and in others they are inferior. It is common knowledge that the inherent corrosion resistance of Si alloys eliminates the need for AP protection, simplifying operation, albeit at a higher mate-

In any acid cooler replacement project the owner and operator of the sulphuric acid plant faces the dilemma of choosing appropriately between technological solutions. Failure to select the appropriate technical solution and/or incorporate the required spares, diagnostic instruments and maintenance procedures can result in significant downtime for the operating

Anodically protected coolers

Most anodically protected coolers are austenitic stainless steel coolers with anodic protection. In conventional anodically protected coolers acid flows in the shell side and water flows in the tube side. Anodic protection controls the rate of the corrosion on the acid side by forming a stable protective oxide film. Electrodes mounted on the shell measure the anodic notential which is related to corrosion rate, and relay the signal to the controller/power supply and operator interface for automatic adjustment and direct read out of critical parameters. Fig. 1 shows a typical anodic protection system diagram.

Modern anodic protection systems are fully automatic as the potential (voltage) and current is monitored and controlled by the controller/power supply. Once set up, there is no need for operator adjustments of the system. This system alarm will sound when the acid conditions fall outside normal operating boundaries. Typical process upsets are usually due to acid concentration, temperature or flow fluctuations.

Alloy coolers

As alloy materials are becoming more widely available in the marketplace, acid plants have the option to replace AP coolers with high silicon alloy coolers.

Table 1 lists common alloys for acid coolers and their chemical composition

Silicon austenitic stainless steel allov coolers are normal shell-and-tube exchangers with no anodic protection. Instead of relying on an oxidation film generated by electrical potential applied to the cooler electrodes, the cooler relies on using more exotic metallurgy that is resistant to corrosion against hot sulphuric acids. In sul-

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| | | | |
| | | | |

Fig. 2: Chloride water side corrosion - blocked tubing.

SARAMET®, ZeCor®, SX Silicon austenitic stainless steel Cr-Ni-Fe- 5% Si Austenitic stainless steel SS 304L, SS 316L, SS310 Cr-Ni-Fe Superaustenitic steel Cr-Ni-Fe-Mo 20-1-0 Cr-Ni-Mo Superferritics phuric acid cooler applications, the alloys corrosion at the acid side only. Corrosion typically used are 300 series austenitic issues at the water side (tubing) are not stainless steel, superaustenitic steels. addressed with these technologies. In fact, superferritic and silicon austenitic stainmost acid cooler failures are found to be

High silicon alloys have around 5 to 10 times higher silicon content compared to other types of austenitic stainless steel. Another development of using alloys in acid cooler applications is the use of superaustenitic steel in seawater cooling applications because of its good resistance against chlorides present in sea

Table 1: Allovs, trade names and chemical composition

Trade name

For seawater coolers without anodic protection alloys (e.g. SX-CI) possessing an excellent resistance against chloride induced corrosion and with a very high corrosion resistance in sulphuric acid can be applied. These alloys have proven operation periods of up to 25 years in acid cooler applications

Alloy acid coolers for use in high chloride water applications like seawater require thermal designs that maintain low tube wall temperature.

Metallurgy selection

Metallurgy selection is one of the most important criteria at the time of selecting either alloy coolers or AP coolers. As discussed earlier AP and alloy coolers control

caused by tube (water) side failures (Fig. 2). Most tube side failures are found to be caused by chloride stress corrosion cracking, crevice corrosion, and pitting corrosion. Other common causes that are not caused by chlorides are tube blockage. cooling water throttling, poor quality water, and process upsets.

The leading cause of stress corrosion cracking and pitting is in fact reducing the water flow which increases the tube wall temperature. Environments that favour stress corrosion cracking require five elements:

- austenitic stainless steels:
- oxvgen.
- chlorides:
- high metal temperature.

Another common cause of pitting and under deposit corrosion in stainless steel is chlorides present in cooling water. Chlorides react with chromium in austenitic stainless steels to form very soluble chromium chlorides (CrCls). As the chromium is dissolved, chloride "bores" into the surface of stainless steel creating pits and jagged depressions which continue to burrow into the stainless steel (Fig. 3). The protected

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Fig. 3: Chloride pitting in bore of extracted tube

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environment inside the pits becomes acidic with the addition of corrosion product metal ions and the chlorides concentrate at its base. With elevated temperature and stagnant water conditions, the condition in the bottom of the pits becomes so aggressive that it will cause cracking. The chlorides then interact with the initial crack and accelerate the crack tip.

To improve the pitting corrosion resistance of stainless steel, alloving elements like molybdenum (Mo) and nitrogen (N) need to be added. To quantify pitting corrosion resistance of stainless steels, ASTM has established Pitting Resistance Equivalent Number (PREN) as an indication of corrosion resistance of different types of stainless steel. Exact testing procedures are specified in the ASTM G48 standard. In general a higher PREN value will result in more corrosion resistance against aggressive chloride containing environments. The PREN value is calculated using the following formula: $PREN = 1 \times \%Cr + 3.3 \times \%Mo$ + 16 x %N (w/w).

Table 2 shows the comparison range of calculated PREN values for most commonly used alloys for acid coolers.

From Table 2 it is apparent that high silicon austenitic stainless steel has the lowest PREN number among all commonly used metallurgy for acid coolers. Therefore, high silicon alloy coolers are most vulnerable for tube bore chloride stress corrosion cracking, pitting corrosion and crevice/ under deposit corrosion when compared to other metallurgies used for acid coolers when water contains chlorides.

The other problem as discussed earlier with stainless steel and chloride service is stress corrosion cracking (SCC). SCC

Table 2: PREN comparison ranges

| Alloy | PREN |
|---|-------|
| High silicon austenitic stainless steel | 18-21 |
| 300 series austenitic stainless steel | 22-25 |
| Superaustenitic steel | 39-49 |
| Superferritics | 40-43 |
| Caurage Chamatian | |

Table 3: Stress corrosion cracking threshold temperatures

| Alloy | Threshold temperature |
|------------------|-----------------------|
| SS 304 | room temperature |
| SS 316 | 50°C |
| CIRAMET | 225°C |
| Si SS Alloys | room temp. – 50°C |
| Source: Chemetic | s |

in austenitic stainless steels is highly dependent on threshold temperature. At temperatures below the threshold temperature alloys are not likely not crack, but at temperatures above the threshold temperature cracking is likely to occur. In general, this threshold temperature increases with molybdenum, nitrogen and nickel content. Table 3 illustrates the threshold temperature for SCC.

In summary, the correct tube material selection at the water side comes down to four critical parameters:

- tube wall temperature (TWT);
- water temperature at inlet and outlet of cooler;
- chloride content in cooling water;
- water velocity.

If high chlorides are present and the water velocity is too low, this will lead to high exit water and tube metal temperature, ultimately resulting in pitting and SCC. In practice, the lower the PREN number or the closer the material is to the stress corrosion threshold temperature, the more likely a failure will occur on the water side.

It is very important to review cooling water conditions when considering using high silicon stainless steel materials in acid cooler applications. High tube wall temperatures, chloride content and water quality in the cooling water are typical constraints in alloy cooler applications. Improving the SS alloy against the water quality minimises operating risks.

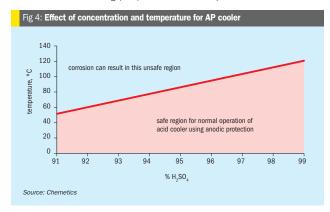
Acid temperature and concentration

Acid temperature and concentration are other important criteria when selecting AP or alloy coolers. Tube wall temperature will be higher at higher acid temperatures, which increases the rate of acid side corrosion of either AP or alloy coolers.

Fluctuations in acid concentration particularly towards weaker acid make it very difficult and sometimes impossible to establish or maintain a stable passive film on the wetted surface for AP coolers. Fig. 4 summarises the safe range for AP coolers to operate at different acid concentrations and acid temperatures.

Anodic protection will struggle to maintain the anodic film for operating parameters above the shaded area as shown in Fig. 4. In these circumstances alloy coolers with materials of construction with increased range may be a good choice over the AP coolers provided chloride content in cooling water is low and water quality is acceptable. In practice operating the plant above the graphed "safe region" will create operating difficulties in other areas, so in most cases it is likely impractical.

Generally on the acid side AP coolers and Si SS coolers have comparable acid strength and temperature operating windows. The major difference is that the anodic protection provides a corrosion control and monitoring system that reacts to lessen corrosion and will sound the alarm to warn against improper operation.





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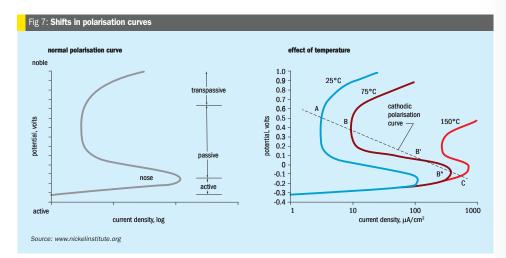
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Fig. 5: MECS® ZeCor® acid cooler tubesheet.

Fig. 6: Fully fabricated ZeCor® acid cooler.



Acid velocity and plant capacity

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From a design perspective, there are additional hidden benefits to a Si alloy exchanger. If the acid velocity is too high, it is possible to break down the protective layer leaving the exchanger vulnerable to higher corrosion rates with AP or alloy coolers. However, AP acid coolers are more velocity constrained than alloy acid coolers. At the same process conditions, a Si alloy unit can be designed with a slightly smaller shell with higher shell velocities, greater shear stresses, better heat transfer and

A Si alloy exchanger is also more ideal for increasing plant capacity (Figs 5 and

6 depict large Si alloy acid coolers from MECS). Some clients require that a cooler be designed with 5-10% more area for future increases in plant capacity

BFW preheaters

There have also been issues with anodically protected coolers at elevated temperatures, more specifically boiler feed water (BFW) preheaters. Anodically protected BFW preheaters typically have a shorter life expectancy due to the higher water and tube wall temperatures. As the temperatures increase, the polarisation curve shifts to a higher current density and the passive window decreases. The current is related to the corrosion rate with higher current resulting in higher corrosion. With high enough temperatures, a phenomenon where the cathodic curve crosses the anodic curve in multiple locations can occur (see Fig. 7).

This can lead to fluctuations between the passive and active regions hindering the build-up of the protective layer.

For example, a North American client of MECS experienced these phenomena requiring replacement of their AP cooler every 2-3 years. The client ultimately opted to replace the AP exchanger with a MECS® Zecor®-Z unit in 2005, and it is still in operation today. Based on this customers' experience, MECS standardised on Zecor®-Z alloy acid coolers for BFW service

Chemetics offers both alloy and anodically protected systems for BFW service. While alloy coolers are preferred for this application, Chemetics' anodic protection system with proportional control provides good corrosion resistance with >95°C wall temperatures.

Reliability

Cooler reliability is an important criterion when selecting an acid cooler. If an acid cooler fails (leaks), the consequence is severe. Cooling water will turn acidic and this low pH cooling water potentially will damage all equipment in the entire cooling water circuit. In the event of an acid cooler leak, the acid plant must shut down to isolate the leaking cooler so repairs can be made.

For metallurgical acid plants alloy coolers are not a good fit where fluorides are present in the acid plant feed gas. Fluorides have a high chemical affinity to the silicon present in Si alloy stainless steels and cause corrosion. In the absence of physical evidence, the scientific theory would be that fluorides in sulphuric acid accelerate silicon stainless steel corrosion, by reacting with the silicon/oxygen and silicon/sulphur compounds in the passive layer, making them volatile. European case histories exist where fluoride breakthrough in metallurgical plants have caused severe Si SS corrosion.

The maximum permissible fluoride level in strong acid is less than 1 ppm. which is consistent with normal levels in industrial quality concentrated sulphuric acid. Fluoride contaminated weaker sulphuric acid has a higher corrosion rate in high silicon austenitic stainless steel compared to stronger sulphuric acid (Fig. 8).

An anodic protection system has a built in corrosion monitoring system. In the event of rapid corrosion due to whatever reason the anodic protection system will notify the plant operator to take action to reduce corrosion. The anodic protection system controller will increase current and voltage (potential) to compensate for oxide protection film loss due to highly corrosive conditions. The controller will alarm and alert the operator to take corrective actions to revert operating parameters back to normal conditions and avoid an acid leak. For alloy coolers there is no built-in corrosion monitoring or back-up instrumentation system. If the operating conditions are causing the cooler to corrode there is no means to detect it while the plant is on-line. The only way to detect corrosion is when the cooler has already leaked and the cooling water pH is dropping. This reactive response means by the time operators detect a problem, it is already too late and will require a plant shutdown to repair the cooler leak.

The anodic protection system has an option to transfer operating data to the DCS, allowing the DCS to alarm on acid temperature and concentration fluctuations. This helps operators to diagnose acid plant problems at an early stage. Moreover, data trending is a very good tool for troubleshooting and is a source of redundant instrumentation. For alloy coolers there is no built-in monitoring system to measure acid temperature, concentration, and corrosive condition fluctuations. In such situations,

additional instrumentation will be required to enable acid temperature and concentration monitoring through the DCS system.

AP coolers experience some corrosion if acid temperature changes are cyclic for the acid plant. In this case the passivation film generated by the anodic protection system breaks down due to temperature changes and the short time needed to rebuild at the new temperature. This leads to an increased corrosion rate.

As discussed in a previous section, the majority of acid cooler failures have been caused by poor water quality. AP coolers have the flexibility to use different types of stainless alloys other than austenitic stainless steel to better withstand various water quality issues. With AP coolers Chemetics has experience with at least ten different water side alloys to handle all industrial waters (from demin to full salinity seawater). Acid resistance can also be tailored this way to make AP coolers more reliable.

The application of the high silicon cooler is limited when water quality is an issue. There is limited possibility to make a hybrid alloy cooler similar to an AP cooler with different metallurgy on the water side for longer life of the cooler.

Rimetallic tubes with materials that are ideal for both water and acid exist but are not cost effective.

Safety

Fig 9: Cost comparison between AP and alloy cooler

cost anodi

Generally, AP acid coolers present different hazards than Si alloy exchangers. There is the increased risk of leaks in an AP exchanger since these systems innately have more potential leak points, such as

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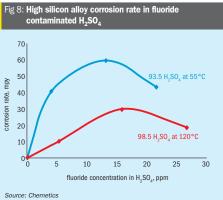
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400,000 300,000 200,000 100.000 60 shell ID, inches Source: Chemetics

US\$

900,000

800,000

700,000

600,000

500,000

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between the cathode and threaded reference electrode connections.

Additionally, typical maintenance activities for an AP cooler require acid side component removal and cleaning.

Both alloy and AP coolers require water side inspection and cleaning plus acid side inspection corrosion management and occasional cleaning.

Capital cost

Capital cost is another important aspect when selecting an acid cooler for a plant. Typically the capital cost of the high silicon alloy cooler is around 50% higher than an AP cooler for larger size coolers with plant capacity more than 500 t/d. For smaller size coolers there is no significant difference in capital cost between AP and alloy coolers.

From Fig. 9 it is confirmed that for diameters less than 20" the alloy cooler cost is competitive with the AP cooler. For larger coolers AP coolers are noticeably less expensive than alloy coolers.

Another commercial consideration is delivery. It is important to check whether at any given time special alloys may be less available than standard 300 series SSs in all required product forms. This is important for rapid replacements or to make an outage window.

Total installed cost

When comparing equipment costs, it is important to consider not only capex but also total installed cost (TIC) and operating expenses (opex). This is because maintenance and installation costs are customarily higher with an AP system.

A recent case study for an MECS plant in the USA indicated that the overall TIC of an AP exchanger turned out to be equivalent to the overall TIC of a high Si allov exchanger of the same size. This is largely due to the installation costs required for AP coolers. AP systems require considerable installation activities such as installing the electrical panel, running wires, performing loop checks and DCS programming (refer to Fig. 1 for a typical anodically protected acid cooler configuration).

Opex should also be considered when installing new equipment. AP systems require electricity and care to be taken to ensure reliable electrical connectivity when the plant is operational.

Furthermore, AP exchangers require turnaround maintenance every plant main-

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tenance shutdown. The AP system turnaround activities include removing, cleaning. inspecting, re-inserting the cathode and electrodes, confirming that all the electrical components are functioning properly and reviewing the system parameters. Numerous plants even contract the OEM specialists to perform these turnaround activities.

With any electrical system, sudden component failures can occur if not properly maintained. Additionally, a few of the cathode components are considered consumables and need to be replaced occasionally (5-10 years). This requires that a plant inventory spare parts or risk scrambling to get the components, usually at an expedited cost.

Maintenance

One of the prime reasons to consider acid cooler maintenance is the highly corrosive nature of the product. Moreover, if cooling water quality is poor or there are unsets in acid concentration and temperature then more frequent maintenance (e.g. hydroblast tube bore cleaning, tube plugging, etc.) will be necessary.

There is a myth that the AP system

requires heavy maintenance when compared to alloy coolers. While it is correct that alloy coolers do not have extra components related to anodic protection which require periodic inspections, the AP system components are relatively simple and inspections are only required to be done on an annual basis during plant turnarounds. All anodic protection system components are reliable and quickly replaceable as 300 series austenitic stainless steel materials are readily available in the market, reducing the need to keep a large amount of spare material on site for cooler repairs. Moreover, there is no need for special welding procedures and additional welder qualification requirements because 300 series austenitic stainless steel is one of the most commonly used material in industry. Another advantage with AP cooler maintenance is conventional tube plugs can be utilised for any required tube plugging.

For alloy coolers that contain high silicon austenitic alloy material it is critical to have ample quantity of tube plugs and weld consumables on site because replacement materials may not be readily available and likely will have to be shipped from overseas. Special precautions are required while welding high silicon allov compared to austenitic stainless steel due to the higher alloy content in the high silicon alloys, as they are sensitive to welding contamination. In most cases additional welder qualifications and special weld procedures are required for high silicon austenitic alloy cooler repair.

Case studies

To illustrate the importance of some of the parameters discussed with regard to acid cooler design and operation, two cases studies are presented. The first case is related to water (tube) side failure while the second case is on acid (shell) side failure.

Case 1: Water side acid cooler failure

In this instance, the pH at the water side of the absorption acid cooler water circuit started decreasing after a plant turnaround in a metallurgical acid plant. Operators did not have adequate experience to handle this scenario. So instead of starting to diagnose the issue it was decided to add caustic soda to the cooling water circuit to maintain the pH. Within a few hours the entire absorption acid water circuit was mixed with acid and the resulting weak acid corrosion generated enough hydrogen to accumulate and explode at the top of the inter absorption tower. The plant was shut down for one month to replace the absorption acid cooler and repair the damage caused by the hydrogen explosion at the inter absorption tower

It was concluded during the investigation that the root cause of the hydrogen explosion was the leak in the absorption acid cooler. The cause of the leakage was debris accumulated in the cooling water piping during repairs of the cooling tower during the shutdown. Debris accumulated in the cooling water piping travelled to the absorption acid tube inlet and lodged in the cooler tubes

Accumulated debris restricted cooling water flow in the absorption acid cooler, resulting in high tube wall temperature and ultimately tube failure. The addition of caustic soda to the water circuit actually made the situation worse as adding caustic had the effect of buffering the pH of the cooling water, which made the plant seem normal but in reality the tube leak continued and acid in the water generated weak acid which prolonged the tube corrosion without being detected. As a result of the prolonged corrosion, the single tube leak developed into multiple tube failures.

A key lesson learned in this incident is that it is critical to investigate low pH in

cooling water. Adding caustic is just masking the issue and can have catastrophic consequences. Most of the tube failures in acid coolers start from inside the tube. Typically the cause of tube failure is because of the poor water quality or fouling or throttling of water.

Case 2: Acid side acid cooler failure

Sulphuric acid itself is very corrosive so there is always the possibility of acid cooler failure due to higher corrosion rate of the sulphuric acid. Moreover acid concentration. temperature and velocity are also heavily

affecting the sulphuric acid corrosion rate. In this case study a weak acid incident occurred due to a steam leak in the economiser in a sulphur burning acid plant.

The acid temperature increased from 59°C to 128°C due to dilution by steam leaking into the process gas entering the acid tower/pump tank. Unfortunately, the response time for the acid temperature controller was very slow, more than two hours. All four coolers in the plant were exposed to the higher acid temperature because of the slow response of the temnerature controller

Higher acid temperature leads to a higher corrosion rate. A consequence of the weak acid incident was a shortened life for all four acid coolers in the sulphuric acid plant.

AP versus alloy coolers

All major sulphuric acid cooler suppliers offer a choice of acid cooler types, each with their own design features. Table 4 shows a comparison of NORAM's anodically protected acid coolers and NORAM SX™ acid coolers

Table 4: Comparison between NORAM SX™ and anodically protected acid coolers NORAM SX™ Anodically protected Requires anodic protection Longevity 20 to 35 years are expected, depending on service and operating practice. Effect of weak acid, oleum, chlorides, • Can cause accelerated corrosion and fluorides at elevated temperatures Requirement for concentration control and control of impurities in cooling water and acid Resistance to liquid acid erosion Unlimited resistance to liquid acid Must observe acid velocity limits to maintain anodic protection. erosion 6 Weight Lighter Heavier Size Smaller (can use higher acid velocities) Larger (requires lower acid and higher heat transfer coefficients) velocities). 8 Shell and tube Design Welding requirements . Similar to other stainless steel allovs. Stainless steel welding. Should follow specific welding procedures. Installation time and cost Lower Higher (due to larger size and electronics) 11 Capital cost Similar cost NORAM SX[™] acid coolers tend to be less expensive in the smaller sizes because they do not require the fixed costs associated with the electronics of anodic protection 12 Lifetime cost (including maintenance Depends on site specifics. and cost of monitoring) NORAM SX[™] acid coolers require much less monitoring by operators and less Sulphur burning, metallurgical and acid regeneration acid plants. Dry. Intermediate absorption and final absorption systems



NORAM SX[™] acid cooler. Anodically protected acid cooler

Source: NORAM

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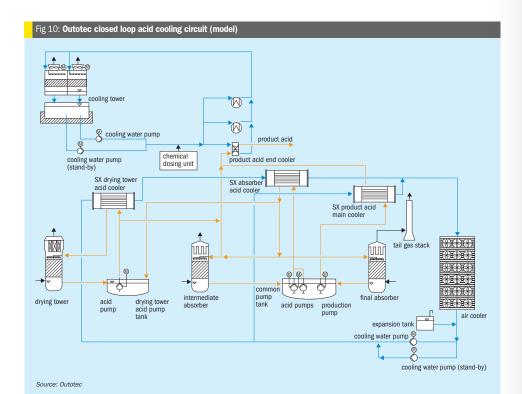
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Sustainable use of water

Cooling water is becoming a more and more limited resource. Therefore Outotec's latest developments for acid cooling are targeted to closed loop water cooling circuits, a sustainable solution to substantially reduce cooling water consumption. The closed loop concept is therefore an attractive solution in areas where cooling water is scarce or in cases when local regulations limit thermal pollution. For such applications elevated temperature of the cooling water is beneficial in order to maintain a sufficient temperature driving force for the water/air coolers. Taking advantage of the properties of Edmeston SX® in the design of the shell-and-tube coolers makes it possible to achieve a feasible cooler design for elevated cooling water temperatures. The first system of this kind has been in successful operation since it was commissioned in 2015. A typical process design is shown

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in Fig. 10. The closed loop consists of the SX acid cooler for the drving tower. absorption tower and product cooling connected to the air coolers. With the closed loop operated at elevated acid temperatures for optimised cooler design the product acid needs special attention. An additional cooler included in the low temperature circuit reduces product acid temperature to normal level

However, this solution still incorporates a large surface area as interface between the hot sulphuric acid and water, increasing as such the possible hazards in the case of a failure. As a solution, Outotec has developed direct fin-fan acid coolers made of Edmeston SX® eliminating the risk of leakages with subsequent water contact, formation of weak acid and heavy corrosion generating hydrogen and eventually hydrogen explosion.

All piping, headers and finned tube banks are made of Edmeston SX® with fins of suitable material for any environmental condition. Without the typical restrictions of

flow velocity and acid temperatures below 140°C, the Edmeston SX® coolers can be optimised and the overall installed cost can be lower than the closed water loop alternative. The operating cost is also minimised as the intermediate water pumping

The application of direct fin-fan air coolers made of Edmeston SX® completely eliminates the risk of diluted acid formation, through the absence of water and results in economic advantages. Thereby this solution contributes substantially to reliable and safe plant operation and complements the Outotec portfolio of the original SX shell-and-tube acid coolers for standard cooling water, demin water and seawater applications available to the market since 1985. Finally, these acid coolers can be supplemented by Outotec PORS, a digital operator support tool identifying upset conditions on basis of DCS data at an early stage to secure the availability of the acid plant.

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Conclusions

In summary, AP coolers have been the workhorse of the sulphuric acid industry for the past 40+ years. However, in some situations, Si alloy coolers are price competitive when considering the upfront fixed cost of the AP system.

For higher acid temperature, clean water and cyclic energy recovery applications, high silicon SS acid coolers are a good choice because high silicon austenitic stainless steel has better resistance against corrosion at higher acid temperature. There is no risk of chloride stress corrosion cracking, under deposit and pitting corrosion issues with clean water due to lower chloride content. However, it is essential that cooling water used must be boiler feed water quality demin water.

Silicon alloy coolers are also preferred for hot water applications (energy recovery) where temperatures and flows are typically cyclic with the elevated tube wall temperatures. This will cause the AP system to

ity and impurities present a high risk of

causing pitting and stress corrosion cracking, AP coolers may be a better choice because they have the flexibility to utilise different metallurgies to address water side corrosion issues. At the same time the anodic protection system controls the rate of corrosion on the acid side by forming a passivation film. The other situation where alloy coolers have a higher risk of failures is in metallurgical acid plants, where fluoride contaminated strong acid is a strong possibility

Alloy coolers do not require routine electrical maintenance because of the absence of electronics and control systems, but do require shutdown hydro-blast tube cleaning to maintain thermal efficiency. Silicon alloy coolers are a good fit for acid plants located in remote and politically uncertain areas, but these are also usually locations with poor water quality. Operators have to be prepared for more challenging repairs for alloy coolers in the case of failures because of the sensitivity to contamination while welding in the field and the possibility repair due to easier access to materials and qualified welders, lower welding sensitivity to contamination, and degree of difficulty to do the necessary repairs.

AP coolers have some diagnostic and corrective capability for plant upsets when the acid temperature and concentration are outside normal operating limits. Alloy coolers do not have any diagnostic ability for plant upsets. This may lead to catastrophic plant damage in the event of weak acid events. Though monitoring acid strength and temperature can be achieved by using on-line instrumentation via the DCS, the AP system is an inherent back up instrumentation system without lag time.

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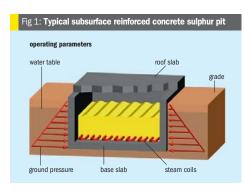


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Sulphur pits for durable service



Subsurface reinforced concrete sulphur pits can provide excellent service for many years. Thomas Kline of Structural Technologies discusses original reinforced concrete design aspects, detailing and materials of construction. Common pitfalls in design, detailing and construction defects that shorten service life and actions to correct original design/construction deficiencies prior to commissioning a new subsurface reinforced concrete sulphur pit are highlighted.

or decades, molten sulphur containment has been successfully provided by reinforced concrete structures placed in the ground for process stream delivery. These subsurface sulphur nits temporarily accommodate elemental sulphur extracted from the hydrocarbon process stream. The structures then convey the molten sulphur via suction pumping to various modes of transportation that can include barges, railcars or tanker trucks.

Regardless of the mode of transportation, the storage requires that the sulphur stay molten and the surrounding environment be protected from accidental ingress/egress of contaminants from the process stream. When correctly designed and constructed, subsurface sulphur pits can remain in service far beyond their original design service life.

Close attention to reinforced concrete design detailing, materials, waterproofing, construction practices as well as mechanical process penetrations can frequently be the difference between long term durable molten sulphur containment service and that of a short-lived deteriorated civil asset.

Original design parameters

Understanding the process tonnage at a given facility will help in defining the geometry and relative size of the new sulphur pit.

With reinforced concrete sulphur pits being site constructed and cast-in-place important decisions need to be made during the design phase that directly affect the longterm durability of sulphur pits that include:

- structural design;
- selection of durable materials of con-
- concrete type;
- steel reinforcing detailing:
- protective concrete coverage;
- joint location and design;
- water-stops type and positioning;
- process penetrations into sulphur pits: waterproofing & sealants – types and
- backfill and drainage around the external perimeter of the sulphur pit;
- quality assurance/quality control.

Structural design

The globally accepted reinforced concrete design code is the American Concrete Institute (ACI) ACI 318 "Building Code Requirements for Structural Concrete" (ACI 318-14). Sulphur pits are essentially large boxes in the ground subjected to ground and groundwater pressures as well as thermodynamic changes associated with elevated service temperatures. They are designed to contain molten sulphur and

keep it from entering the surrounding envi-

Environmentally, sulphur pit structures have a more stringent requirement that is identified and stipulated in ACI 350 "Code Requirements for Environmental Engineering Concrete Structures" (ACI 350-06). The code portion of this document covers the structural design, materials selection, and construction of environmental engineering concrete structures. Sulphur pits have uniquely different loadings, more severe exposure conditions, and more restrictive serviceability requirements than non-environmental building structures. As such, sulphur pits require proper design, materials, and construction practices to produce serviceable concrete that is dense, durable, nearly impermeable, and resistant to chemicals along with limited deflections and cracking.

Additionally, leakage must be controlled to minimise the contamination to the environment, to minimise loss of product and to promote long-term durability and service life.

Materials of construction

Concrete mixture

Fundamentally, portland cement concrete is strong in compression and weak in tension. Steel is strong in tension and when embedded into concrete in the form of deformed steel bars, works compositely as soon as the structural section experiences an applied load. This behaviour makes concrete one of the most widely used building construction material systems in the world. However, standard portland cement concrete is susceptible to degradation when exposed to sulphate salts via a process known as "sulphate attack" as detailed below:

Sulphate and calcium ions form gypsum (CaSO₄•32 H₂O) - expands 124% in volume

Sulphate and calcium aluminate form calcium sulphoaluminate (ettringite)

(3CaO • Al₂O₃ • 3CaSO₄ • 3H₂O) - expands 227% in volume

As seen in the reactions above, the expansive behaviour places the concrete mass into tension and as we learned above, concrete is weak in tension approximately only 10% of the compressive strength. To remedy and reduce the effects of these chemical reactions, the fine and coarse aggregates must be nonreactive as stipulated in American Society for Testing and Materials (ASTM) ASTM C33-16 "Standard Specification for Concrete Aggregates", the mixing water potable and the concrete paste fraction be low in C₂A, typically less than 5%. Methods achieving these goals can include:

- using Type V portland cement;
- · incorporating blends of hydraulic/portland cements
- · replacing significant amounts of portland cements with ground-granulated blast-furnace slag (GGBS) cement
- · replacing significant amounts of portland cements with supplementary cementitious materials (SCM) such as fly ash, microsilica, volcanic tuft, etc.
- using processed aggregates tested & verified to be non-reactive according to ASTM C33 including the requirements established in the appendix document.

Design of the ready-mix concrete should be performed in accordance with ACI 211.1 "Standard Practice for Selecting Proportions for Normal, Heavyweight and Mass Concrete" ACI 211.1-91 (R2009) as well as he produced and supplied in accordance with ASTM C94-15 "Standard Specification for Ready-Mixed Concrete". The objective of the concrete mix design is to determine the proportion of ingredients that will produce a workable concrete mix

Much talk in the industry regarding reinforcing steel coating has been noted.



Fig. 2: Stainless steel expansion joint detail along the side walls and floor of a sulphur trench.

that is durable and of the required strength and at a minimum cost. Overall the concrete mixture should provide:

- a workable mixture that's easily con-
- use as little portland cement as possible;
- use as little water as possible attain a dense mixture by proportioning
- the coarse aggregate and fine aggregate appropriately
- maximise the size of aggregates as large as possible, to minimise surface area of the aggregates.

The aim of the designer should always be to get concrete mixtures of optimum strength at minimum cement content and acceptable workability. The water-tocement ratio which is a critical feature to any concrete mix design, should be no greater than 0.40 as determined by ACI 201.2 "Guide to Durable Concrete" ACL 201 2R-08

Steel reinforcement

Steel reinforcing bars are a critical component in reinforced concrete design as stated earlier with most of the conventional steel reinforcing bars produced in accordance with ASTM A615-16 "Standard Specification for Deformed and Plain Carbon Steel Bars for Concrete Reinforcement". Typically two carbon steel minimum yield strength grades of reinforcing bars are available that include Grade 40 - 40,000 psi (280 MPa) and Grade 60 - 60,000 psi (420 MPa) with Grade 60 being the most commonly specified for sulphur pit construction. High strength steels (> 60,000 psi/420 MPa) and specialty alloy grades as well as pre-stressing reinforcement systems are seldom specified due to availability, cost and long-term durability in the extremely harsh environmental service conditions experienced by an operating sul-

Although worthwhile in standard construction service, the elevated sulphur pit service temperature conditions, coupled with potential exposure to acidic solutions have shown weaknesses in coating systems ranging from galvanisation to epoxy fusion coatings. Uncoated plain carbon steel bars have consistently proven to be Industry best practices as the reinforcement of choice. Additionally, the use of new resin-based fibre-reinforced bars currently available in the market is not applicable for sulphur pit construction. The high temperature molten sulphur environment (285°F/140°C to 325°F/163°C) is typically above the polymer glass transition temperature of the bar resin matrix. This high temperature service exposure would ultimately result in the eventual volatising of the binder resin. rendering the concrete member ineffective when loaded in tension.

Protective concrete coverage

Due to the particularly aggressive environment associated with an operating sulphur pit, the protective concrete coverage overtop of the embedded reinforcement should be 3 inches (75mm) as specified in ACI 318-14 when concrete is exposed to the earth and potential sulphate attack which is the case for sulphur pits, internally and

Joints

When feasible, a sulphur pit should have an absolute minimum of construction joints and no expansion joints. Sulphate attack preferentially occurs in regions of cracks. voiding/poorly consolidated areas and at any discontinuity along reinforced concrete member surfaces (i.e., joints). When joints are required, as in sulphur trenches (see Fig. 2), it's important that the regions adjacent to the joints be well consolidated during original casting and that "keyways"

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Fig. 3: Stainless steel water stop – bent configuration.



Fig. 4: Typical sleeve detailed with a welded circumferential water stop steel plate.

and embedded water-stops be installed to form a barrier within the cross-section of the structural member.

Water stops

Conventional building construction waterstops generally consist of polyvinyl chloride (PVC) which performs well at standard ambient service temperatures. However, at the elevated service temperatures associ-

ated with an operating sulphur pit, the PVC will begin to "disassociate" where the chloride portion of the polymer chain exits the water stop mass. This change in chemical properties renders the water-stop physically "brittle" which will easily tear once subjected to movement. Movement occurs regularly within a working sulphur pit as the molten sulphur "charges" into the sulphur pit from the process stream and then exits via a suction pump to ancillary storage locations. It is not uncommon to see a 75% molten sulphur volume fluctuation within a sulphur pit on a daily basis that can result in significant thermodynamic movement behaviour within the reinforced concrete structure

The water stop of choice in sulphur pit construction is stainless steel and preferably of 316 L alloy that is at least 20 gauge (0.0375 in / 0.953mm). The water stop configuration can be a "bent" configuration such as a sigma or omega style (see Fig. 3) or flat with a welded round bar as in a "dumbbell" configuration. The placement of the water-stop should be mid-width of the structural section, within the keyway and between the mats of the conventional embedded reinforcing steel. Care should be taken that no direct contact be made between the dissimilar steel types (i.e., mild steel contacting stainless) as a galvanic corrosion cell will initiate at the point of contact.

Process penetrations

Meticulous detailing is required for entry/ exit seals around molten sulphur process piping, heating elements and instrumentation associated with gravity-fed subsurface reinforced concrete containment structures. These penetrations need to be environmentally sealed to ensure process

vapour containment as well as providing an effective barrier to moisture ingress. Process piping that needs to penetrate into interior regions should make a "sleeved" entry into the sulphur pit via the roof slab as sidewall penetrations initiate radial cracking. Sleeves typically have a single welded plate that functions as a waterstop with the sleeve's inner diameter larger than the outside diameter of the process line. The sleeve is then integrally cast into the concrete with the water-stop nositioned mid-width of the concrete placement (Figs 4 and 5). The annulus distance between the sleeve interior surface and external pipe wall is then filled with a sealant which all too often is detailed to be cementitious grout. Unfortunately, cementbased grouts shrink during hardening and further when exposed to elevated service temperatures. Current industry best practices is to fill sleeved pipe annulus regions with high-temperature tolerant elastomeric sealants developed for the roofing industry that can handle sulphur pit process service temperatures.

Another option is to cast-in "spools" that have flanged ends protruding above and below the reinforced concrete roof slab for piping "bolt-up" with a single welded water-stop positioned mid-width of the concrete placement (Fig. 6).

Waterproofing and sealants

Positive-side waterproofing strategies can be one of the more important decisions a designer can make during reinforced concrete sulphur pit design. The installation of high temperature resistant elastomeric membranes has proven effective at providing long term durability when applied along exterior surfaces prior to backfilling sulphur pit



Fig. 5: Sleeved process piping penetrations and entry portals positioned prior to sulphur pit roof slab concrete placement.



Fig. 6: Precast concrete sulphur pit roof slab panels that incorporate "spool" penetrations installed during concrete casting/placement.

construction excavations. Besides high service temperature exposure, external positive side waterproofing systems need to be chemically resistant to sulphurous acid attack and should be fabric-reinforced to provide resilience during potential thermodynamic movement associated with sulphur pit service.

Typically systems come in two types. fluid applied (spray/roll-on) and prefabricated sheet membrane. Both systems require quality control services during installation. Fluid applied (spray/roll-on) systems require film application thickness checks during multilayer installation to assure adequate "build-up" of the resultant membrane and complete saturation/ integration of the fabric reinforcement within the system. Prefabricated membrane sheet waterproofing systems arrive to the site in pre-cut widths. These systems require significant concrete substrate preparation as well as an adhesive primer to bond the sheet membrane products to the concrete substrate. Additionally, seams between adjacent widths of prefabricated membrane either need to be heat sealed or overlapped to provide membrane integrity (Fig. 7).



Fig. 7: Prefabricated seamed and sealed fabric reinforced waterproofing membrane.

Surface sealants around penetrations, portals, and joints require high temperature service capabilities as well as chemical resistance. Establishing a tenacious bond with the concrete and metallic inserts is necessary in order to maintain moisture and vapour tight integrity. Current sealant chemistry best-practices include high-temperature urethanes, high-temperature silicones and fluoroelastomers. These products develop excellent bond with numerous material substrate types and are capable of withstanding high temperature service and sulphurous acid chemical exposure.

Backfill and drainage

Many cold-weather locations throughout the world have some type of insulation surrounding a sulphur pit in order to maintain a minimum required service temperature for molten sulphur in conjunction with internal steam heating coils. This generally can be attained through the use of subsurface backfill soil materials. However in particularly cold climates, the use of exterior insulation applied to external wall and slab areas prior to excavation backfilling can be an effective means of maintaining molten sulphur temperatures. External insulation is typically installed as a high temperature-rated foam board designed for direct burial and placed over the concrete surface and the waterproofing membrane installed over the top of the insulation as shown in Fig. 8.

Regarding backfill associated with new subsurface structure construction, a new sulphur pit is the "smallest" it will ever be at the time of original construction and will grow thermodynamically, once commissioned. Essentially, the reinforced concrete structure will be at ambient



Fig. 8: View of a spray applied waterproofing membrane placed on top of insulating board adhered to the external concrete surface of a new sulphur pit.

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Thermal growth against tightly compacted backfill can create conditions

conducive for cracking in subsurface reinforced concrete structures.

wall

External foundation drainage system incorporating monogranular drainage media with a perforated drain line located adjacent to the foundation to relieve hydrostatic groundwater pressure.

temperatures subsequent to construction and then will be subjected to a "heat-up" during the commissioning process. This process will bring the internal temperature to 285°F/140°C to 325°F/163°C within the sulphur pit, once charged with molten sulphur. Depending on the geometry of the sulphur pit, this thermodynamic growth can be significant and without the ability to expand within the backfill materials "in-ground boxes" have a tendency to arch, when not able to expand linearly as seen in Fig. 9.

To counter stresses induced in Fig. 9 requires the ability for the reinforced concrete structure to move freely during thermodynamic periods of growth. Growth is typically accommodated by placing compacted monogranular backfill materials in excavated areas which function similar to "ball-bearings" that facilitate movement without dislodging the sulphur pit's perimeter backfill. Unfortunately, however, this type of backfill is extremely porous and will collect water if not adequately drained and a top surface seal of impervious soil or pavement is installed across the entire width of the backfill placement. As shown in Fig. 10, the installation of a perforated drain is recommended to collect and convey groundwater away from regions surrounding the newly constructed sulphur pit.

Ouality assurance/quality control

Although following the recommendations in this article will result in a more durable reinforced concrete molten sulphur containment vessel, it is critical that a comprehensive programme of quality assurance/ quality control (QA/QC) be developed and implemented during new sulphur pit construction. A sulphur pit inspection programme (SPIP) provides a verifiable audit trail of accountability with designated milestones and hold points - assuring no important details "fall through the cracks". The SPIP should be followed closely as it will establish an important level of accountability that includes owner, engineer and contractor representatives. SPIP integrates milestones, activities, inspection practices and reference materials.

Conclusion

Subsurface reinforced concrete sulphur pits can provide excellent service with many pits approaching 70 years in age and still functioning well beyond their intended service life. However, the industry has seen all too often conditions/situations of substandard design, materials-of-construction and construction practices that prematurely doomed sulphur pits to early signs of degradation and subsequent failure. Sulphur pit repair can be expensive and require extensive restoration efforts and outages from the process stream. The best money spent on a sulphur pit is during new construction as quality design. materials of construction and expert craftsmanship will ultimately delay or negate forced maintenance outages of these critical sulphur recovery structures

Acknowledement

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Extending the life of sulphur recovery units

KT has identified the key elements

necessary to extend the life of SRUs as

All four elements are necessary and fun-

damental to identifying the best way to

achieve an extended plant life due to poor

design, wrong supplier of critical equip-

ment or wrong plant design performed by

inexperienced EPC contractors. In these

cases plant life can only be extended by

utilising a new design and/or replacement

plant life because of poor operation and/or

inadequate or insufficient maintenance. In

this case with adequate measures it will be

select the proper technology and experi-

enced licensors with specific references,

not only in licensing, but also in plant con-

struction and operation, as this is the only

guarantee that the basic design delivered

to the EPC contractor can be effectively

and easily developed and implemented. It

is not uncommon for an EPC contractor to

for the critical items of equipment, are a

key element for extending SRU plant life.

Before first start-up it is necessary to

Other plants cannot achieve an extended

There are many plants that will never

Before first start-up:

After first start-up:

plant operation:

plant maintenance.

extend the life of an SRU.

of the wrong critical item(s).

possible to extend the plant life.

licensor and basic design:

detailed design and construction.

A plant that has been well designed and fabricated, is operated and maintained well and equipped with all necessary tools can easily reach a life of 40 years. In this article KT and Jacobs Comprimo® Sulfur Solutions discuss how to maximise the life of sulphur recovery plants.

istorically, sulphur recovery units (SRUs) have been considered as a source of problems for plant operation and in many cases just an imposition of the environmental authorities.

The trend towards "zero emissions" and total respect for the environment has become a focus for all industrial complexes and is strongly linked to the primary target of plant profitability. Since acid gas flaring is no longer tolerated or allowed, any potential problems affecting the SRU is considered a potential loss of profit.

Due to current market trends it is also a requirement to put in place all necessary strategies to allow production to be maximised over a prolonged time. Therefore, even if the SRU is not regarded as a production plant it is still considered just as important as any other plant in the complex.

Typically, sulphur recovery units have a long life. Around the world there are many plants that have been in operation for more than 30 years. Of course these plants have been modified during their plant life, some critical equipment items will have been replaced, but they are nevertheless still in operation. There are other plants that after only a few months of operation, and sometimes even after the first start-up, have been seriously damaged and this has caused a prolonged shutdown of the plant/industrial complex.

In the last ten years, the turnaround for maintenance has gone from being every two years to up to four or five years and may well be extended further in future to every seven years. Extending the life of the SRU can be considered as prolonging the ability of the SRU to guarantee plant operation in order to maximise profit.

Various types of problem can affect plant

- mechanical problems:
- catalyst and chemicals problems.

Mechanical problems can lead to damage to equipment and piping and usually require a plant shutdown for maintenance or remedial action.

Damage is often due to corrosion phenomena, thermal stress, or to a combina-

The most frequent problems encountered

- tube leakage of waste heat boilers and sulphur condensers:
- sulphur pit coil leakage;
- refractory damages.

Less frequent problems are corrosion of

- thermal reactor shell:
- stack shell (top zone):
- amine regenerator.

The occurrence of such problems can be avoided or mitigated through correct design, operation and maintenance.

Correct design

Avoid corrosion

The main types of corrosion relevant to SRUs are stress corrosion cracking (SCC) due to H_oS and Cl⁺, hydrogen induced cracking (HIC) due to HaS wet dissociation, corrosion due to SO₂ at high temperature, corrosion due to SO₂²/SO₄², caustic corrosion cracking (CCC) due to amine dissociation, and acidic corrosion due to wet H2S and CO2.

The selection of the correct construction material prevents and mitigates the

Corrosion due to HaS affects the part of the plant which handles the feedstock; in this case killed carbon steel with adequate corrosion allowance and correct



Fig. 1: Aluminised tube sheet fooled.

use of specific design

should be constructed of carbon steel pro-

tected by a refractory layer and the metal

wall temperature should be maintained in

the proper temperature range through the

SO₄₂- can drastically affect the thermal

reactor and stack life if the wall tempera-

ture drops below the H₂O or SO₂ dew point.

vented selecting a killed carbon steel,

while the acidic corrosion shall be avoided

tive way to protect the tubesheets of

critical items like waste heat boilers and

sulphur condensers from corrosion and is

An example of the effectiveness of the

Even if the plant has not been operated

aluminisation is shown in the Figs 1 and 2.

in the correct and proper way leading to

heavy fouling of the tubesheet, aluminisa-

tion has mitigated and avoided any prob-

lems to the tubesheet, which is still in

Another possible critical point for the SRU

is the tube welding of the waste heat boiler

the welding zones include the following:

select the proper welding type in accord-

verify whole tubesheet behaviour.

normal operating, shut-down, etc.):

utilise only experienced, qualified and

certified welding personnel;

ance with well recognised mechanical

including tubes, during the different

phases of the plant operation (start-up,

minimise the tubesheet thickness:

Ways to reduce the stress caused by

perfect condition after cleaning.

and sulphur condensers.

standards.

Avoid thermal/mechanical stress

sometimes utilised to protect stacks.

selecting an austenitic stainless steel.

The corrosion due to CCC can be pre-

Aluminisation is an efficient and effec-

For example, corrosion due to SO₂2-/

execute carefully the post weld heat treatment for waste heat boiler

execute appropriate tests and non destructive examinations to check welding;

 protect the welding zones of the waste heat boiler with the ferrules when the tubesheet is exposed to high process gas temperatures.

Increase catalyst life

The main phenomenon which reduces the Claus catalyst is alumina sulphation. Catalyst vendors are continuously improving the catalyst resistance through new catalyst formulations and by improving production procedures. If in the past the guaranteed life was three years, now, due to such improvements, it is possible to achieve five or six years.

Sulphation can also be reduced or mitigated with the selection of specific operating conditions. Sulphation increases with temperature and SO2 concentration, but the temperature also promotes COS and CS2 hydrolysis and it is well known that the maximum Claus conversion efficiency is reached at an H₂S/SO₂ ratio equal to 2. Therefore the best compromise should be reached to select the best operating conditions in order to have long catalyst life and good conversion efficiency.

Other conditions that impact on catalyst life are the presence of traces of oxygen and the presence of non-combusted benzene, toluene and xvlene (BTX), BTX must be converted in the thermal reactor otherwise BTX cracking occurs on the catalyst. resulting in fouling and deactivation of the catalyst. Oxygen can be present in cases where the process gas reheating is done by means of in-line heaters or using low efficiency burners. In this case, the installation of a protective layer of a catalyst with oxygen scavenging features prevents cata-

extended. Alternatively, TiO2 catalyst can be over a long time but is more expensive and has a lower mechanical resistance.

Avoid amine degradation

Nowadays almost all SRUs are equipped

organic acids in the treated gas.

Contact with oxygen can be avoided by the amine storage tank with pure nitrogen.

The amine performance should be monitored accurately in order to detect the formation and presence of extraneous compounds.

The first action to reduce the accumulation of degradation compounds is the installation of a well sized and designed filtration system, composed of mechanical

like heat stable salts reaches a value of a few percent, then the solution can be cleaned by treatment with electrodialysis or by ion exchange resins.

To overcome such conditions the plant

Fig. 2: Aluminised tube sheet after cleaning.

lyst sulphation and allows plant life to be considered which maintains its performance

with a tail gas treatment section where the H₂S is washed with an amine solution.

Amines are subject to a slow degradation process that gradually reduces the washing performance and causes severe corrosion problems.

The causes of amine degradation include hot spots in the regenerator reboiler, possible contact with oxygen and the presence of

proper design and accurate blanketing of

filters and an activated carbon filter.

If the presence of degradation products

can be equipped with a dedicated fixed system. Alternatively, it is possible to utilise the services of a specialist company. equipped with mobile facilities that are capable of restoring the amine to its original quality at a price much lower that complete substitution of the product. In this way the plant life can be easily increased.

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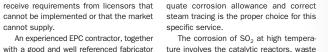
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ture involves the catalytic reactors, waste heat boilers and sulphur condensers. To avoid this type of corrosion the metal walls

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Careful plant operation is of paramount importance for plant life. Plant operators should adhere fully to all operating instructions.

Routine checks e.g. of tracing, jacketing and instrumentation and the flushing of lines as required are mandatory to extend plant life. Several flushing lines are provided on purpose on KT plants to prevent hot spots (like the burner tip) avoid corrosion and avoid plugging.

Another source of fouling and corrosion can be encountered in specific operations like start-up or shutdown of the plant. For instance, the sweeping of the plant during a planned shutdown is important to remove the $\rm H_2S$ and $\rm SO_2$ which are corrosive in the presence of $\rm H_2O$ when the plant is cold.

A useful operation for extending catalyst life is catalyst rejuvenation executed periodically according to operating instructions.

Personnel training and clear instructions and procedures are also important for achieving longer plant life.

Understanding operating data

Nowadays, a huge amount of data is available to monitor the performance and correct operation of each unit of industrial complexes.

Nevertheless it may be not easy to understand what is really happening "behind the steel":

- some basic information may not be available (e.g feedstock composition, fuel gas composition, flue gas composition, etc.)
- the DCS reading is sometimes inconsistent, misleading or unavailable (maintenance, wrong installation, etc.)

In order to overcome such situations KT has developed a proprietary "digital platform", which is an engineering tool based on a customised and proprietary process simulator capable of modelling the correct and real operation of the process units starting from a few basic data and process constraints. The proprietary tool allows actual performance to be compared to key performance indicators, detecting instrumentation failure, assessing the criticality of deviations and creating alerts for safety and corrosion risks. In this way the lifetime of the SRU can be really maximised.

This tool can be easily utilised by operators to achieve excellence in plant operation, allowing selection of the proper

actions and operating parameters in any operating conditions. Utilising this tool is another strategy toward extending the life of a plant.

Extending plant life

In the following sections Jacobs highlights additional factors to consider for extending the life of an SRU.

Many circumstances can bring up the question of whether to scrap an old SRU (and build a new one) or extend its life. Examples include changes in feed, stricter emissions requirements, decreasing feed-stock quality in maturing sour gas fields, and aged or failing equipment. The emergence of new technology can also be the inspiration behind extending the life of an SRU life, to achieve more efficient or reliable operation and to facilitate easier or cheaper maintenance.

In fact, turnarounds and regular maintenance already extend the plant lifetime, but usually this is replacement in kind of anything broken or corroded. So, here we will consider:

- changing the plant to meet new demands, i.e. any small modifications that will aid operating outside the original design window
- upgrading the plant with new technology to make it more maintenance friendly, reliable, operable or efficient.

Process controls

Improved process controls make a big difference in operability. The Jacobs Comprimo® Sulfur Solutions ABC technology (Advanced Burner Control) improves the ability to have tight control of an SRU and the addition of a feed gas analyser in the ABC+ system further promotes an SRU's ability to manage changing acid gas and sour water stripper gas feed compositions. ABC will help squeeze out a bit more recovery by reducing the amplitude and frequency of off-ratio control. But for this control to be effective in turndown operation, it may be necessary to replace valves and flow measurement equipment. Furthermore, replacing 20 year old equipment may be a good idea in any scenario.

Oxygen enrichment

The addition of oxygen enrichment increases the SRU capacity and thus can avoid the need to go to a full unit replacement with a

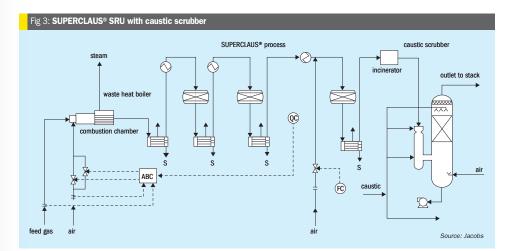
new larger SRU. Oxygen enrichment in itself merits a wider discussion, also in view of the various technologies that are on offer to achieve up to 100% oxygen enrichment. This could theoretically double the SRU capacity.

Ferrule technology

While two-piece ferrule technology does not necessarily have a direct impact on extending the life of the waste heat boiler, this development does promote easier refractory installation and maintenance, especially in cases where owners prefer to inspect the tubesheet at every turnaround. These inspections would require removal of refractory every four vears to enable access to the tubesheet. with a traditional castable tubesheet lining design. With the two-piece design (whether hex-head or square-head), the internal ferrules can be removed to inspect the tube sheet. If the periphery refractory is still intact at turnaround, this inspection can be done without collapsing the refractory face. Also, the two-piece ferrule design is more accommodating of thermal expansion mismatches across the tubesheet and limited unit vibration On the other hand two-niece ferrules can cause some complications if the tube sheet has become warned (which is inevitable after some years of operation). The warping can be accommodated with some shimming during installation to ensure there are no gaps in between and behind the ferrule heads

Furnace temperature measurement

Furnace temperature measurement is a difficult topic, even with new projects. Clients often want redundant technology (thermocouples and pyrometers), but experience has shown that it is difficult to get consistent temperature indication from the two technologies. This can be because of failing ceramic sleeves for thermocouples. As to pyrometers, these have a tendency to drift and need regular calibration; also, the perceived temperature may be influenced by nozzle fouling. Here Jacobs' TempProtect may help: this tool calculates the reaction furnace temperature based on the actual DCS data for the air and gas streams (flow, composition, temperature and pressure). The calculated temperature can then provide a baseline to cross check the results of the temperature measurement instruments.



Engineered refractory

Specifically related to the reaction furnace and thermal protection of the WHB tube sheet is applying engineered refractory and employing an experienced refractory installation contractor.

It is very important for the long term reliability of the SRU to have properly designed and properly installed refractory. In the case of oxygen enrichment, this becomes even more critical due to the higher operating temperatures within the reaction furnace. The refractory material requirements could also change if transitioning to oxygen enrichment operation.

Reheaters

Hot gas bypass reheaters or gas/gas heat exchangers are mostly replaced by direct fired reheaters or steam reheaters. Although hot gas bypass reheaters are good for energy conservation the operating windows and flexibility are less advantageous.

Sulphur pits

Problems with aging sulphur pits are well understood, an effective solution can be to put sulphur vessels in them. These vessels could be outfitted with the Shell degassing technology, which can be designed for both operation under pressurised conditions with return of the vent air to the reaction furnace, and operation at

atmospheric conditions. Consideration has to be given to the amount of sulphur storage required within the plant, but there are definite advantages from a maintenance and operability perspective to move away from a concrete pit to a steel walled vessel for sulphur degassing and short term storage. Depending on the height of the local water table, the concrete pit can have water ingress issues over time.

Sulphur seal legs

The traditional sulphur seal legs can be replaced with sulphur trap seals. This may be appropriate when the legs have become too short (or rather the operating pressure has become too high), or just to simplify maintenance as the removal of sulphur seal legs is typically complicated due to limited access. An added benefit is that with these closed sulphur seals operators will have less risk of being exposed to hazardous vapours from sulphur funnels.

Thermal maintenance system

Also related to the liquid sulfur area is the thermal maintenance system, either with steam jacketing or bolt-on tracing. Reviewing the design and operation of this system could help to prolong the SRU life, by avoiding corrosion issues or plugging problems due to sulphur freezing. Attention should be given to the steam levels used by the system, confirming these are adequate. Properly insulated systems and

regular maintenance of the steam traps will all work to improve the reliability of the overall system.

Adding a caustic scrubber

An eminent example of extending the life of a (SUPERCLAUS® equipped) SRU is adding a caustic scrubber downstream of the thermal oxidiser (Fig. 3). In this way, very low SO_2 emissions can be achieved without having to install an amine based tail gas treating unit (TGTU). The savings in capex make this a convincing business case.

On the other hand, where capacity is decreased and higher local emissions are acceptable, TGTUs (with typically 99.8% sulphur recovery efficiency) have been changed to SUPERCLAUS® or EUROCLAUS® installations (99.2%-99.5% SRE).

Reducing capacity

On the issue of reducing capacity, Jacobs has been involved with several cases recently where the capacity has to be turned down. In one example, replacing some equipment and judiciously applying co-firing made it possible to run the SRU at or below 20% of the original capacity.

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- Sulphuric acid catalyst guidelines Based on many years of operating and design experience we ask leading suppliers of sulphuric acid catalyst what simple rules of thumb can be applied when designing sulphuric acid catalyst beds with regard to catalyst type, size, shape, catalyst bed depth, number of beds and optimal operating conditions.
- New Chinese sulphur production The sour gas fields of Sichuan and a slew of new refineries on the east coast are generating increasing quantities of domestic sulphur for China. With demand from phosphates slowing, could this lead to falling Chinese imports of sulphur?
- Sulphur and sulphuric acid in southern Africa New smelting and leaching capacity in the copper belt of southern Africa and the uranium mines of Namibia have the potential to radically change the regional balance of acid production and consumption.
- Sulphur-carbon co-polymers While the use of sulphur in improving the properties of rubber (vulcanisation) is a long-standing technology, it can also be used to similarly modify man-made polymers. Sulphur reports on work being conducted by the Petroleum Institute in Abu Dhabi on using sulphur to increase the strength of polyethylene, nylon and polypropylene.

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