Number 386

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Sulgas Conference, Mumbai Phosphate markets Predicting corrosion in amine systems Refinery integration with renewables

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SULPHUR JANUARY-FEBRUARY 2020



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**Cover:** Colorful Indian sweets eaten on the Holi festival, Patasa are made of sugar and boiled water. Ramniklal Modi/Shutterstock.com



#### **Refinery challenges**

Changing product slates and regulatory burdens.



#### Sour water systems

Removal of contaminants.

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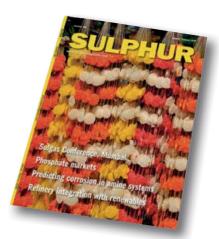
## **BCInsight**

# Happy new decade?

New Year is typically a time for taking stock, for looking back at the year just gone, and thinking about the year to come. This year of course marks a bigger transition, from the 2010s to the 2020s. The past decade has been a volatile one, existing under the shadow of the global financial crisis of 2008-09, from which the world was still just emerging in 2010. Over the past decade, 'quantitative easing' has helped prevent deflation and driven a decade long stock market rally, but also kept both public and private debt levels high, as interest rates stay low. Weaning the global economy off QE has proved to be far more difficult than many anticipated.

In the meantime, the first half of the decade was dominated by the end of the commodity boom, as China's overheated economy continued to suck in raw materials – including sulphur and sulphuric acid – from all over the world. However, over the long term, demographic factors tend to loom largest, and since 2015 the Chinese economy has slowed as its retirement age population has grown much faster than its working population, a delayed effect of the 'one child policy' of the 1990s. With it has slowed the commodity boom. Prior to the financial crisis, GDP growth in emerging markets averaged 7.3% per year. Since then, it has fallen to 4.2%, and much of this has been due to the slowdown in China.

Sulphur and sulphuric acid are commodity chemicals, dependent for supply upon oil, gas and metals markets, and for demand upon metals, agricultural and general chemical markets. As such they move in long cycles of high prices, leading to new investment, then overinvestment, leading to falling prices, which in turn leads to underinvestment, and then rising prices again. While the cycles of any single commodity are not necessarily related, when looked at over very long periods, they often seem to move together in what statisticians describe as 'supercycles'. Four commodity supercycles have so far been identified -1899-1932, driven by the rapid industrialisation of the United States, and ending in the Wall Street Crash and Depression; 1933-1961, with global rearmament and the Second World War and its aftermath; 1962-1995, driven by the reindustrialisation of Europe and Japan following the trauma of the war and ending with the collapse of the Soviet Union and reabsorption of eastern Europe into the world trading system; and 1996 to the present, driven by the rapid industrialisation of China.



It seems very clear that we are now reaching the end of that supercycle, and perhaps about to move into a new one – driven by Indian urbanisation and/or the transformation of Africa's agriculture, perhaps?

Other factors have shaped the past decade and will continue to shape the next one - digitalisation continues to reach into more and more areas of our lives, and we seem to be only at the beginning of the possibilities of artificial intelligence and robotics. A warming world - the past decade was the warmest on record - is also leading to investments in renewable energy that have seen its costs fall dramatically to rough parity with fossil fuels. The electrification of road vehicles and move to renewable power generation will, as our article this issue discusses, lead to a peak in oil consumption some time around 2030, and peak demand for natural gas may follow not long after. This will lead to a new environment for the sulphur industry, as it learns to cope with a sustained period of demand outrunning supply.

Because demand does seem set to continue to rise. The previous decade also added 800 million people to planet Earth. While the rate of global population growth has been falling since the 1980s, peak population may still be some decades away. What seems certain is that more fertilizer will be required, meaning more phosphate, and more sulphur.

And yet, in spite of all of this, global economic growth has been remarkably stable for decades, averaging 3.3% per year in the 1990s, 3.7% in the 2000s, and 3.5% in the 2010s. Since the 1950s, it has averaged 3.8% per year. Slowing population growth (and hence the expansion of the labour force) has been balanced by increasing productivity growth. We continue to become richer than at any time in history. Perhaps that is a thought to take some cheer from at the beginning of another uncertain decade.



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It seems very clear that we are now reaching the end of that supercycle...

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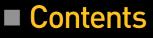
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#### MARKET INSIGHT

**Meena Chauhan**, Head of Sulphur and Sulphuric Acid Research, Argus Media, assesses price trends and the market outlook for sulphur.

#### SULPHUR

Global sulphur markets were weighed down by the lacklustre processed phosphates market throughout 2019 and this led to a sustained period of price erosion. Toward the end of the year, availability was limited due to forward selling, leading to some stabilisation of spot price ranges. Entering the new year, expectations are for there to be no fundamental shift in pricing in the short term. The second half of the year is forecast to see some recovery in the fertilizer market and any uptick in sulphur consumption would lead to fresh supply being absorbed during this period.

Middle East producers all posted rollovers for January, further supporting short term stability in the market. In Kuwait, KPC set its January price at \$39/t f.o.b. Shuaiba. State-owned Muntajat announced its January Qatar Sulphur Price (QSP) at \$40/t f.o.b. The marketer will not issue a sulphur spot sales tender for February loading, however, owing to tight availability. The last spot tender held by the company was back in September. Meanwhile in the UAE ADNOC set its January monthly price at \$42/t f.o.b. Ruwais for shipments to the Indian market.

First quarter contracts in the Middle East were heard ranging \$34-38/t f.o.b, but final conclusions were still awaited from buyers in Tunisia and Brazil at publication time. ADNOC contracts with traders were deemed to reflect the top end of the range while North African prices to date supported the lower end of the range. In 4Q 2019 major buyer OCP in Morocco did not agree a contract price with ADNOC, with no deliveries received during the period. However, an agreement was later reached at under \$60/t c.fr. This is expected to contribute to reduced spot activity from OCP through to March as deliveries resume from the UAE, as well as holding high stocks. In addition, the reduction of output by 500,000 t from mid-December to the end of February on the back of weather related problems will curb consumption. The port of Jorf Lasfar was closed, impacting the arrival of raw materials. In the year ahead, we expect to see increases in OCP's demand for sulphur as processed phosphates production continues to ramp up.

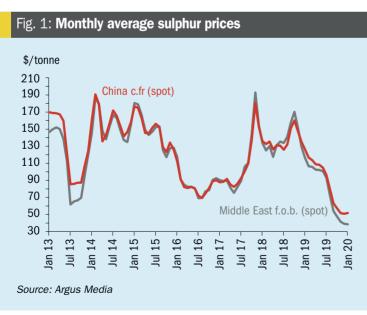
Supply developments in the Middle East are expected to add to the market balance through 2020. KPC will have increased export availability this year with the start-up of its Clean Fuels project. The long delayed Qatar Barzan project is set to start its first phase in 2020 – Argus is forecasting a start-up at low rates of around 250,000 tonnes for the year with the project expected to reach capacity in 2022. Total sulphur production capacity in Qatar is expected to reach just over 2.5 million t/a with the addition of this project.

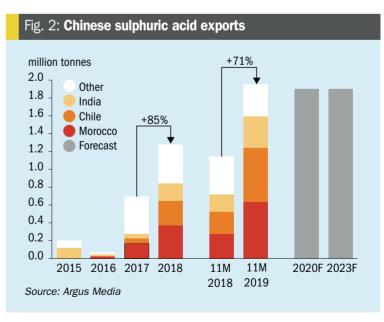
In mid-January sulphur stocks at Chinese major ports was estimated at 2.7 million tonnes, around 1.4 million tonnes up on a year earlier and understood to be close to capacity of around 2.8 million tonnes. There was a minor rebound in prices for Chinese granular product in December despite unchanged market fundamentals. The spot price range ticked up further in January to \$40-64/t on the back of firmer bids, but we expect this trend unlikely to continue in the short term. Healthy stocks are expected to remain for the short term, with reduced DAP production cuts providing a ceiling to offtake. The upcoming Lunar New Year holiday in China at the end of January will also temporarily stall import demand. Domestic sulphur production in China is forecast to rise in 2020 with three projects scheduled to add capacity. The Fujian refinery began construction in 2017 and this is due to complete in mid-2020, adding 500,000 t/a of sulphur.

On the import front, Jan-Nov 2019 trade data reflects an increase of 4% on the 2018 period, despite pedestrian demand through much of the year due to weak downstream fertilizer markets.

Indian spot prices ranged \$65-68/t c.fr at the start of January. At the end of 2019 several buyers stepped in with purchase tenders including FACT and CIL. FACT scrapped its render while CIL secured a cargo from Qatar, with its next requirement heard secured at the start of January from a Middle East trader. Shipments in January – October 2019 to India totalled over 1 million t for the first time since 2016, reflecting a 12% increase on the year. The UAE and Qatar are the leading suppliers at 604,000 t and 280,000 t respectively.

Over in Australia, First Quantum Minerals (FQM) has announced its production guidance for 2020-2022, indicating its Ravensthorpe Nickel Operations is estimated to produce 15,000-20,000 t of nickel in 2020, rising to 25,000-28,000





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t in 2021. The project was put under care and maintenance back in Q4 2017 on the back of a sustained period of low nickel pricing. The leaching operations utilize a 1,400 t/d sulphur burner when running at full capacity. In the January-November 2019 period Australia imported 566,000 t of sulphur, down 6% on a year earlier.

#### **SULPHURIC ACID**

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The stable/soft global sulphuric acid price trend has continued in recent months and into the new year. The view for the short term outlook remains stable to soft. Limited demand from Chile and low prices in India in December resulted in downward pressure on the South Korean and Japanese smelter export prices. Average monthly prices dropped from \$7/t f.o.b. in November to \$5.50/t f.o.b in Januarv. down to \$4/t on the low end of the range. Limited spot tonnes were on offer towards the end of the year. Pan Pacific Copper (PPC) in Japan has announced it will restructure the joint venture by April 2020 to allow its partners to better use copper smelting and refining assets independently. PPC has a planned maintenance at its Hibi Tamano smelter in December 2020 for 35 days. The smelter produces around 73,000 t/month acid. On the export front, Japanese acid trade dropped by 10% in January-November 2019 to just under 2.6 million t. South Korean exports were flat at 2.72 million t for the same period

The presence of China in the export market remains a major focus point for the

industry on the back of growing acid supply from copper smelters in the country. Exports in the first eleven months of 2019 totalled 1.95 million t - surging by 71% on a year earlier. Morocco was a major outlet at 637,000 t delivered during the period. Alongside the upward trend in exports there has been a dramatic decline in import trade to the country. Imports to November in 2019 drop to 501,000 tonnes, down by 47% on a year earlier. South Korea is the main supplier to the country at 89% of total acid. The weak processed phosphates market has weighed on pricing and demand in China. Argus expects acid imports to remain at low levels through the medium term forecast with exports forecast to remain at around 2 million t/a.

In India FACT issued a tender closing 12 December, understood to have been awarded at \$33/t c.fr. with 180 days credit. Buver MCFL was also expected to enter the market in January. Long term contract negotiations for 2020 continued into the new year with buyers including IFFCO and CIL in discussions over formula based and fixed price terms. On spot pricing, the Indian range has dropped 68% in January 2020 compared with a year earlier in line with international developments. The Sterlite Tuticorin smelter in Tamil Nadu remains offline, coming up to almost two years of closure. India's Madras High Court has reserved judgement on petitions from the company asking for permission to re-open the plant.

In NW Europe, spot prices moved up slightly in December on the high end of the

range to \$40/t f.o.b. on the back of firmer prices in Brazil before easing once again in mid-January to \$27-38/t f.o.b. Exports out of Germany in January-September 2019 dropped 14% to 701,000 t. The US is the leading export market at 102,000 t. First quarter contracts were heard being discussed at a rollover, but indications were for decreases on long term contracts. No major turnarounds have been announced in Europe for 2020 as yet.

Average monthly Chile spot prices have eased from \$72/t c.fr in November to \$70/t c.fr in January with import demand tepid going into the new year. A number of tankers were due to arrive in late January at the port of Mejillones, however, to meet demand during planned maintenance at domestic smelters. Chile acid imports increased by 25% in January – November 2019 to 3.26 million t, higher than any full year previously, despite imports easing in the latter part of 2019 as domestic production improved after a period of significant maintenance.

Acid shipments to Morocco were a major focus through 2019 with demand from downstream processed phosphates producer OCP impacting global trade flows. Acid imports to the port of Jorf Lasfar tallied 1.56 million t at the end of 2019, down 7% on a year earlier. China was the leading supplier, with over 700,000 t delivered, up by 91%. Meanwhile European trade dropped 23% on the year. Bulgarian shipments were notably absent and all countries except Belgium and Italy dropped their share in the Moroccan market.

## **Price Indications**

Cash equivalent	August	September	October	November	December
Sulphur, bulk (\$/t)					
Adnoc monthly contract	n.a.	49	47	42	42
China c.fr spot	75	66	66	72	64
Liquid sulphur (\$/t)					
Tampa f.o.b. contract	75	75	46	46	41
NW Europe c.fr	98	80	80	80	70
Sulphuric acid (\$/t)					
US Gulf spot	95	75	75	75	75

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## Market Outlook



#### SULPHUR

- How the processed phosphates market develops over the coming months will be a major factor for the short term outlook for sulphur trends. Improvement is anticipated in the phosphates market from around mid-2020 which may help to support sulphur demand and in turn pricing.
- China remains a major influencing factor on global pricing and trade for the year ahead. Price recovery will depend on recovery in the domestic fertilizer season in the spring. High sulphur stocks at ports and domestic DAP production cuts alongside the slowdown over the Lunar new year period are bearish factors weighing on the market.
- New export volumes from the Middle East region are expected in 2020 as projects in Qatar and Kuwait come online, adding to the global sulphur balance
- **Outlook:** Prices are expected to remain stable in the short term with demand fundamentals pointing to any increases in price trends to be short lived. The

rollover from Middle East producers for January points to support for stability in the short term. Reduced shipments to North Africa to major buyer OCP is a bearish factor due to the weak phosphates market and high inventories, as is reduced participation of Chinese players in the market for several weeks from mid-January.

#### **SULPHURIC ACID**

- The presence of China as a major exporter remains a market bear for the outlook. We expect to see volumes offered to international markets in the medium term period, as surplus availability remains a feature of the local market.
- Prices in SE Asia have been stable to soft in recent months ranging \$30-38/t c.fr in mid-January. Spot activity has been limited with many buyers covered through the first quarter of 2020. Year to date imports for Thailand, Indonesia and Malaysia were all down 3-15% year on year.
- Brazil imported 451,000 t acid in 2019, reflecting an 18% decline on a year

earlier; weak demand and domestic production margins impacted offtake. Spain remained the leading supplier at 215,000 t, up 24%, while Belgium and Mexico shipped 122,000 t and 60,000 t respectively.

- DRC production of sulphur based acid is set to rise with the start-up of the new KCC burner. This will lead to Zambian smelter acid from the Mopani smelter into other markets.
- Chilean production is forecast to rise slightly in the medium term on the back of improvements and upgrades at smelters on the back of more stringent environmental regulations on SO<sub>2</sub> emissions.
- Outlook: Stability in the global sulphur market and potential for improvement in processed phosphates from mid-2020 may provide support for consumption of sulphuric acid. The outlook remains stable to soft with cautious sentiment in several markets. Limited smelter outages in NW Europe are currently planned for 2020, keeping export potential healthy for the coming months.

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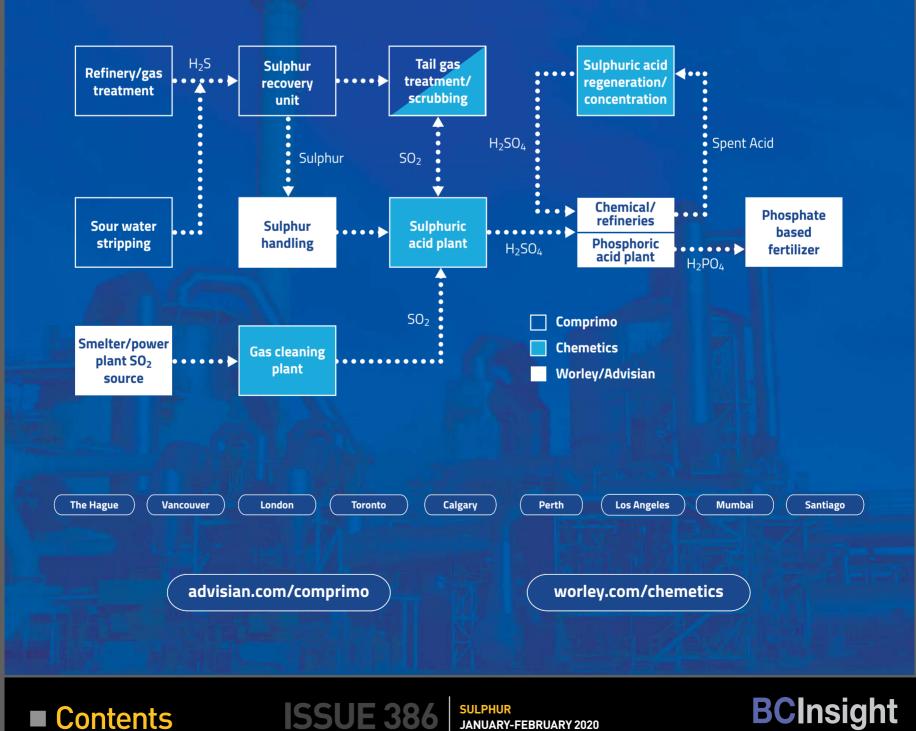
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#### CANADA

### Fears that new IMO regulations could reduce demand for oil sands bitumen

Canadian Press reports in December have highlighted concerns that the new tighter IMO rules on sulphur content of marine fuels, which came into force on January 1st, could lead to reduced demand for oil sands bitumen and syncrude. Canadian oil output has been steadily increasing over the past two decades, mainly due to expanded bitumen recovery, which now accounts for 50% of Canada's 4.6 million bbl/d of oil production. However, the discount for Western Canadian Select bitumen blend crude prices versus North American benchmark West Texas Intermediate could almost double to \$30/bbl in January, according to consultancy Wood Mackenzie, averaging US\$23-24/bbl for most of 2020, as US and other refiners use less heavy, sour oil and switch to lower sulphur feeds to try and optimise low sulphur fuel oil (LSFO) production. However, reduced output from Canada's competitors Mexico and Venezuela is currently helping to mitigate this. Oil sands producers with refineries or upgraders are expected to benefit as



the new standards will increase demand for refined low-sulphur fuels. For example, Husky Energy has expanded its Lloydminster Upgrader to produce an extra 4,000 bbl/d of diesel, and reconfigured its Lima refinery in Ohio to use more heavy oil.

#### SAUDI ARABIA

#### **Aramco IPO underperforms**

The sell-off by the Saudi government of 1.5% of the shares in Saudi Aramco in early December has become the world's biggest ever initial public offering (IPO), raising \$25.6 billion for the Saudi state. However, it fell some way short of the valuation that Saudi Arabia's crown prince, Mohammed bin Salman, had been hoping for. The selloff notionally values Aramco at \$1.7 trillion, but bin Salman had reportedly been looking to raise \$100 billion from the sale, which will be invested into strategic projects via the Public Investment Fund as part of an attempt to diversify the oil-dependent Saudi economy. The flotation had also been intended to attract international institutional investors to the Saudi market, but was in the end only offered to local and regional investors.

#### **MIDDLE EAST**

#### **Gas investments declining**

Gas investments in the Middle East and North African region are declining, according to a report from the Saudi Arabia-based Arab Petroleum Investments Corp. (API-CORP). The report highlights worries about the challenge of meeting domestic gas demand given this slowdown. Private investors are taking a wait-and-see approach, driven by low gas prices, potentially putting more strain on governments.

The Gas Investment Outlook 2019-23 charts a reduction of \$70 billion in gas

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spending from the previous report, 2018-22, alhough the outlook for petrochemicals has increased by 50%.

The most notable fall in gas plans was in Kuwait, down nearly 80%, while Saudi Arabia was down 60%, with Algeria and Iran down around 50% each. The largest overall decreases in dollar terms were in Saudi Arabia and Iran, reflecting in some cases completed 'megaprojects' like Saudi Arabia's Wasit gas plant. As a result of the slowdown, LNG is playing an increasing part in meeting demand. Regasification terminals are on track in Kuwait and the UAE, while Qatar is working on expanding its export capacity to 126 million t/a by 2027 at a cost of \$15 billion. Abu Dhabi is also pursuing unconventional gas resources such as shale, in addition to offshore sour gas. The state imports gas via the Dolphin link, with LNG coming via two regasification terminals.

#### KUWAIT

## Start-up for diesel production at Mina Al-Ahmadi

The Kuwait National Petroleum Corporation says that it has begun production of ultra-low sulphur diesel (ULSD) at its Mina Al-Ahmadi refinery. The new \$700 million diesel production unit has a capacity of 45,000 bbl/d at full capacity, and produces diesel with a sulphur content of 10 ppm. KNPC also commissioned a 73,000 bbl/d diesel production unit at its Mina Abdullah refinery in September 2019, as part of an ongoing programme to increase capacity at the two refineries to 800,000 bbl/d. Work on the upgrades is expected to be complete by mid-2020, according to KNPC.

#### **UNITED KINGDOM**

#### **Conference on sulphur in agriculture**

In December, ICL UK held its first technical conference dedicated entirely to sulphur as a crop nutrient. According to the company, the one-day event – attended by over 75 representatives of the fertilizer supply chain and advisory services – had two clear aims: to raise awareness of the role of sulphur and the rising incidence of deficiency and to demonstrate the benefits of choosing and using a precise and balanced crop nutrition strategy.

Professor Steve McGrath, head of the Department for Sustainable Agricultural Sciences at the UK's Rothamsted Research, said that soils requiring the use of sulphur fertilizers are increasingly widespread. While at one time adequate supplies came from atmospheric deposition, today's cleaner air means sulphur needs to be applied for yield and quality crops. In 1970, it was estimated that 8 million t/a of sulphate were deposited on the UK from industrial emissions. Today, the figure is less than 500,000 t/a, while fertiliser application on UK farms is only around 220,000 t/a of sulphate. "Where sulphur is deficient, expensive nitrogen is wasted." said Prof McGrath.

Jonathan Telfer of Lancrop Laboratories stressed the importance of checking for essential macro- and micro-nutrients. He explained that there are three key stages where sulphur measurements should be

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#### SULPHUR INDUSTRY NEWS

taken: pre-season check on soil to make nutrition plan; in-season leaf and tissue analysis to check whether nutrients are deficient; and post-season grain analysis to evaluate efficiency of nutrient use and content. According to Lancrop's own data, sulphur deficiency in the UK has increased from 60% in 1995 to 97% in 2017 across all soils.

For wheat and potatoes, the element can play an important part in quality. Dr Tanya Curtis, of Curtis Analytics, outlined how food processing and retailing industries are increasingly concerned about acrylamide, a neurotoxin that can form at high temperatures in baking, roasting and frying. An inadequate sulphur supply can lead to free asparagine (an amino acid) and sugars in crops which are precursors of acrylamide.

ICL mines polyhalite at Boulby in northern England, and produces a range of polysulphate based fertilizer products. As well as information from ICL UK's own work on polysulphate-based products. the conference participants were also given insights into a range of independent trials investigating benefits of polysulphate as a source of sulphur. Peter Scott, Technical Director for Origin Fertilisers UK and Ireland, revealed the positive outcome of using polysulphate on maize, grassland and lucerne. Tom Land, Fertiliser Manager with Agrii UK, described their work on wheat, oilseed rape and pulses demonstrating polysulphate consistently gave good results. Andrew Stillwell, Technical Sales Manager for Bartholomews Agri Food Ltd, presented research by the International Potash Institute and Bartholomews comparing ICL's FertilizerpluS product PotashpluS products against conventional posassium sulphate (MOP) for fertilization of spring barley. It was found that PotashpluS improved overall yield at all of the different nitrogen rates and splits. It also contributed to better final grain nitrogen content of malting barley and improved other quality parameters, resulting in better returns to the grower.

#### Breakthrough in reversible SO<sub>2</sub> capture

According to a paper published in Nature Materials, an Anglo-American team of scientists led by the University of Manchester in the UK has developed a new material capable of selectively capturing and releasing sulphur dioxide. The material, MFM-170, is a porous metal-organic framework using transition metal cations linked by organic compounds. The material can purify gas streams to <0.1ppm SO<sub>2</sub> (99.99% recovery) and shows higher SO<sub>2</sub> absorption than other porous materials. It can fully reversibly uptake 17.5 mmol/g of SO<sub>2</sub> at room temperature and pressure, with release of SO<sub>2</sub> achieved by applying a vacuum to the absorption column. No heat is required for regeneration, lowering energy requirements.

#### **UNITED STATES**

#### **Refinery slate changes see lower sulphur production**

Sulphur production from US refineries was down 10% for the year to September 2019 compared to comparable figures for 2018, as refiners began to switch to lighter, sweeter crude feeds rather than heavier, sourer feeds in anticipation of the January 1st IMO deadline for a 0.5% cap on sulphur content of marine fuels. According to figures from Argus, refinery sulphur output was 6 million tonnes to September 2019.

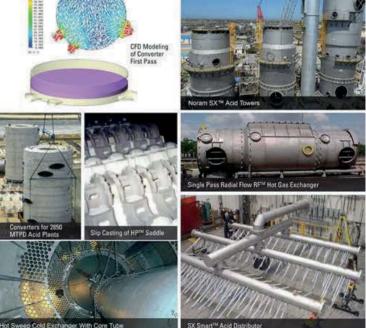
As well as the new IMO regulations, US refiners are also having to cope with new Tier 3 gasoline rules, which reduce sulphur content in gasoline to 10 ppm from this year. As a result, more lower sulphur fractions are being blended which are also lower octane, putting a premium on higher octane fractions such as alkylate and reformate to make up for this, and reducing demand for naphtha.

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## Sulphuric Acid News

#### SAUDI ARABIA

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## **DuPont awarded Ma'aden service contract**

The Ma'aden Wa'ad Al Shamal Phosphate Company (MWSPC) has signed a service agreement for a period of three years with DuPont Clean Technologies for its sulphuric acid plant at Sirhan. The service programme will include activity testing of catalyst samples, evaluation of catalyst performance, plant optimisation, troubleshooting and management of catalyst replacement. DuPont says that it will also track plant performance and assess its overall health using pre-agreed metrics and its proprietary  $PeGASyS^{\mathbb{M}}$  gas chromatography system, which can be used to detect possible leaks in gas-gas heat exchangers, identify SO<sub>2</sub> gas bypassing and measure overall plant conversion in order to optimise plant operation, reduce

SO<sub>2</sub> emissions, increase production and improve converter performance.

MWSPC is a joint venture between Ma'aden, Sabic and Mosaic and includes a phosphate complex with mining, beneficiation, phosphoric acid and sulfuric acid operations with a total capacity of 16 million t/a and a fertilizer facility with a capacity of 4.3 million t/a.

MWSPC senior management commented on the agreement saying, "Ma'aden's vision is to be among the leading players in the global phosphate trade. MWSPC is one of three mega projects that contribute to this goal and as such we need to accomplish planned turnarounds swiftly, as planned and with optimal performance gains.

#### EGYPT

## Contract signed for phosphoric acid plant

The China State Construction Engineering Corporation (CSCEC) and Wengfu Group have signed an engineering, procurement and construction contract with Egypt's Phosphate Misr Company to build a phosphoric acid plant at Abu Tartour in the southwest of Egypt. The plant is estimated to cost \$850 million, and will take 30 months to construct, followed by a trial operation and production period. At capacity, it will produce 900,000 t/a of phosphoric acid, for use in phosphate fertilizer manufacture, making it the second largest phosphoric acid plant in the world, according to CSCEC. The Chinese companies' scope of work covers the plant itself, as well as on-site storage, processing and transport facilities and associated utilities. Wengu has also signed long-term offtake contract for 500,000 t/a of phosphoric acid. The complex also includes 1.6 million t/a of sulphuric acid capacity.

#### TUNISIA

## China looking to invest in phosphate industry

The Tunisian government says that a consortium of Chinese and Tunisian investors has approached it with a proposal to recover phosphates from mine tailings in the southwest of Tunisia. However, the announcement has not been well received by the state-run Compagnie des Phosphates des Gafsa (CPG), which operates the mines and owns the mine tailings. CPG has previously prevented local companies from such a move, regarding the tailings

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as a strategic resource which it can turn to in the future when its phosphate mines' productivity declines. CPG has been operating since 1899, and has produced a huge tonnage of mine tailings which contain 15-25% recoverable phosphate, according to the government. However, while CPG has conducted trials on flotation-based recovery techniques, it has not as yet proceeded with them because of the large volumes of water and additives that would be required.

The Tunisian government is keen to boost the country's phosphate output – prior to 2012, Tunisia was the world's fifth largest phosphate producer, but production has been hampered by strikes and industrial action since then. The government says that it hopes to raise production in 2020 from the 4.3 million t/a produced in 2019 to a target of 6.1 million t/a.

#### DEMOCRATIC REPUBLIC OF CONGO

#### Acid plant set for 1H 2020 start-up

Glencore has provided an update on its Katanga Mining subsidiary in the Democratic Republic of Congo (DRC). Katanga owns 75% of the Kamoto Copper Company, partnered by state-owned Gécamines. Work on the new sulphuric acid plant at Kamoto is said to be 75% complete, and work on the second and third phases of the project, including sulphur dioxide production and a steam turbine generator is "progressing", according to the company. Phase 1 engineering, procurement, fabrication and delivery and civil engineering is complete, with structural, mechanical, plate work, piping and electrical and instrumentation installation progressing. Commissioning of the acid plant is scheduled during the first half of 2020, and the  $SO_2$  plant and power generation during the second half of the year.

#### **UNITED STATES**

#### MECS technology selected for new mine

NioCorp Developments Ltd. has selected DuPont's *MECS*<sup>®</sup> sulphuric acid technology for its Superalloy Materials Project in southeast Nebraska. The acid plant will be designed to maximise energy recovery and emissions control to ensure best-in-class environmental performance, according to DuPont. NioCorp has already obtained the federal permits needed for construction of the Elk Creek Project according to CEO Executive Chair of NioCorp, Mark Smith. The minerals NioCorp plans to produce at Elk Creek; niobium, scandium and titanium, are all considered "critical" by the US government.

"We are pleased to partner with Nio-Corp on this important project," says Eli Ben-Shoshan, President, DuPont Clean Technologies. "We have extensive experience providing world-leading sulphuric acid technologies and ongoing support to mining companies around the globe. Emissions control is a fundamental part of what we do, so we are delighted to assist Nio-Corp in achieving its environmental goals."

#### Mosaic cuts phosphate production in Florida

Low market prices have prompted Mosaic to cut phosphate production at its central Florida operations by 150,000 tons per month, or around 25%. Mosaic's plant in Bartow will be idled for the duration of the production cuts, although no layoffs are anticipated. Once of the concerns about Bartow remains water seep-

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age from a phosphogypsum stack at the site. Meanwhile, phosphate prices at Tampa have been running below \$270/t, compared with \$420/t a year earlier, with bad weather in North America hindering applications, and low crop prices reducing demand globally. Mosaic also idled operations at St James' Parish in Louisiana last year, reducing production by 500,000 t/a, and closed its Plant City facility in Florida, although St James' Parish has since restarted. Longer term, however, Mosaic says that it anticipates better demand in 2020 and a return to higher prices.

#### INDIA

#### Argument over Tuticorin air quality

As the legal arguments over the future of Vedanta's Sterlite Copper Smelter continue, the latest bone of contention has become air quality figures for the region. A local non-governmental organisation (NGO) has said that data collected by the Tamil Nadu Pollution Control Board from three monitoring stations near the Sterlite plant show that air quality has seen a significant improvement since the shutdown of the smelter – now idled for nearly two years, with an increase in the number of days with "acceptable" air quality increasing from 44% to 73% after the closure.

However, the company disputes these figures, arguing that average annual  $SO_2$  levels recorded at the Fisheries College, the closest monitoring stations to the smelter, showed a decrease only from 13 microgrammes per cubic metre to 12 µg/m<sup>3</sup> from 2017/18 to 2018/19.

#### CHILE

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## Fewer copper projects received environmental clearance in 2019

Chile's environmental regulator (SEIA) approved one third fewer mining projects in 2019 than the previous year. According to its most recent report, SEIA approved 47 mining projects in the period January-November 2019, valued at a total of \$1.5 billion, compared to 73 projects with a value of \$12.2 billion in 2018. Approved projects include Codelco's Ministro Hales expansion, where there is a 10-year \$360 million exploration programme, and a \$250 million works programme at Codelco's Andina operations, where extraction works will be diverted away from glaciers and the size of the waste material deposit will be expanded.

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#### NEW CALEDONIA

## Vale to sell its nickel operations in 2020

Vale says that it intends to exit its high pressure acid leach (HPAL) nickel operation at Goro in New Caledonia some time during 2020. Speaking at an investor conference in London in December, CFO Luciano Siani said that the group has been conducting a review of "non-performing" assets, and had decided that it does not "have the competence to raise the production levels with this technology to where we want it to be. Others may have this competence," Siani said. In November Vale took a \$1.6 billion write-down of the value of the New Caledonian assets for 4Q 2019. A combination of accidents, technical difficulties and protests have seen production struggle, down to 23,000 tonnes of nickel in 2019 from 40.000 tonnes in 2017. and less than half of the plant's nameplate capacity. The Goro facility is expected to be idled until a buyer can be found.

Vale says that it intends to increase output from its Canadian and Indonesian nickel operations to more than offset the decline in New Caledonian production, and that it continues to see nickel as a core activity, with anticipated demand coming from batteries for electric vehicles. In Indonesia it is partnering Sumitomo Metal Mining to build a 40,000 t/a HPAL plant. There is also a ferronickel joint venture with another Chinese company which is targeting 700,000 t/a of production.

#### BRAZIL

### Feasibility study completed on HPAL project

Horizonte Minerals says that its pre-feasibility study (PFS) on the Vermelho nickel laterite project indicates that the resource will generate \$7.3 billion in total cash flow over 38 years. The company acquired the asset last year from Vale for \$8 million, and is aiming to produce nickel and cobalt sulphate for the battery industry. The PFS puts initial capital expenditure at \$652 million, and estimates that at full production Vermelho would produce an average of 25,000 t/a of nickel and 1,250 t/a of cobalt per year using a high-pressure acid leach (HPAL) process. Horizonte says that it hopes to find a strategic joint venture partner to co-develop the deposit, and has indicated that it would ideally like to work with Japan's Sumitomo, to replicate the success of the latter's Coral Bay HPAL plant in the Philippines.

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#### CHINA

#### Dongying Fangyuan denies bankruptcy rumours

Shandong-based copper smelter Dongying Fangyuan has denied rumours that the company is close to bankruptcy, although it has admitted a "liquidity shortage" which has prevented the company from issuing letters of credit. The company also denied that it had cut back copper production. The company produced 750,000 tonnes of refined copper in 2018. Recent court filings indicate that there are currently two outstanding lawsuits attempting to enforce payment of \$83 million in debts by Fangyuan.

Chinese copper smelters have been facing weaker margins as an economic slowdown and trade tensions with the US have impacted upon copper demand, and treatment and refining charges (TC/RCs) fell to their lowest level in seven years, down 27% during 2019 alone, before rising marginally for the first quarter of 2020 as production cuts in the smelting sector finally began to show an effect. However, smelter capacity has been increasing rapidly, up 900,000 t/a in 2019, and another 350,000 tonnes in 2020, according to Chinese research house Antaike. Investment firms are nevertheless bullish on copper demand for 2020, with Citigroup predicting a 2.6% rise in Chinese demand this year.

#### PERU

## Southern Copper on cusp of major expansion

In December, the president of Southern Copper Peru, Oscar Gonzales Rocha, announced that the company intended to invest more than \$8 billion over the next five to expand its mining and smelting operations in Peru. There is a feasibility study on an expansion of mining at Cuajone in the Moquegua region to take mine output from 85,000 t/a to 120,000 t/a. The company is also conducting an environmental impact assessment on its Los Chancas project, and is conducting scoping studies on its newly acquired Michiquillay deposit, where Southern Copper hopes to be producing copper by 2023-25. Additionally, there will be a new smelter at IIo, and in October the Peruvian government finally approved the huge \$1.4 billion Tia Maria project in Arequipa, after delays since 2011 because of local opposition to the mine's environmental impact. Copper output at Tia Maria is expected to be 120,000 t/a.

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### People

The Agricultural Industries Confederation (AIC) has announced the election of Angela Booth as its new Vice Chairman. AIC says that Angela brings many years of broad experience in the industry, including several years as Chair of the AIC Feed Executive Committee, a member of the AIC Board, and several roles on industry executives and committees. She was previously the AB Agri Director of Feed Safety. In her career, Angela has had widespread involvement, including feed safety, operations, quality, nutrition, purchasing, legislation and sustainability.

"I'm delighted to assume the position of Vice Chairman at AIC, an organisation that continues to act as the leading voice for the UK farming industry," Angela Booth saod. "We operate in unpredictable times, making AIC's role as the leading voice for agri-supply trade members more vital than ever. AIC's members are key in supporting arable and livestock producers with their extensive knowledge and expert guidance. As it becomes more important than ever to both produce food efficiently and manage our natural resources, AIC will be a strong voice for its members in discussions with



Angela Booth.

government departments, NGOs, and relevant bodies both in and outside of the UK."

"I'm very pleased that Angela will be taking the role of Vice Chairman following her election," said Robert Sheasby, Chief Executive of AIC. "Angela has been a key figure at AIC in promoting members' interests across the UK agriculture industry. As the agri-supply element of agriculture faces a growing number of challenges and oppor-

## Calendar 2020

#### **FEBRUARY**

#### 24-27

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

#### MARCH

8-10

Phosphates 2020 Conference, PARIS, France Contact: CRU Events Tel: +44 20 7903 2167 Email: conferences@crugroup.com

#### 22-24

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

#### APRIL

5-8

2020 Australasia Sulfuric Acid Workshop, BRISBANE, Australia

Contact: Kathy Hayward, Sulfuric Acid Today Email: kathy@h2so4today.com Web: www.acidworkshop.com

#### 20-22

IFA 88th Annual Conference, NEW DELHI, India Contact: IFA secretariat Tel: +33 1 53 93 05 00 Email: ifa@fertilizer.org

#### 22-24

The Sulphur Institute Sulphur World Symposium, CHICAGO, Illinois, USA Contact: Sarah Amirie, TSI Tel: +1 202 296 2971 Email: SAmirie@sulphurinstitute.org

#### Date T.B.A.

Sour Oil and Gas Advanced Technologies (SOGAT) 2020, ABU DHABI, United Arab Emirates Contact: Nick Coles, Director – Conferences, Dome Exhibitions Tel : +971 2 674 4040 Fax: +971 2 672 1217 Email: nick@domeexhibitions.com tunities in the coming years, we need the insight and forward vision of leaders like Angela who will lead AIC members with a strong voice and intelligent outlook."

The International Fertilizer Association prize was awarded by IFA's President, Mostafa Terrab to OCP's Senior Vice President - Sustainability Platform, Hanane Mourchid, at the IFA Strategic Forum in Versailles, France in November. The award recognises OCP's strong commitment in terms of safety and confirms the group's leadership in terms of sustainable development. OCP has committed substantial resources into reaching the best safety standards. based on anticipation, risk prevention and the ongoing involvement of all its employees. With the support of Dupont OCP Operations Consulting (DOOC), a joint venture between OCP and Dupont dedicated to safety, health at work and environment, the Group has also set up a safety excellence programme called "Zero incidents". This aims to take employees and external subcontractors to a state of security interdependence, where each individual is not only responsible for his/her own safety, but also for their colleagues' safety in their workplace.

#### JUNE

#### 12-13

44th Annual International Phosphate Fertilizer and Sulphuric Acid Technology Conference, CLEARWATER, Florida, USA Contact: Miguel Bravo, AIChE Central Florida Section Email: vicechair@aiche-cf.org Web: aiche-cf.org/Clearwater\_Conference

#### JULY

13-17 Brimstone Amine Treating and Sour Water Stripping Course, HOUSTON, Texas, USA Contact: Mike Anderson, Brimstone STS Tel: +1 909 597 3249 Email: mike.anderson@brimstone-sts.com Web: www.brimstone-sts.com

#### SEPTEMBER

21-25 Brimstone Sulphur Recovery Fundamentals Course, HOUSTON, Texas, USA Contact: Mike Anderson, Brimstone STS Tel: +1 909 597 3249 Email: mike.anderson@brimstone-sts.com Web: www.brimstone-sts.com

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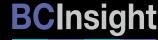
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## **BCInsight**



After a poor 2019, when global demand contracted by nearly 2.5%, phosphate markets are expected to rebound in 2020. Saudi Arabia and Morocco dominate new capacity additions while India and Brazil continue to be the key importers. US and Chinese production is in slow decline, meanwhile.

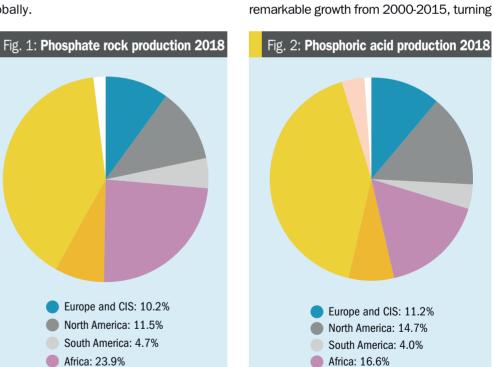
ulphuric acid demand continues to be predicated heavily upon phosphate fertilizer production, with about 60% of sulphuric acid going to make phosphates. The global phosphate industry has seen a period of falling prices and oversupply in 2019, as poor harvest and lower farm incomes and bad weather have reduced phosphate fertilizer applications.

Global phosphate rock production stood at 63.3 million t/a  $P_2O_5$  in 2018, with production split as shown in Figure 1. The world's largest producer remains China, which represents the vast bulk of East Asian production and which produced 23.2 million t/a  $P_2O_5$  of phosphate rock, 38% of the world's supply, mostly for domestic consumption. Next comes Morocco, at 10.5 million t/a  $P_2O_5$  (17%), and the United States, with 7.4 million t/a  $P_2O_5$  (12%) of production. Russia was the fourth largest producer, followed by Jordan, Brazil and Saudi Arabia.

On the processed phosphate side, global phosphoric acid production was 47.0 million t/a  $P_2O_5$ , with production split as per Figure 2. On the whole the split is similar to Figure 1, but as Figure 2 shows, Africa produces less finished phosphates as share of world production, and exports phosphate rock to India, China and other places to produce finished phosphates. Hence the regions that have the greatest

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influence on phosphate production and trade, and hence consumption of sulphuric acid, are China, North America, India, South America and North Africa. China, India, Brazil and the USA between them account for 60% of all phosphate demand globally.



China

#### Africa: 16.6% Middle East: 7.2%

east Asia: 41.8%

South Asia: 3.6%
Rest of world: 0.9%

China is the largest producer and consumer

of phosphates in the world, driving the coun-

try's huge consumption of sulphur and sul-

phuric acid. China's phosphate industry saw

Source: IFA

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Middle East: 8.0%

East Asia: 40.0%

Source: IFA

Rest of world: 1.7%

the country into the largest producer and consumer of phosphates in the world. However, since that rapid period of development, growth has slowed and stagnated even as new plants continued to be built, leading to overcapacity. China's phosphate industry has soaked up most of China's sulphuric acid production over that period, and led to China being the largest importer of sulphur in the world. However, government policy is now to make more efficient use of fertilizer and to cap fertilizer use at its 2020 level. Chinese phosphate consumption peaked in 2012 at 14.4 million t/a  $P_2O_5$ , but since then has fallen to 10.6 in 2018, and this is likely to continue to see a decline.

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Phosphate production, meanwhile, also rose rapidly to reach 17.0 million t/a  $P_2O_5$ in 2018. Some 45% of this was represented by diammonium phosphate production, which has seen a particular excess and much ended up on the international market; 3.4 million t/a  $P_2O_5$  in 2018. But an increasing government crackdown on pollution has led to shutdowns or increased costs of compliance with environmental legislation, and much of the excess or unproductive capacity has been forced to close over the past few years, especially in the Yangtze River basin, where much of China's phosphate capacity is concentrated. In 2015-17, about 1.8 million t/a of DAP capacity and 2.5 million t/a of MAP capacity (both in terms of tonnes product) was idled, most of it from smaller scale producers

Meanwhile, closures on the phosphate rock mining side may turn China into a net importer of phosphate rock from about 2023. CRU reported at the Phosphates 2019 conference that Chinese phosphate rock production costs are expected to rise above the global average site cost by 2020.

In the shorter term, as global phosphate prices have fallen, so major Chinese producers have coordinate efforts to cut production capacity. In July they cut phosphate output by 40%, and this output cut has lasted into the start of 2020, removing over 1.5 million tonnes  $P_2O_5$  of phosphate production so far.

#### **North America**

The US was the largest producer of phosphate rock in the world throughout the 20th century, but its dominant position has declined over the past two decades as competition has evolved elsewhere. US production of phosphate rock peaked in 1980 at 54.4 million metric tons, and this had more

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than halved to 25.7 million t/a in 2018, as mines became exhausted. In Canada, the last phosphate mine – in Kapuskasing, Ontario – was closed when the reserves there were exhausted, and operator Agrium began instead importing phosphate rock from Morocco. Canada also has only one remaining downstream phosphate site, at Redwood, Alberta, although Arianne Phosphates is developing a new mine and downsteram complex at la a Paul in Quebec, and there is also a feasibility study underway on developing a 500,000 t/a phosphoric acid plant at Belledune in New Brunswick.

As phosphate rock mining and processing has shrunk in North America, the North American industry has consolidated. In the 1990s there were 18 different companies operating phosphate plants in the United States at 22 different sites. However, a continuous process of consolidation has seen that reduced to just four; Mosaic, Nutrien, Simplot and Itafos, with only nine phosphate processing sites now in operation. Downstream production of phosphoric acid in 2018 was 6.7 million tonnes P<sub>2</sub>O<sub>5</sub>. The North American share of global downstream phosphate production has steadily fallen since the mid-1990s, from 45% of global phosphoric acid production to 15% in 2018 - still significant but not the dominant force it once was.

Falling production and increased competition on the global market has meant that North American exports of phosphates have contracted– from 12 million t/a of DAP/MAP and TSP in 1996 to less than 3 million t/a in 2018, and North America's share of the international phosphate trade fell from close to 60% to just 10% during that time.

As regional phosphate rock mining has contracted, North American demand for phosphate rock has begun to run slightly higher than supply. In 2017, the region imported 3.5 million t/a of phosphate rock to feed phosphoric acid production. US fertilizer demand for phosphate is relatively mature, and for most of the 1990s and 2000s fluctuated between 3.8-4.2 million  $t/a P_2O_5$ , with another 4-500,000 t/a from Canada. In general, there has been a gradual increase in demand over the past few years, due to increased plantings of maize and soybeans, which are more phosphatehungry, as opposed to declining plantings of wheat, which uses less phosphate fertilizer, but 2019 saw poor weather, especially flooding, across the Mid-West in spring which reduced planting, while the trade war with China has reduced export opportunities for farmers. The result was a significant decline

in phosphate applications last year, and US phosphate producers were forced to make production curtailments as a result. Mosaic idled operations at Faustina in Louisiana from October to December, at which time it announced it will reduce phosphate output in Florida. However, US phosphate demand is expected to rebound during 2020, making up for the losses in 2019.

#### India

India has a significant domestic finished phosphate industry but little domestic phosphate rock mining. Consequently the country is one of the most important importers of phosphate rock and phosphoric acid, and the largest importer of processed phosphates like DAP. India's phosphate consumption ran between 6.7-7.0 million tonnes  $P_2O_5$  for the period 2015-2018, according to the Fertilizer Association of India, and was forecast to have reached 7.1 million t/a  $P_2O_5$  in 2019. India structurally applies too much urea - which has a higher subsidy level - and too little phosphate, and successive governments have failed to tackle this issue, which has contributed to stagnating crop yields. The Modi government is trying to move from nutrient-priced subsidies to fertilizer producers to a direct subsidy to farmers. It is hoped that this will gradually boost phosphate consumption at the expense of urea applications, but this will probably also require the government to tackle the unique subsidy status of urea.

Domestic phosphoric acid production was 1.7 million tonnes  $P_2O_5$  in 2018, with downstream phosphate production running well below the levels required to meet domestic demand. Consequently, India imports several million tonnes per year of DAP - the figure for the 2019-20 fertilizer year (which runs to April 1st) is expected to be around 5.5 million t/a (tonnes product) according to Argus. This is actually lower than for the previous year, as stocks are running high -2018-19 was a record year for Indian DAP imports, which were 50% up on the figure for 2017-18. Total Indian phosphate fertilizer imports were 6.3 million tonnes product of MAP and DAP according to Nutrien figures.

#### **South America**

One of the fastest growing areas for new phosphate demand is South America, with Brazil the largest consumer. Brazil's fertilizer requirements have more than doubled in the past two decades, and phosphate applica-

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tions, aside from a dip in 2015 when the country was in severe recession and paralysed by political deadlock, have climbed from just over 3.5 million t/a  $P_2O_5$  in 2010 to closer to 6.0 million t/a in 2018. The rest of Latin America adds another 1.8 million  $t/a P_2O_5$  of consumption. Consumption is continuing to grow, with CRU forecasting that another 1.8 million t/a of  $P_2O_5$  demand will be added from 2018-2023; an increase of almost 20%. The US-Chinese trade war has ironically been a boost for Brazilian soybean exports to China, which require significant quantities of phosphate nutrient.

Regional production of phosphates is relatively low. Total phosphate capacity stands at only 2.6 million t/a  $P_2O_5$ , so exports run correspondingly high. In 2018 Brazil alone imported 4.5 million t/a (tonnes product) of MAP and DAP fertilizer, making it the second largest importer after India.

#### North Africa/Middle East

On the production side, North Africa and the Middle East are hugely important to the global phosphate industry in terms of phosphate rock production, but also increasingly in terms of finished phosphates (and hence sulphuric acid demand). Morocco is the world's largest holder of phosphate reserves and the second largest producer. But with little domestic phosphate demand, it is by far the world's largest exporter of phosphate rock and, increasingly, processed phosphates. State producer OCP is undergoing a huge expansion programme to not only boost phosphate rock production but also to develop more downstream phosphate production and export capacity in an attempt to capture more value from its phosphate resources.

Neighbouring Algeria is a major phosphate rock reserve holder and has exported around 1 million t/a but now, with \$6 billion of Chinese money, it is attempting to develop four major projects, with state oil and gas producer Sonatrach and state fertilizer producer Semidal taking a 51% majority stake in the project and CITIC and Wengfu group the remaining 49%. The projects include developments in four areas, including the eastern province of Tebessa, where there is an investment budget of \$1.2 billion in new mining, the eastern province of Souk Ahras with an investment put at \$2.2 billion, the northeastern province of Skikda, with \$2.5 billion, and the northeastern port of Annaba, with \$200 million for infrastructure development. First

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Table 1: Global phosphoric acid supply/demand balance 2018

Region	Capacity, million t/a		Dema	1	
	Total	Operating	Fertilizer	Technical	Total
W Europe	1.0	1.0	2.3	0.8	3.1
E Europe/CIS	5.2	4.5	1.1	0.4	1.5
North America	8.8	7.1	5.1	0.9	6.0
South America	2.7	1.8	6.2	1.1	7.2
Africa	11.4	8.2	1.5	0.7	2.2
Middle East	5.4	4.3	1.1	0.5	1.6
South Asia	2.3	1.9	7.8	0.3	8.1
East Asia	23.6	19.3	14.0	2.4	16.4
Oceania	0.6	0.5	0.9	0.0	0.9
Total	61.5	48.6	40.0	7.0	47.0
Source: Nutrien					

production from the new sites is due to start in 2022.

Tunisia is attempting to rebuild its phosphate industry after years of stagnation due to industrial and political unrest. Phosphate rock production stood at 8 million t/a prior to the Arab Spring, but declined to less than half that in 2011 and has recovered only patchily since then. Like Algeria, the government has looked towards Chinese money as part of the Belt and Road initiative to try and boost production, but state producer GCT has been critical of a recent suggestion of recovering phosphates from phosphogypsum tailings (see Sulphuric Acid News, this issue).

In Egypt, another phosphate rock exporter (ca 3 million t/a), there are also moves to expand mining and greatly expand downstream phosphate production, at Abu Tatour, where 900,000 t/a of phosphoric acid capacity is planned, and Ain Sokhna, where anther 360,000 t/a of phosphoric acid capacity is planned. Moving further east, Jordan is a major phosphate producer, and now Saudi Arabia has also moved into phosphate expansion and processing via state-owned mining company Ma'aden. Two large phosphate complexes are already up and running, the most recent, the Wa'ad Al Shamal joint venture with Mosaic in 2017, and a third mega-complex is planned for 2024.

Taken as a whole, the region is the main source of new processed phosphate capacity over the next few years, with North Africa alone adding 3.7 million t/a  $P_2O_5$  of phosphoric acid capacity between 2018 and 2023, and Saudi Arabia another 1.5 million t/a.

#### **Other issues**

Europe's decision to lower its limit on cadmium content of phosphate rock looks like changing the pattern of European consumption of phosphate, consolidating the hold that Russian phosphate producers have on the European market, and displacing Moroccan phosphate, which has a higher cadmium content.

The other major change in the phosphate industry globally is a move towards more complex fertilizers and away from the mono- and diammonium phosphate and single and triple superphosphate that have been the industry's mainstays towards nitrophosphates and NPKs. India has particularly moved towards NP fertilizers.

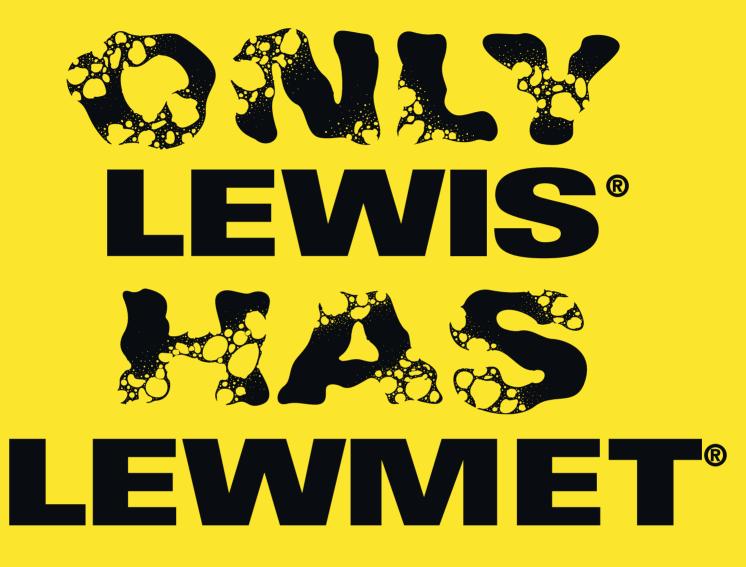
#### Sulphuric acid demand

Sulphuric acid demand for phosphate production is predicated on phosphoric acid production from phosphate rock. Table 1 shows the breakdown of phosphoric acid production and demand by region in 2018 according to figures from Nutrien. As noted above, the main new capacity additions will be in Morocco, Saudi Arabia, Algeria and Egypt, with additional projects in Russia and Kazakhstan, Brazil and Turkey. Capacity closures are likely in North America and possibly India. In its most recent forecast, IFA projected a baseline assumption of an additional 3.7 million t/a  $\rm P_2O_5$  of phosphoric acid production from 2018 to 2023, at an average annual growth rate of 1.5% per year, representing an additional 11 million t/a of sulphuric acid demand over that period, mainly in North Africa and Saudi Arabia.

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The refining industry, the source of half of the world's elemental sulphur, continues to face major structural changes from changing feedstock and product slates and increasing regulatory burdens.

he refining industry has in general benefitted from the lower oil price environment over the past few vears. Because it derives its profit from the so-called crack spread - the difference between the price of crude oil and the price of refined end products - the downstream sector can withstand crude oil price volatility much easier than the upstream industry. Indeed, the collapse in crude oil prices from late 2014 caused by the slowdown of the Chinese economy has helped the refining industry. As oil companies found upstream projects facing uncertain financial returns, they were forced to concentrate more on their downstream sector. The fall in oil prices to as low as \$26/bbl in 2016 also led to a corresponding decline in absolute price levels of end products, which helped boost demand for, eg, road fuels - US gasoline demand rose by 9% for the first half of 2015. All of this contrasts with the poor conditions for the refining industry from 2008-2014, when Europe, for example, saw 2.1 million bbl/d of refinery closures. Even so, the refinery sector continues to face a variety of challenges over the coming years and decades.

#### **IMO** regulations

Undoubtedly the greatest immediate challenge for the refining industry has come with the requirement to meet the change in demand for refined products prompted by the International Marine Organization's 0.5% cap on sulphur in bunker fuels, which came into effect on January 1st 2020. As we discussed in our previous issue ('Countdown to MARPOL', Sulphur 385, Nov/Dec 2019, pp18-20), as there has been only a relatively modest take-up of exhaust scrubbing systems so far among shipowners, the most pronounced effect for refiners will be a large reduction in demand for high sulphur fuel oil (HSFO) and a corresponding increase in demand for middle distillate - marine gasoil (MGO) and diesel and very low sulphur fuel oils (VLSFO). The best estimates point to the decline in HSFO requirements and increase in MGO/VLSFO demand being around 2.7 million bbl/d in both cases, with a slow rebound for HSFO demand as more scrubbing systems are installed over the coming years.

This is one of the biggest changes that refiners have had to face in many years, and puts a premium on refineries with resi-

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Total's Antwerp refinery in Belgium.

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due cracking and desulphurisation units. Indeed, the IMO regulations are expected to bring a temporary benefit for the more complex refiners of North America and Europe for the next couple of years. During times of changeovers in fuel specifications, markets often place a premium on higher grade products compared to their marginal cost of supply. However, as supply increases and begins to balance increased demand the premiums gradually disappear. Refining industry analysts are indicating that the pricing effects of the IMO changeover could begin to disappear by the end of 2022. At that time, slowing demand growth and the impact of new capacities and more fuel-efficient vehicles and a switch towards electrical and other alternative power trains will start to make the business environment more difficult again.

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#### Changing crude and product slates

The switch from HSFO to MGO/VLSFO is, however, only one of the challenges facing refiners in terms of changing crude and product slates. For many years, the switch towards diesel road vehicles, especially in Europe, and away from gasoline was an issue for European refiners, who were predominantly geared towards gasoline production, and who relied on selling their surplus gasoline production across the Atlantic to North America, buying in diesel from Russia and the CIS to make up for the shortfall. However, the pendulum has recently begun to swing against diesel road vehicles in Europe, with diesel engines blamed for emissions of nitrous oxides and particulate matter and consequent poor air quality in major European cities, and the aftereffects of the 2015 'dieselgate' emissions scandal, when major car makers were found to have been fudging diesel emissions figures. Many European cities are now looking at bans on the use of diesel vehicles during the 2020s. European sales of diesel vehicles dropped by 20% in 2018, and 30% in the UK, and in 2019 diesel car sales dropped by another 30% across Europe, with corresponding increases in hybrid and electric vehicles. Set against this, globally the demand for diesel fuels continues to increase, and of course has especially been boosted by the new IMO regulations, but longer term there are product changes that the industry will need to come to terms with.

On the feedstock side, there has been a major boost in light sweet crude production in the US, as fracking for tight oil has completely transformed the US oil industry. US shale oil production has risen from virtually nothing in 2010 to almost 7 million bbl/d by the end of the decade. This has been fortunate for US refiners - global oil demand is in general increasingly shifting towards lighter and sweeter products as a result of rising demand for petrochemicals and the need to meet tightening sulphur specifications. Meanwhile, US refiners' access to heavy sour crudes have been restricted by sanctions on Venezuela and Iran and constraints on Canada's rail and pipeline capacity to export oil sands bitumen. This has been problematic for US Gulf Coast refiners who had geared up to work with heavier, sourer crudes, expecting them to be much cheaper than they have in fact become, when in fact they have been trading at rough parity to conventional crudes.

The IEA's most recent long term energy outlook projects that the US will continue to lead oil supply growth over the next six years, thanks to the incredible strength of its shale industry, triggering a continuing transformation of global oil markets. US tight oil production is forecast to rise between 3-5 million bbl/d in the period to 2024, depending on oil prices (high oil prices will encourage more production), by which time the US will be exporting more oil than Russia and closing in on Saudi Arabia. Overtaking Arabia as the world's largest oil exporter will be a pivotal milestone that will signify greater diversity of supply in world markets, bringing down the average API gravity - and sulphur content - of the world oil supply considerably. Shale crudes contain an average 0.3% sulphur by weight, compared to the current global average of 1.2%.

#### Longer term challenges

Looking to the longer term, three major challenges face the refining industry – one on the supply side, one on the demand side, and the third from regulation. On the supply side, one of the major trends in the industry over the past two decades is one that seems sure to continue, and that is the gradual long-term shift towards the Middle East and Asia of global refining capacity. According to the IEA, between 2018 and 2040, around 15 million bbl/d of new refining capacity will be completed in the Middle East and Asia, about 3.5 million bbl/d of that in China, and a similar amount in the Middle East, taking those regions' combined share of what will be a 110 million bbl/d industry by then from 37% today to 48% in 2040. At the same time, refining capacity in Europe is projected to fall, from 16.2 million bbl/d to 14.5 million bbl/d, with another 5.3 million bbl/d predicted to be "at risk". For refiners in Europe, and owners of smaller, older capacity around the globe, remaining competitive with large new refiners in Asia will be one of their greatest long-term challenges. Likewise, attempts by US refiners to sell gasoline into Asian markets may founder on refining capacity additions in those markets.

#### **Demand – peak oil?**

Prior to the boom in oil production from fracking, one of the major concerns for the industry were projections of new supply sources being unable to keep up with falling production from existing fields – this led to the projected phenomenon of socalled 'peak oil' production. The US tight oil boom has ended such gloomy predictions, and no-one talks of peak oil supply any more. Instead, the looming crunch for the industry now appears to be peak oil demand. Various companies and industry bodies project that global demand for oilbased products will peak some time in the late 2020s-early 2040s.

The drivers for this are increasing efficiency of road vehicle engines, ageing populations (who tend to drive less) and more particularly the increasing uptake of alternative fuel vehicles. Some inroads into liquids consumption has come from biofuels such as sugar or corn starch derived ethanol (in Brazil and the US respectively), coal-based methanol production (in China), natural gas vehicles, hybrid electric vehicles, and now increasingly from electric vehicles. Electric vehicle sales are estimated to have reached just under 3 million units per year worldwide in 2019. Europe and the United States are major consumers, but demand growth is rising fastest in China, which is seeking to ease the country's dependence on foreign oil imports. More than half of all electric vehicle sales are now in China. On the power generation side, meanwhile, oil-based power production is falling, and switching to natural gas or renewables.

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As to when peak oil demand will be reached, the IEA puts the dating of the plateau in consumption at 2040, by which time consumption will be 104.8 million bbl/d. However, the organisation also projects essentially zero growth during the 2030s, pointing to a long peak plateau for demand from 2030-2040, with demand in 2030 up only 9.8% on 2018; an average annual growth rate of only 0.8% to 2030. Furthermore, the IEA says that 90% of this growth will come from petrochemical feedstocks such as ethane, LPG and naphtha and jet fuel. This contrasts greatly with the trend since 2000, when gasoline and diesel provided two-thirds of the growth in oil products. Gasoline demand will probably peak sometime in the late 2020s, according to the IEA forecast.

#### Regulations

While the IMO's switch to lower sulphur bunker fuels has been the biggest systemic shock to the global refining industry over the past few years, tightening envi-

ronmental regulations on a variety of other products and emissions also continue to challenge refiners. While regulations on sulphur content of road vehicle fuels are down to 10-15 ppm sulphur in most major economies now, regulations in those regions not meeting these levels are continuing to tighten, including Africa, Latin America and the Middle East. As yet there is no sulphur standard on aviation fuel, though there have

been discussions and studies on a reduction from the existing 400-800 ppm typical. There are also continuing extensions of what the IMO defines as "emissions control areas" (ECAs), where the limit on fuel sulphur is 0.1%. Refiners also face pressure to lower SO<sub>2</sub> emissions and, increasingly, emissions of carbon dioxide, something which can be mutually exclusive in terms of refinery operations.

#### Digitalisation

Finally, especially for older refineries, capturing the benefits of digitalisation of operations could be a significant factor in future success, via improved margins from real-time optimisation systems that

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This is increasingly leading to a trend towards greater integration between refining and petrochemical production.

integrate process control and production planning; using predictive maintenance to make plants more reliable, with lower levels of downtime; and making processes and support functions across the refinery more efficient. However, experience suggests that it is not always an easy process for refiners to manage, and can be scrappy and piecemeal, with poor implementation unless these efforts are well coordinated.

#### **Petrochemicals**

Although demand for refined products is approaching a peak, demand for chemicals and petrochemicals is projected to continue to grow strongly beyond 2030. Petrochemicals are forecast to represent about one third of global oil demand growth out to 2030, and 50% of demand growth out to 2050. This is increasingly leading to a trend towards greater integration between refining and petrochemical production. Saudi Aramco has been a pioneer in this area, last year taking over a 70% stake in Saudi chemicals producer Sabic for

> \$69 billion. Aramco is aiming to increase its refining capacity from 5 million bbl/d to 10 million bbl/d over the next decade, with half of this growth coming from petrochemical products. The addition of crudeto-chemicals plants in China will also add to competition among refiners, providing additional product streams to generate refinery income, and increasing

pressure on refiners with more basic refinery-chemical operations. Traditional refineries produce around 8-20% naphtha from their operations, whereas the new crude to chemicals plants are geared towards 40-45% petrochemical feedstocks.

#### The future of refining

Stagnating demand and the new wave of refining capacity in Asia and the Middle East seem likely to lead to a new wave of rationalisation, especially among European refiners, who face structural disadvantages including weak local demand, inefficient capacity, and declining local crude supply. Wood Mackenzie has suggested that it is the region most susceptible to closures, and that around 900,000 bbl/d of crude distillation capacity would need to be closed to bring European refinery utilisation levels up to 80 percent in 2035. However, marginal assets in other mature markets also face pressure including Australia, Northeast Asia, and the US. The centre of gravity of the refining industry continues to move eastwards, away from Europe and North America and towards the Middle East and Asia.

However, refiners are able to mitigate this by focusing on market access, capital efficiency, and technology utilisation, staying ahead of regulatory changes by making pro-active investments in low sulphur transportation fuels by upgrading the bottom of the barrel. New refining assets that are aiming to produce both refined products and petrochemicals should invest in the latest technical processes as well achieve economies of scale in terms of size and complexity.

#### Effect on sulphur supply

The continual move to remove sulphur from oil-based products before they reach the consumer has led to the current situation where refineries produce half of all elemental sulphur. In terms of regulations, most of the sulphur is already recovered from oil that is processed, and the biggest slice of sulphur that was not being recovered was present in the HSFO which is now likely to be converted to VLSFO and MGO. This change is currently estimated to increase sulphur production worldwide by about 1.3-1.5 million t/a in the short term.

Of greater effect in the longer term is the increasing supply of light sweet crude from tight oil production. US refiners have produced approximately 10% less sulphur over the past year because of switching to lower sulphur feeds, reducing output by about 600,000 tonnes. As US oil exports grow, so this may have a knockon effect elsewhere. On the other hand, increased petrochemical production will require more stringent sulphur recovery down to very low levels, as sulphur is a poison to many catalysts used in industrial processes. Use of side streams such as gasified waste or biomass may also bring more sulphur into a refinery that needs to be recovered.

Finally, looking beyond the next decade, peak oil demand will signal a major turning point for the sulphur industry.

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PRICES

## Sulphur's price collapse

Jerry d'Aquin of ConSul Inc. looks at the impact of falling sulphur prices on the US market.

S refiners produced 8.35 million metric tonnes of sulphur in 2018. Gas processing added another 600,000 tonnes, for a total of 8.95 million t/a. A lower amount is expected for 2019; refineries and gas should only achieve 7.9 million t/a and gas 300,000 t/a for a total of 8.2 million t/a, due to sweeter crude slates and operating issues. With Tampa's index price declining to \$36/long ton for 1Q 2020 from \$140/It during 4Q18, most US refiners will experience a \$104/It decline in revenue. Simple math concludes this will educe the industry's profitability by \$208 million during just 1Q20, a staggering consequence for any economic sector.

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Sulphur extracted during hydrocarbon processing has long been referred to as 'recovered' as against the hydraulically mined Frasch sulphur of the past. When sulphur was obtained via the Frasch mining process it was driven by a direct price-production cost relationship; the cost of natural gas to superheat water, and the cost of infrastructure being the most significant components. In the US the extraction process ended in 2000 when the last sulphur mine and its related infrastructure shut. Thereafter, supply became the exclusive purview of gas plants and refining installations. During the last decade of Frasch mining, sulphur's economic model shifted from producing, storing and delivering an essential raw material used in fertilizers, chemicals and a myriad of other essential industries to disposal.

Removing sulphur from refineries has always been the objective of most recovered sulphur producers. Few ever considered entering the industry commercially due to sulphur's low commercial image. Frasch producer infrastructure was the happy recipient of such dregs – they guaranteed disposal, taking responsibility for logistics, storage, marketing and making a handsome profit on this 'waste' stream.

As Frasch output declined and companies exited the market, in part due to increased recovered sulphur output, oil companies increasingly had to undertake those tasks, despite being unprepared to do so and unwilling to invest the requisite capital. By 2001, when the Freeport Sulphur Company closed, the sulphur industry was left with only recovered producers and service companies providing logistics and/or resale services for a fee. The profit motive had been replaced with minimising the cost of guaranteeing disposal. No corporate entity whose mission was delivering profit from production of sulphur remained, although disposers always wanted to be paid the top spot price, leading to an interesting mixture of marketing psychology and the game of 'chicken'.

For consumers, sulphur is an essential raw material. The material is a good example of what economic theorists refer to as price inelasticity; when users need it, the price is almost immaterial, and when they do not, even zero or negative value is unlikely to attract a purchase. Simplistically, the impact of poor far economics during 2018 and 2019 severely reduced phosphate fertilizer demand and thus sulphur consumption. Sulphur producers faced a similar downturn; insufficient demand and lack of storage meant sulphur had to be sent away from refineries regardless of the price. Frasch mining once provided production and inventory adjustments allowing refiners and fertilizer companies to operate in a relatively smooth relationship. That ceased almost 20 year ago.

#### **Global trends**

Last year's sulphur price decline is the direct result of the inflexible linkage between US recovered sulphur producers, the phosphate fertilizer industry and similar global trends. Refineries lowered prices to push material into phosphate companies' storage, leading to further price drops. Globalisation has brought similar conditions to Canada, where oil sands upgraders are now loading molten sulphur trucks and subsidising the transaction to US buyers by up to US\$90/t - a figure which is expected to increase. And the rest of the world is in a similar quandary. ADNOC, the world's largest sulphur producer at 6+ million t/a, will experience a 1Q20 profit decline of at least \$150 million, reaching \$0.6 billion should the present price differential exist for the year. Pundits' sulphur price expectations are negative: new gas and refining projects are starting up in the Arab Gulf, West Asia, India and China, to name but a few. The IMO 2020 regulations will increase and disrupt supply, the pace of phosphate fertilizer demand increase is slowing due to environmental constraints and greater application efficiencies, and the volatility of that industry's sulphur needs continues. At best, the surplus of recovered sulphur may be tempered once its disposal costs to users far exceeds all of the costs of stockpiling and reclamation - as has at times happened during prior long-term excesses.

In conclusion, one must wonder why a supplemental product of refinery operations can exert such a huge impact, let alone "turn on a dime". Its financial effect is immediate, as fluctuations go directly to sulphur producers' bottom lines. How can the producing industry better prevent such price shocks? Can it? In truth, some readers will be quick to point out that prices also go up, bringing a corresponding benefit. But nearly 50 years working in all three industries have demonstrated to the writer that upswings are always much slower than collapses, unless, perhaps, navigation in the Arabian Gulf is severely disrupted. I believe solutions exist, being a matter of study, creativity and reasonable determination.

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## Sulphur + Sulphuric Acid 2019

CRU's Sulphur + Sulphuric Acid 2019 conference was held in

ISTOCKPHOTO.COM/ART WAGER

#### **TECHNOLOGY PAPERS**

The technology section of the conference occupied a day and a half of parallel sessions on the Wednesday and Thursday, accompanied by two workshops, one a sulphur operations and troubleshooting 'clinic' moderated by Elmo Nasato, the other a workshop on heat recovery from sulphuric acid plants, including Rick Davis, Garrett Palmquist of MECS, Hannes Storch of Outotec, Michael Fenton of Chemetics, and Nelson Clark of Clark Solutions.

#### Digitisation

A number of papers looked at the application of new digital technologies to the sulphur and sulphuric acid industries. Michael Ku of Applied Analytics Inc described the application of artificial intelligence to sulphur recovery control, via a system of sensors measuring  $H_2S$ and  $SO_2$  levels at various points in the process, which are coupled with an adaptive AI model to fine control Claus plant efficiency.

Collin Bartlett of Outotec showcased Outotec's digital tool solutions for its sulphuric acid plants, including development of its *PORS* system to include a gas cleaning and acid plant optimiser module.

In China, Wylton has developed its own 'intelligent sulphuric acid' system, based around a distributed control system (DCS) and 'big data' analysis system, and Kan Ming Han of Wylton described the system's genesis and operation.

Finally, Patryk Szafaran and Marten Granroth of Haldor Topsoe presented Topsoe's own suite of sulphuric acid plant monitoring and control software, including *DynSOx* and the connected services solution *ClearView*.

#### **Sulphur recovery**

On the sulphur recovery side, John Bourdon of Streamline Innovations Inc presented his new redox process for hydrogen sulphide removal; *Valkyrie*. The process uses a patented chelating agent, *Talon*, used in waste water treatment, as a regenerable scavenger to remove H<sub>2</sub>S

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Houston last November.

ower sulphur prices marked a corre-

spondingly slightly quieter than usual Sulphur + Sulphuric Acid conference

at the start of November 2019. One of

the major announcements at the head of

the conference was CRU's acquisition of

Coking.com, a US-based company provid-

ing consulting, technical support, field ser-

vices, training, and industry conferences

to oil refineries around the world. The

acquisition includes the Refcomm Refining

Community conferences in Galveston and

worldwide, and may change the makeup of

To set the scene for the conference, CRU's

economist Ross Cunningham gave a mac-

roeconomic outlook. Global GDP growth

was 3.2% in 2018, he said, but this is

forecast to drop to 2.5% in both 2019

and 2020. The fall is mainly due to falling

GDP in advanced economies; from 2.3%

to 1.6% and then 1.3% in 2020. Emerging

the Sulphur conference going forward.

**Global economy** 

markets, conversely, have stayed relatively buoyant, averaging 4.7% growth in 2018, down to 3.8% in 2019 but back to a predicted 4.4% for 2020. The main growth in these economies is no longer in China, where growth continues to slow, but places such as South America and India.

At the time of the conference no oil shock to the world economy was predicted; CRU's view on the global oil price was for Brent Crude to average \$63/bbl in 2020. Supply is plentiful in non-OPEC countries, especially the US, and there are large new fields under development in Norway and Brazil. However, other risks to the world economy of course include continuing tensions in the Middle East, as well as the effects of easing of monetary policy, and potentially any impact from OPEC oil production cuts. The US-China trade dispute also continues to generate uncertainty.

On a regional basis, US growth is slowing as the boost to the economy from fiscal policy fades, with manufacturing output down. At present unemployment is low and

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in an automated, modular process. The process has been operated at two demonstrator units in Texas since 2017 removing  $H_2S$  at levels of up to 1.6% in a 25 million scf/d plant, with OPEX savings compared to a triazine unit of between 50-90%.

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Frends Jensen of Haldor Topsoe showcased an alternative to tail gas treatment to push a 99.3% efficient sulphur recovery technology to the 99.9% typically required today. So-called *TopClaus* integrates Topsoe's wet gas sulphuric acid (WSA) process and can recycle acid to the Claus reaction furnace to achieve 100% elemental sulphur recovery. The oxygen in the acid helps enrich the Claus feed in much the same way as conventional oxygen enrichment.

Oxygen enrichment continues to be a way of increasing the efficiency and throughput of a Claus plant, and Diego Scilla of Siirtec Nigi described his company's *SplitOxy* process, which injects oxygen stepwise, allowing for intermediate removal of reaction heat, and postponing part of the combustion to a secondary chamber at the rear of the waste heat boiler, where the gas temperature is still high enough for further  $H_2S$  conversion. It has recently been used in a revamp of an SRU in South America, boosting sulphur production from 52 t/d to 90 t/d.

On a similar subject, Fluor's *COPE* oxygen enriched Claus process can be combined with ExxonMobil's *FLEXORB SE* tail gas treatment, as described by Richard Bazata of Fluor and Jenny Seagraves of ExxonMobil respectively. They also described the option of using Fluor's *OEC*<sup>2</sup>*RP* oxygen enhanced Claus carbon dioxide recovery process as an add-on, generating CO<sub>2</sub> for enhanced oil recovery use.

With the growing importance of shale gas in the US, Juan Marrugo-Hernandez of ASRL looked at producers' experience with what appears to be an increasing concentration of  $H_2S$  within a fracked gas reservoir over time. It is suspected that interactions between biocides and corrosion inhibitors in the fracking fluid with sulphur compounds in higher temperature reservoirs (>100°C) may be leading to degradation of the sulphur compounds into  $H_2S$ .

Some producers, however, are facing the opposite problem – falling  $\rm H_2S$  levels as sour gas wells become exhausted,

leading to turn-down issues in operating a Claus plant. Dharmeshkumar Patel of Sulfur Recovery Engineering addressed the design challenges, and simple changes that can be made such as converter bed deflector plates or deflector plate realignments, which can help ameliorate them.

Edina Avdic of Enersul looked at re-melting of contaminated sulphur. Enersul has recently designed a *ModEx* Dirty Sulphur Remelter to assist with clean-up of contaminated sulphur and sulphur block base pads, avoiding landfill solutions which are increasingly attracting environmental penalties from authorities in Canada and elsewhere.

> The oxygen in the acid helps enrich the Claus feed in much the same way as conventional oxygen enrichment.

#### **Case studies**

A number of case studies also provided practical advice for SRU operators. Ashraf Abufaris and John Nichols of BASF related their experiences with design of the Central Gas Plant III in Bahrain, where the high ambient temperature (and consequent high lean amine temperature) was used as a  $CO_2$  absorption accelerator, avoiding using a costly amine chiller.

Marco Van Son of Comprimo described the integration of biofuels with a refinery sulphur complex - this forms the basis of the article on pages 52-57 of this issue. Ben Spooner of Sulphur Experts meanwhile presented 'war stories from the foaming front' - six different studies on amine foaming problems, their diagnosis and root causes, and how they were tackled, and Domenica Misale-Lyttle of Industrial Ceramics, in conjunction with ASRL, investigated waste heat boiler tube sheet corrosion mechanics, in particular the circumstances under which lower temperature wet sulphuric acid and wet sulphur corrosion can occur, symptoms of which can be masked by failure of ceramic ferrules and tube sheet metallurgy.

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#### Sulphuric acid technology

Chemetics has been working on two huge 5,000 t/d acid plants for OCP at Jorf Lasfar in Morocco, scheduled to come on-stream in 2021-22. As part of the design they have included what they claim are the largest heat recovery systems in the world, using their Chemetics *CES-Alpha* system to generate medium pressure superheated steam at 10 barg and 205°C.

Collin Bartlett and Marcus Runkel of Outotec described work on a different kind of acid plant, this time for a pyrite roasting-based plant for Eti Bakir in Turkey. The 2,080 t/d plant and its associated roaster and gas cleaning plant are part of an integrated fertilizer complex, and also includes an auxiliary *HEROS* heat recovery system downstream of the acid plant to generate additional low pressure steam.

Other sessions covered emissions management, including NOx abatement, mist eliminator systems, and gas measurement. Marco Kennema of BASF also presented new data on the company's second generation of O4-115 Quattro sulphuric acid catalysts, launched the previous year, and used in the final bed of a plant to make up for deactivation over time onstream in the first three beds, leading to more stable operation and lower SO<sub>2</sub> emissions. An installation at DOMO Caproleuna showed that overall conversion levels continued to be over 99% even with first bed activity down to 47% over two years of measurements.

#### Corrosion

Corrosion protection is a perennial concern for sulphuric acid plant operators. Roland Gunther of Steuler KCH reviewed the different capabilities of a variety of materials for such purposes, including organic polymers and resin coatings, various types of rubber membrane fillers, thermoplastic sheets and ceramic tiles or bricks. Following on from this, Johannes Derfler of AGRU Kunstofftechnik described the use of partially or fully fluorinated fluoropolymer materials, which can have longer lifetimes and lower operating costs, depending upon the application.

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consumer confidence still holding up, but the current expansion of the US economy is the longest in history, and the probability of recession is at its highest since the global financial crisis. In the Eurozone, the soft growth patch persists. Manufacturing is down and trade negative. France and Spain are doing well, but Germany and Italy, the Eurozone's largest manufacturing and exporting economies, growth is low. China is continuing to manage its economic slowdown and turn to environmental improvements and poverty reduction, but the trade war with the US has been a surprise, and China continues to be more exposed to its effects than the US. Much rests on the current 'Phase 1' deal.

#### Sulphur markets

Next Peter Harrison of CRU reflected upon sulphur's price collapse in the second half of 2019. There has been much weaker

demand, especially for American phosphates, becoming more evident as the year went on, leading to oversupply in spite of the supply situation not being huge. India and Morocco saw import growth, but there was less buying in China and Brazil. On the supply side, the Kashagan project in Kazakhstan was

still ramping up to full capacity of 1.4 million t/a, although US production was down as refiners switched to lower sulphur crudes and Saudi exports were diverted into domestic demand growth.

China's import decline has been due to closures in the phosphate industry, as DAP prices have been below the average Chinese production cost, leading to fewer opportunities for export. Chinese port stocks between May and July 2019 from 1.1 to 2.2 million tonnes of sulphur – a multi-year high.

On the other hand, there could be better demand from the metals sector, said Peter, with a restart for the Ravensthorpe HPAL nickel site and new HPAL plants in Indonesia, as well as Glencore's new sulphur burning acid plant in the Democratic Republic of Congo, all of these together accounting for 1.7 million t/a of additional sulphur demand from 2019-22. Phosphate demand growth was also positive, although the increases were mainly from 2021 onwards, in Morocco, Saudi Arabia and the CIS. Supply was still being impacted by delayed projects in the Middle East, but these would boost production growth after 2019, in places like Kuwait. Crucially, many of these supply additions would be in coastal locations. Overall, CRU saw the market balance peaking in 2020, with supply running ahead of demand out to 2024, leading to stock builds in Canada, Turkmenistan and Uzbekistan, but potentially no real change to the price environment. The current low prices would, he said, rebound slowly out to 2024, as demand recovers.

Dr Salah al-Awadhi of the Kuwait Petroleum Corporation (KPC) followed with a look at Kuwait's current projects in the sulphur arena. He reiterated that the Middle East will be responsible for more than 40% of sulphur supply growth from 2021 due to new and upgraded refineries, sour gas production and the processing of sour crude, taking production from 17 million t/a in 2019 to 22.5 million t/a in 2024.

> Kuwait's share of this will rise from 750,000 t/a to 2.5 million t/a, mainly due to the Clean Fuel Project, which is expanding two existing refineries, and the new Al Zour refinery, due for completion in mid-2021, with 600,000 t/a of sulphur production. Kuwait is moving to a monthly sulphur price like Adnoc and Muntajat, as quarterly pricing

can lag market developments in the current more volatile sulphur market.

#### Sulphuric acid markets

CRU's Nick Waters looked at the market for sulphuric acid. Chinese smelter exports are rising, and imports declining. Chinese acid exports were forecast to reach 2 million tonnes for the full year of 2019, and the country has been a net acid exporter since 2018. Most of these exports have been from Two Lions coastal sulphur burning plant, and the smelters are focused inland, but more smelter exports are forecast for 2020. Pyrite capacity is declining, balancing some of the new smelter capacity.

Elsewhere, exports from sulphur burning acid plants are expected to fall in 2020 as smelter supply recovers, although India is still having to import to cover the loss of the Sterlite smelter. Chilean imports have been rising, from 2.2 million t/a in 2017 to 3.4 million t/a in 2019, although this is expected to fall to 2.6 million t/a in 2020 as work is completed on smelter upgrades and the smelters return to production.

The major demand area for sulphuric acid continues to be phosphate fertilizer, and Mike Rahm, formerly of Mosaic, covered the market for phosphates. He described the market as 'sick', with the structural changes in the Chinese internal market one of the major culprits, coupled with flooding in the US that reduced phosphate applications and weak currencies for major exporters. Global demand fell by 0.8% in 2019, and by 2.6% in 2018, but shipments were up that year, leading to a large overhang of stocks into 2019 and lower shipments. Chinese demand has fallen faster than supply, leading to more availability for export, but more Chinese production is shutting down in the longer term.

Looking to the longer term, Mike saw agricultural fundamentals slowly improving as lower phosphate prices lead to a demand response. There is also positive growth in some regions, such as South America (especially Brazil), Africa, Asia outside China and India, and the CIS.

#### **Industry trends**

Tuesday's commercial sessions concluded with two panel discussions. The first covered the International Maritime Organisation rules on sulphur content of bunker fuels, moderated by Peter Harrison of CRU, and included Adrian Tolson of Marine 2020. Ross Cunningham of CRU and Nils Dahlberg of Bery Maritime. CRU now estimate that IMO-driven refinery investments will contribute an extra 1.3 million t/a of sulphur supply during 2019-20. About 10% of the world shipping fleet in tonnage terms have installed exhaust scrubbers, rising to 15% by 2023, but in the meantime hish sulphur fuel oil (HSFO) demand is forecast of all from 3.2 million bbl/d to 1.1 million bbl/d, while marine gasoil (MGO) demand will rise from 1.25 million bbl/d to 3.3 million bbl/d, and may attract a \$200-240/t premium over HSFO. Alternative fuels such as LNG are cheaper than conventional fuels and more carbon efficient but supply remains limited to large ports and port infrastructure is expensive. Overall freight rates may rise by 15-20%.

The second panel discussion, chaired by *Sulphur* editor Richard Hands, looked at emissions in the sulphur industry, with Angie Slavens of UniverSUL consulting covering sulphur plant emissions and Eli Ben-Shoshan of DuPont Clean Technologies sulphuric acid plant emissions.

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China's import decline has been due to closures in the phosphate industry...

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The Sixth Annual MESPON Forum took place 7-10 October at the Rosewood Hotel Abu Dhabi, where the global sour gas and sulphur community gathered for four days of networking, learning, and collaboration. This year's theme highlighted new trends, innovations and best practices in the field of sour gas processing that enhance operations.

he Middle East Sour Plant Operations Network (MESPON), organised by UniverSUL Consulting and supported by ADNOC is one of the industry's premier events for knowledge exchange and networking in the field of sour gas production, processing and sulphur recovery. Each year at this event, the sour gas community comes together from across the globe to share knowledge and resources in support of continual improvements in HSE, reliability, efficiency and general best practices.

Given that the Middle East became the largest sulphur producing region in 2015, ADNOC has created an environment of effective industry stewardship, ensuring collaboration and information sharing in established subject matters, while also promoting development of new innovations that will drive the industry forward for decades to come.

Some of the major themes for MESPON 2019 were:

- Operational excellence in sour gas treating, sulphur recovery and sulphur handling
- Ultra sour gas processing innovations, including digitalisation and artificial intelligence
- CO<sub>2</sub> capture for enhanced oil recovery (EOR)

MESPON 2019 started off with a Sour Gas Innovation & Technology Day which featured presentations and interactive exhibits that showcased recent advancements and R&D breakthroughs in the sour gas industry. The main themes of the day were optimised asset utilisation and potentially disruptive technologies.

Prof. Alessandro Lanteri of Hult International Business School gave the keynote

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address on the Innovation and Technology Day in which he stressed that innovation is not about a product or a technology, rather it is about something new. Doing new things means making mistakes and having to learn everything all over again. Innovation is all about learning. We get better at learning by first unlearning what we think we know and then by continuing to learn, testing what we wish to be true. It is important to react quickly and be open to serendipitous events. The advantage lies in rate of learning. A learning culture must be cultivated where mistakes are not accepted, they are celebrated. Everything looks like a failure in the middle but it is important to keep going.

The Sour Gas Innovation & Technology Day was followed by three days of the traditional MESPON Forum which covers the full sour gas value chain:

- Extracting maximum value from sour gas
- Gas sweetening and sour water
- Sulphur recovery and tail gas treating
- ulletSulphur handling

A key feature of the MESPON agenda is its panel discussions and operations roundtable. The topics of this year's panel discussions were:

- CO<sub>2</sub> from SRUs/TGTUs for enhanced oil recovery (EOR)
- The sulphur product value chain.

#### Selected forum highlights

#### **Dual column cryogenic distillation**

Tecnimont has developed an innovative cryogenic technology to meet new market demands for the exploitation of highly sour gas fields:

- to produce sales gas or LNG;
- remove  $N_2$  to meet the required gas specification:
- recover as much C2+ as possible;
- reduce CO<sub>2</sub> emissions through EOR and/or direct injection;
- valorise CO<sub>2</sub> through its re-use for the synthesis of chemicals.

Tecnimont's DCCD<sup>™</sup> technology is a onestep cryogenic gas purification process using a proprietary dual column distillation scheme, providing full removal of mercaptans, sulphur components and other impurities to produce sales gas and/or LNG based on client's requests.

Compared to conventional solvent based processes, DCCD<sup>™</sup> has lower capex due to fewer items of main equipment and rotating equipment and reduced opex due to lower energy requirements.

The simple process configuration, concurrent removal of any sulphur species, lower opex sensitivity to CO<sub>2</sub> feed content and the unique synergies existing with LNG production are just some of the characteristic feature of DCCD<sup>™</sup> technology, which sets it apart from the majority of sour gas treatment process.

DCCD<sup>™</sup> technology has been validated by means of two experimental campaigns and a technology package for an industrial plant has been completed.

#### Mega-sized SRUs

Comprimo provided an overview of today's mega-sized SRU trains and gave their outlook for the future. Project economics can be improved by building mega-sized SRU trains. Capex can be reduced due to lower equipment count and economy of scale. There are however limitations to the largest practical sizes of SRU trains, due to both fabrication and transportation limits. Achievable train capacities can be increased by technology selection, e.g. oxygen enrichment, and equipment design modifications, e.g. WHB design. There is no one-mega-size-fits-all solution so close cooperation between operating companies and experienced licensors and contractors is crucial in delivering optimised designs.

Looking to the future, more megasized SRU trains are in the pipeline. The largest sizes (currently up to 2,500 t/d) are expected to increase. There will be increased application of oxygen enrichment. Various new build and revamp gas plant projects using oxygen enrichment are already underway. There is also increasing focus on potential for CO<sub>2</sub> reinjection

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for EOR, which may further favour acid gas enrichment and oxygen enrichment.

#### ASG CO<sub>2</sub> recovery project

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ADNOC Sour Gas (ASG) owns and operates the Shah Gas Processing plant (SGP) which receives and processes sour fluids (up to 25%  $H_2S$  and 10%  $CO_2$ ) from the nearby Shah Arab Sour Gas Field. ASG has been investigating options to capture and produce  $CO_2$  in a flexible and cost effective approach in case of future growth. The captured  $CO_2$ would be utilised for EOR and would reduce greenhouse gas emissions. After a detailed evaluation of the various options available. ASG has selected pre-combustion CO<sub>2</sub> recovery (i.e. after the SRU tail gas treating unit and before the incinerator unit) and amine absorption for CO<sub>2</sub> capture. The target date for start-up is 2023.

#### New technology for reducing amine losses

INEOS has developed Amine Quench<sup>™</sup>, a patent pending process which uses a small piece of proprietary equipment that is installed in the stripper overhead to reduce amine vapour losses in gas processing plants. It provides a cost effective solution for plants experiencing high amine losses and requires minimal modifications to the amine system.

Alkanolamines used for gas and liquid treating are regenerable solvents. The amine solvent is not consumed by the acid gas removal process but some amine loss is inevitable in any system. To determine if amine usage is typical/acceptable industry benchmarks and process simulation can be used. In industry surveys 1-3 lb amine/million standard ft<sup>3</sup> is typical for natural gas processing. High pressure systems can achieve <1 lb amine/million standard ft<sup>3</sup> of gas treated.

Excessive amine losses increase operating costs and can be a symptom of other operational or design issues. It is important to understand the potential pathways for amine leaving the system and to identify and correct the cause of excessive amine loss. Amine loss categories include:

- solubility (liquid treaters);
- entrainment;
- gas-in-liquid (foaming);
- liquid-in-gas;
- liquid-in-liquid;
- degradation;
- mechanical:
- vaporisation.

To troubleshoot, conduct a plant-walkthrough of all process equipment and piping in the amine system to identify leaks, collect process data to enable process simulations to be run to look for problems and use a systematic approach to using a process of elimination to identify and correct the cause of high amine losses.

Once the root cause of amine losses is identified, operational issues or conditions responsible for excessive losses can be addressed.

### Innovative approach to Claus tail gas treating

The conventional method for achieving a sulphur recovery efficiency of 99.9+% is to install a TGTU that hydrogenates all the remaining sulphur species to H<sub>2</sub>S, and then uses an amine system to capture and recycle the H<sub>2</sub>S. Such technologies (BSR, SCOT etc.) are widely used when high sulphur recoveries must be met but are relatively expensive with associated high energy consumption.

With amine-based TGTUs the operator only has sulphur to deal with but if sulphuric acid is acceptable, the economics could be considerably improved by combining the Claus plant with a wet gas sulphuric acid plant. Higher energy recovery is achieved when using the wet gas sulphuric acid process for Claus tail gas (in total 808 kJ heat per mole of  $H_2S$ is generated). Approximately 90% heat is recovered as steam or hot air and less than 10% is discharged to cooling water. However, the industry has not been receptive to handling the relatively large quantities of sulphuric acid produced despite the obvious economic benefits.

A new innovative configuration has therefore been developed by Haldor Topsoe in cooperation with Worley, integrating the WSA process with the Claus process, whereby sulphur compounds in the tail gas from the Claus process are recovered as commercial grade sulphuric acid which can be recycled directly to the Claus reaction furnace for 100% elemental sulphur recovery. The oxygen contained in the recycled sulphuric acid will act in the same way as oxygen enrichment, with the result of lower process gas flow and possibilities for boosting the capacity of an existing plant or reducing the capex of a new Claus plant. The only product is high quality elemental sulphur.

Besides lower opex, capex and CO<sub>2</sub> emissions, using a WSA plant as a TGTU also offers extra flexibility for operators operating a sour water stripper as the sour water stripper off gas can be bypassed around the Claus reaction furnace, increasing reliability of the SRU by avoiding the inherent issues caused by handling ammonia in the Claus plant.

#### Liquid sulphur degassing

Liquid sulphur degassing technology continues to take a more important role in the sulphur recovery industry as Claus SRU sulphur emissions and handling safety receive greater attention. Based on commercial operating experiences and ever changing environmental emission regulations, Fluor/GAA continues to improve the performance of the D'GAASS out-of-pit liquid sulphur degassing technology. The 3rd generation D'GAASS process offers: shorter degassing duration requirements, smaller equipment, lower capex and opex, as well as enhanced operating flexibility and reliability through reduced corrosion potential. The improvements can also be retrofitted to existing D'GAASS units.

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	King River now looking to sulphuric acid	Jan/Feb	15
	King River rescales proposed acid plant	Sep/Oct	14
	King River revises acid plant cost estimates	May/Jun	14
	NQ Minerals looking at integrating acid output	Sep/Oct	16
Belgium	Trafigura to take over Nyrstar	May/Jun	15
Brazil	Acid plant may be closed in restructuring deal	Mar/Apr	17
	Itafos launches new premium products at Arraias	Nov/Dec	13
Canada	Acid plant up and running at Trail smelter	Nov/Dec	12
	Arianne secures second offtake deal	Jan/Feb	15
	Glencore cancels smelter upgrade	Sep/Oct	17
	SNC Lavalin profits warning over Chile delays	Mar/Apr	14
Chile	Codelco ends contract with SNC Lavalin	May/Jun	14
	Copper smelters shut for emissions upgrades	Jan/Feb	16
	Coro announces progress with copper leach project	Nov/Dec	13
China	China removes export tax on phosphates	Jan/Feb	15
	Import restrictions driving Asian smelter capacity	Jul/Aug	13
	Merger creates phosphate giant	Jul/Aug	13
	Shenghong opts for acid alkylation	Sep/Oct	16
	Tighter regulations on copper concentrate	Sep/Oct	16
	Zijin Mining starts up new copper smelter	Sep/Oct	16
Cuba	Sherritt reports higher nickel production at Moa	Mar/Apr	15
DRC	Acid plant commissioning set for 4Q 2019	Mar/Apr	17
	Glencore to idle Mutanda mine	Sep/Oct	14
Denmark	Tamasek buys 30% of Haldor Topsoe	May/Jun	12
Egypt	New phosphate complex inaugurated	Sep/Oct	14
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Finland	Outotec to supply leach technology for Terraframe	Jan/Feb	14
France	Axens to license Exxon acid alkylation technology	May/Jun	12
Germany	Lanxess celebrates 125 years of acid production	Nov/Dec	13
India	Hindustan Copper to expand ore production	Jul/Aug	13
	Sterlite court case continues	Jul/Aug	12
	Tuticorin smelter gets reprieve	Jan/Feb	14
	Vedanta seeks approval to repair smelter	Nov/Dec	14
	Vedanta setback as court pushes case to Tamil Nadu	Mar/Apr	14
	Vedanta smelter case drags on	May/Jun	14

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Indonesia	Freeport secures financing for smelter	Sep/Oct	16
	Nickel leach facility awaiting environmental clearance	May/Jun	14
	Nickel ore export ban brought forward	Sep/Oct	17
	Work begins on HPAL plant	Mar/Apr	15
Italy	Nuova Solmine completes testing of absorption tower	Nov/Dec	15
Japan	Sumitomo smelter output to fall in 2019-20	May/Jun	15
Kenya	Geothermal power plant considering acid production	Jul/Aug	13
Madagascar	Ambatovy plans shutdown in November	Nov/Dec	12
Mexico	Silver sulphate project award	Jan/Feb	14
Morocco	Contracts awarded for new acid plants	May/Jun	12
	OCP reports positive 1H results	Nov/Dec	14
	OCP selects Bedeschi to provide conveyors	Nov/Dec	14
Poland	Grupa Azoty signs phosphate rock supply deal	Mar/Apr	14
Russia	New acid plant for PhosAgro	May/Jun	13
	Nornickel revises sulphur project cost estimate	May/Jun	13
	Outotec to build copper leach plant for Baikal	Jul/Aug	12
	PhosAgro output up 18%	Nov/Dec	14
	Sulphuric acid symposium held in Sochi	Nov/Dec	14
Saudi Arabia	Phosphate rock supply deal signed with Kribhco	Mar/Apr	15
	Trafigura to build huge new smelter complex	Mar/Apr	14
South Africa	Phosphate project delayed again	Nov/Dec	15
	Vedanta concerns over zinc expansion	Jan/Feb	14
Turkey	Ground broken on new acid plant	May/Jun	15
UK	Trafigura takes control of Nyrstar	Sep/Oct	14
US	Alon Refining to use DuPont alkylation technology	Jan/Feb	14
	Concerns over potential breach in gypsum reservoir	Mar/Apr	16
	Copper leaching to begin in 4Q 2019	Mar/Apr	16
	First copper from Florence leach site	May/Jun	13
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	loneer awards acid plan design contract	May/Jun	12
	IPNI closes its doors	May/Jun	13
	Mosaic to begin Ona operations in March	Jan/Feb	14
World	Uranium demand predictions revised upwards	Nov/Dec	12
Zambia	Copper smelter restarts but future remains uncertain	Jul/Aug	12
	ERG suspends copper and cobalt production	Mar/Apr	16
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## Sulphuric acid plant health check

Sulphuric acid plant operators juggle multiple issues trying to keep their plants running efficiently and reliably. With the revolutionary ClearView<sup>™</sup> process health monitoring solution, as well the DynSOx<sup>™</sup> software for simulating dynamic operation, Haldor Topsoe strives to bring digital services with real and tangible operational benefits to the sulphuric acid industry. **P. Szafran** and **M. Granroth** discuss how together these digital services can help acid plant operators meet their daily targets.

he current trend for increasing digitalisation of industrial plants results in the generation of more and more data that on its own can result in increased confusion rather than clarity. The key to taking advantage of digitalisation is to leverage the torrent of data and new computational capabilities to solve real operational issues.

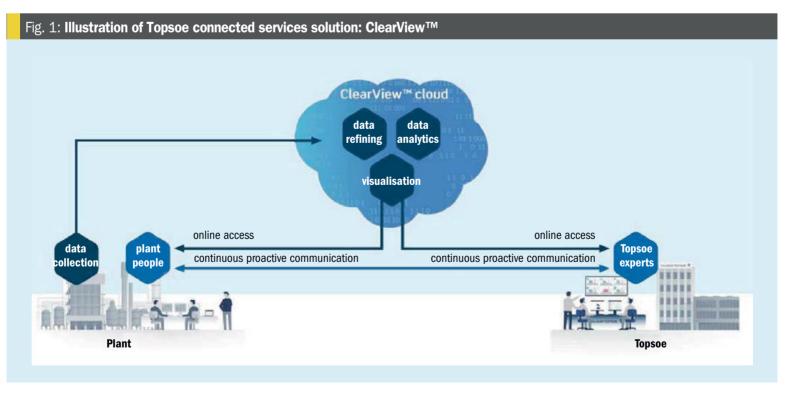
For a bulk chemical market such as sulphuric acid, margins are thin, and plant operators are under constant pressure to improve operation to stay profitable. Ensuring optimal operation means minimising downtime, maximising throughput and avoiding costly equipment damage. Throughout the world, maintaining emission levels below stipulated limits is one important consideration. While emission control may have been mainly related to steady state operation in the past, dynamic conditions, such as start-up, are increasingly attracting the attention of authorities.

Topsoe has been working with digitalisation in different forms in a number of areas. For sulphuric acid, the two latest developments are ClearView<sup>M</sup> and DynSOx<sup>M</sup>.

The driver for these developments is a need to address common challenges faced by sulphuric acid producers; these include poor data quality, wasted time in compiling data rather than analysing it, and a lack of knowledge, especially with high rates of staff turnover. These challenges are experienced on a day-to-day basis, and result in lower throughput, unplanned downtime, avoidable maintenance costs or increased emissions.

#### **Reliability through ClearView**<sup>™</sup>

Topsoe launched its connected services, ClearView<sup>™</sup>, for ammonia, and hydrogen plants in March 2019, in cooperation with Honeywell as a strategic partner. The same concept (see Fig. 1) is now being introduced for the Wet gas Sulphuric Acid (WSA) technology.



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ClearView<sup>™</sup> WSA is a connected solution based on streaming data to an Industrial Internet of Things (IIoT) platform in which rigorous in-house models simulate process data and compare plant parameters to their optimal and healthy values to provide early warnings of process-related problems. ClearView<sup>™</sup> WSA also monitors plant start-up and shutdown, and predicts hydraulic and catalytic performance of the unit in order to provide plants with a proactive approach to shutdowns and catalyst screening, before unit capacity is affected.

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Online dashboards are designed to deliver up-to-date insights directly to the relevant persons and cater to various roles in the plant, including the overall KPI focus of the CEO and plant manager, at a glance alerts for the daily shift engineer and detailed optimisation screens to be used by the technical department.

The goal of ClearView<sup>™</sup> WSA is simple – to detect and mitigate abnormal operation to prevent any surprises in the form of unplanned downtime, and to offer tools and recommendations to mitigate risks, and resolve problems on a planned basis, ensuring world-class availability and reliability.

#### Handling dynamic conditions with DvnSOx™

Although normal steady state operation of sulphuric acid plants can be quite intricate, modelling this operation has taken precedence over transient conditions. Unsteady state operation of plants has long been a black box for designers and operators alike. In particular the behaviour of the catalyst within the SO<sub>2</sub> converter during these conditions was not well understood. To address this, Topsoe started to investigate the different processes taking place in and around the catalyst as gas conditions, temperature or pressure changes. Based on the results of these studies, a model was developed that is able to predict the behaviour of the converter during dynamic conditions<sup>1</sup>. This model together with the knowledge of the technical service team is offered to acid plant operators under the name DynSOx<sup>™</sup>.

Modelling of the complete catalytic system in an  $SO_2$  converter is a complicated task with many unknown parameters due to the number of potential reactions and the different oxidation states of vanadium in the catalytic cycle<sup>2</sup>. Based on an assumed fundamental mechanism and catalytic cycle, a consistent model

comprising temperature-dependent solubilities and reaction rate constants may be set up for dynamic conditions. The challenge in terms of model applicability is that a considerable number of parameters cannot be determined independently and reliably, and as a consequence lose their original physical meaning.

A more practical, semi-empirical model with fewer parameters was developed. The transient  $SO_2$  converter model contains accumulation terms for heat and  $SO_3$ and is capable of predicting the observed dynamic behaviour of pilot- and full-scale plants<sup>1</sup>. Accumulation of  $O_2$  and  $SO_2$  is neglected due to their low solubility in the catalyst melt. The fluxes of  $SO_2$ ,  $O_2$ , and  $SO_3$  to the catalyst melt are calculated from additive contributions from steadystate catalysis, and unsteady absorption or desorption.

With the capability of predicting the behaviour during transient conditions, unsteady state operation such as startup no longer needs to be a black box for acid plant operators. Catalyst loading and operational parameters can now be optimised to reduce emission peaks, increase potential hot stand-by time and give peace of mind through better understanding of process behaviour and risk. This is an excellent complement to ClearView<sup>™</sup>, and will help acid plant operators meet their targets and minimise downtime.

#### **ClearView**<sup>™</sup>

#### **Dealing with fluctuating conditions**

Fluctuations in chemical unit operations are a given in any process industry, but this is especially the case in one dealing with processing sulphur-containing off gases, as is the case with many WSA units. Even operators of sulphur-burning or spent acid regenerating WSA units take advantage of their installed capacity by supplementing sulphuric acid production with off gases from upstream operations, while recovering energy in the form of steam.

Fluctuations in both the volume and the sulphur concentration of off gases are outside of the plant's control, and it is common for the sulphuric acid production rate to vary as a result. Units are designed to handle a peak feed flow and sulphur concentration continuously, so process fluctuations should not matter as long as they take place below these maximum design values. However, few would suggest that

ISSUE 386 SULPHUR JANUARY-FEBRUARY 2020 feed flow and concentration, or, by proxy, sulphuric acid production rate, are the only parameters required to determine a unit's operational health. An adequate assessment of process performance involves assessing the catalytic, thermal and hydraulic capabilities, even if the unit is running below its design load.

To make meaningful and actionable conclusions regarding the performance of any piece of equipment, or the process as a whole, one requires a consistent mass and energy balance. The starting point is to identify a period of time when the unit is steady enough to perform a mass and energy balance - attempting to do so for too short a period of time will introduce error due to process fluctuations, while taking a period that is too long risks compressing periods and subjecting them to excessive smoothing, removing necessary details. The common approach is to look at process trends and guess at a representative period of time by qualitatively judging process steadiness from a parameter's graphical appearance.

Using mathematical algorithms to analyse selected process data for stability. ClearView<sup>™</sup> removes the uncertainty and irreproducibility caused by this guesswork. This process is referred to as steady state detection. Individual process parameters are checked for steadiness, and when all the selected parameters are steady the entire process is deemed to be in steady state, thereby allowing one to confidently proceed to the next step of obtaining a consistent mass and energy balance for a period of operation. Fig. 2 depicts steady state detection applied to four weeks of operating data from a WSA unit, on either side of a stoppage. Although not all the relevant parameters are shown here, the principal being illustrated is that each individual parameter is checked for steadiness (line across the data trend), and when all parameters are steady simultaneously, complete process steady state is shown (line at the base of each trend). In such a way, an entire month of operation is broken into well-defined periods, each with its own associated mass and energy balance.

The term "steady" is itself not a rigid term – steady means stable relative to each parameter's own range and standard deviation, and various inputs control how strict the criteria are that consider a parameter to be steady or not. A quickresponding, easily-controlled process variable such as boiler feed water may have

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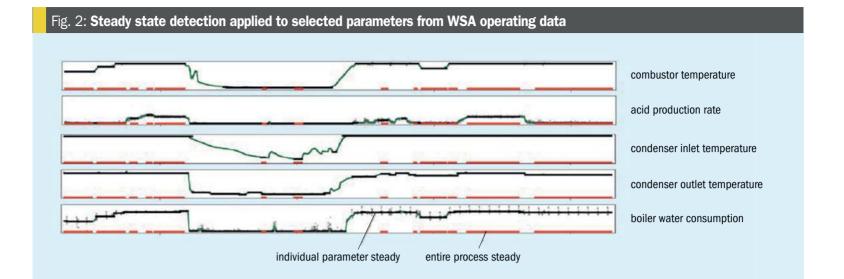
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a lower fluctuation than a parameter such as a combustor chamber temperature, but the goal is to find a period of time when each parameter's fluctuations is within their own acceptable range, allowing an average value for a given period of time to be representative of the entire period of operation. Take for example the boiler water consumption at the bottom Fig. 2; regular spikes can be seen in the process data that represent a sudden increase in boiler feed water flow when the operators perform routine boiler blowdown. A simple mathematical (Gaussian) filter is applied to the data and steady state detection is applied to the filtered data, meaning these spikes do not unnecessarily break the steady state of the parameter in question.

Apart from providing a systematic way of knowing where to distinguish between periods of operation, having access to steady state detection has monitoring benefits for plant operators and engineers. If a process has been steady for the duration of an entire shift, or day, or longer, plant operators and engineers will be familiar with the state of the unit on a day-to-day basis and do not need to spend time looking through trends on a DCS historian. There is a decrease in the amount of time spent on process monitoring that will not yield any useful results. On the other hand, if the process steady state was broken, one is able to see when it broke, as well as which parameter(s) caused it to break, and which ones were able to reject disturbances. This provides an immediate starting point for all process monitoring and troubleshooting. Over the long term, process stability can be improved by analysing whether fluctuations in parameters that break steady state can be reduced through improved controller tuning or modifications

to procedures, or whether more sophisticated interventions are required. This will lead to improved overall unit stability.

### Resolving inconsistent mass and energy balances

Once a period of time has been selected, a mass and energy balance can be performed. Details of process flows, temperatures, and compositions can be combined with the unit's pressure profile to allow one to understand, among other things, the thermal performance of burners and heat exchangers, the hydraulic performance of pumps and blowers, and catalyst performance.

It should come as no surprise that mass and energy balances rarely close, with errors arising from a multitude of sources. Instrument measurement error manifests due to a number of causes, including inherent instrument error, incorrect calibration or compensation, fouling, measurement location, poor process gas mixing (in the case of temperature measurement), and inaccurate laboratory or analyser measurements.

The most basic mass and energy balance tool in a plant that produces sulphuric acid is to compare the flow and  $SO_2$ concentration (if available) of the stream into the  $SO_2$  conversion reactor, with the produced rate of sulphuric acid. One then compares this to the temperature increase across the catalyst to validate the SO<sub>2</sub> concentration in the gas. If the mass and energy balance close, then one is able to take just the feed flow and concentration, and use the  $SO_2$  conversion rate of the reactor to calculate the mass of acid that will be produced, and predict the temperature rise across the catalyst. A failure to predict the product flow meter reading or the reactor outlet temperature does not say anything about which instrument is giving a false reading – any of the instruments concerned could be the culprit for inaccuracies. In fact, it is more accurate to say that every instrument is the culprit, although to various extents. This is something that is already consciously performed when the one doing the calculations looks at a result and concludes that the answer is "close enough". It is known that an error of certain magnitude should be expected, and the error is not formally attributed to any instrument individually, unless it is known that a particular instrument is faulty or unreliable.

Data reconciliation is the process of "smoothing out" the error by attributing error to various instruments until the mass and energy balances close. The degree to which a process parameter is allowed to deviate from an instrument reading is determined by the standard deviation that is assigned to the instrument. This assumes that error in a reading will be normally distributed around the true value. In this way, a properly-positioned, calibrated and maintained thermocouple in the  $SO_2$ converter can reasonably be expected to be within 5°C of the true value, while more margin is given to a thermocouple in a combustor, say. Calculating a combustion chamber temperature to within 50°C of the reading (typically in the region of 1,000°C) would be considered accurate enough to have arrived at a consistent dataset. While standard deviations are mathematical in their backgrounds, in a data reconciliation application they are assigned based on experience in dealing with enough process data. The cumulative differences between smoothed (reconciled) and measured values is then calculated by a sum-ofsquares-type expression (SSQ), as follows:

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		Data Reconciliation - Results									
	18	Number of	data points	s used in	the reconcil	iation					
Name	Unit	Raw value	Smoothed	BIAS =	Standard	SSQ					
			value	Smoothed - raw	deviation						
FLOW1	Nm <sup>3</sup> /h	598.600	558.748	-39.852	59.860	0.4					
FLOW2	Nm <sup>3</sup> /h	329.500	308.806	-20.694	32.950	0.4					
FLOW3	Nm <sup>3</sup> /h	21466.000	20245.356	-1220.644	4293.200	0.1					
FLOW4	Nm <sup>3</sup> /h	28877.200	27214.724	-1662.476	2887.720	0.3					
BFW	kg/h	13761.400	11106.698	-2654.702	1376.140	3.7					
STEAM	kg/h	8060.300	10897.090	2836.790	806.030	12.4					
TEMP1	°C	1100.000	1027.189	-72.811	50.000	2.1					
TEMP2	°C	416.000	411.000	-5.000	5.000	1.0					
TEMP3	°C	412.700	410.223	-2.477	5.000	0.2					
TEMP4	°C	410.000	409.292	-0.708	5.000	0.0					
TEMP5	°C	424.300	430.681	6.381	5.000	1.6					
TEMP6	°C	386.100	390.000	3.900	5.000	0.6					
TEMP7	°C	383.100	386.891	3.791	5.000	0.6					
TEMP8	°C	272.800	272.562	-0.238	5.000	0.00					
TEMP9	°C	79.900	75.000	-4.900	5.000	1.0					
TEMP10	°C	208.000	209.518	1.518	5.000	0.1					
TEMP11	°C	221.700	223.330	1.630	5.000	0.1					
TEMP12	°C	230.300	231.083	0.783	5.000	0.0					
					Sum	24.7					

# $SSQ = \sum ((Reconciled_i - Measured_i)/\sigma_i)^2 \quad (1)$

where i represents each instrument considered in the reconciliation, and  $\sigma$  is the standard deviation for that instrument. The consistent data set that is the best representation of reality is the dataset for which the sum of squares is minimised.

Data reconciliation requires a model that explains the relationship between process variables. ClearView<sup>™</sup> uses the full process model that is used to design WSA units. Each plant is individually assessed to establish the parameter selection with the strongest links to provide a meaningful result. Fig. 3 shows an example of how the results of such a reconciliation look. The "raw values" are average instrument readings for a steady state period, and correspond to the "measured" values in Eq. 1. The mass and energy balance of the unit does not close with these values. The "smoothed values" on the other hand represent a closed mass an energy balance that is consistent with the model of the unit, denoted by "reconciled" in Eq. 1. The bigger the difference between a smoothed value and a measured value, the larger its contribution to the SSO error. The reconciliation revealed that there is a good agreement between measured and modelled parameters across the unit, except for the boiler feed water (BFW) and steam production. These are the most significant contributors to the SSQ.

tation should be checked, calibrated, or replaced. This allows operators to move towards a more consistent dataset on a continuous basis, to the point where insignificant adjustments are required to reconcile the data. The reinforced confidence that one then has in one's instrumentation means that one is able to confidently assess process performance, and optimise operation. Accurate readings also result in safer unit operation.

With this information a plant operator

is then given direction on which instrumen-

# **Going beyond DCS alarms**

It is a common question in operational environments when equipment doesn't behave as expected and a process value is abnormal – "what is the value normally?".

If one has rigorous models to simulate equipment, then one can compare the expected and the measured process parameters continuously. This is now possible with a reconciled dataset – a single error would have made modelling difficult. Ideally, discrepancies should be detected, before alarms on the DCS system are activated. However, this requires that a rigorous model is developed – this could be a hydraulic model to predict the pressure in a line, or a heat exchanger model to predict the outlet temperature of a heat exchanger. However, these are not always available. Also, a plant operator would not

ISSUE 386 SULPHUR JANUARY-FEBRUARY 2020 undertake to develop a rigorous model explaining every parameter in a unit. In these instances, a comparison of current and past behaviour for similar process conditions is valid and extremely useful.

To elaborate on the limitations of the DCS alarm system - there are many design margins added to the overall unit design, and then again to each individual piece of equipment. Take for example a gas treatment plant that is design to continuously comply to SO<sub>2</sub> emissions at a peak gas flow and a peak gas sulphur content. In defining these peak conditions, plant owners will be conservative and add margins to the design basis of the unit to ensure that there are no emissions compliance concerns during regular operation. An individual heat exchanger. such as a cooler between catalyst beds, will also have fouling factors and excess area margins in its design. The DCS alarm for high temperature out of this cooler will be selected based on the material properties of the cooler and reactor, as well as the correct operating temperature of the catalyst bed downstream of the cooler. During regular operation, away from the peak gas flow and sulphur concentration, the excess area is more than sufficient to meet the temperature set point out of the cooler. Even in the event that there may be heavy fouling in the cooler, the excess area masks this; indeed, this is the entire point of including the design margin. In this case, consider the extremely fouled state of the cooler necessary to trigger a DCS alarm on a piece of equipment with all this excess capacity. The DCS alarm does not serve as a pro-active tool for identifying problems as it requires a large deviation in equipment behaviour, especially when the unit is running away from design capacity.

An example of this is shown in Fig. 4, which depicts the SO<sub>2</sub> converter on a combined sulphur-burning/off gas-treating WSA unit running almost identical sulphuric acid production - about 90% of the design rate almost two years apart. The interbed cooler is unable to cool the gas out of the first bed to the set point of 420°C into the next catalyst bed. Already in the first instance (June 2016) one can see that the interbed cooler bypass valve is fully closed to allow maximum steam flow into the cooler to try reduce the temperature of the gas. unsuccessfully. Despite this problem, no DCS alarm is activated to indicate a problem with the cooler. The representation of the same DCS screen during a period of

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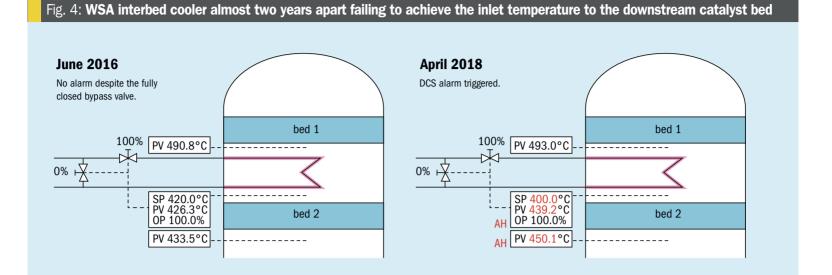
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similar production (April 2018), showed that the temperature into the second bed had climbed over time with deteriorating cooler performance (from 426°C to 439°C for very similar temperatures into the exchanger), and the DCS alarms for high temperatures in and out of the next catalyst bed had eventually activated. One can see that the operator had tried to reduce the set point to the downstream bed to 400°C, without any way of achieving this given the cooler had been operating with a fully-closed bypass for at least 22 months.

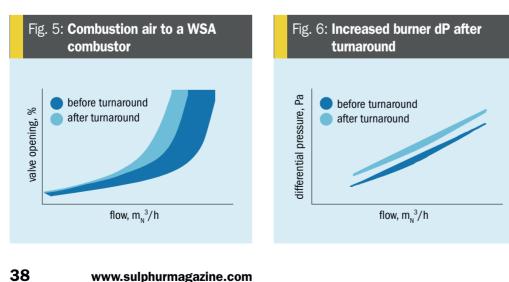
This situation resulted in higher SO<sub>2</sub> emissions (due to lower conversion in the second bed) and reduced energy efficiency of the unit in the form of lost steam production. The highly-valued steam production had to be made up by burning fuel in a steam generator to meet steam demands in the complex. The unit was also running at a higher downstream temperature, putting the plant at risk of equipment damage due to high temperatures. A plant pressure survey by Topsoe field engineers during operation revealed a high pressure drop around this cooler, an unusual area for hydraulic restriction, and an inspection and

cleaning of the interbed cooler was recommended. The pressure build-up over the cooler also meant a reduction in the volume of off gas that was treated in the unit; the hydraulic restriction had mistakenly been attributed to another piece of equipment with a faulty pressure measurement.

In the abovementioned example, the exchanger could have easily been simulated and problems detected before the valve opened fully in June 2016.

An example of a situation in which a rigorous model is less simple to develop, but a unit's own historical operation was used as a stand-in, is provided in Fig. 5. In this situation, another WSA unit was taken offline for a statutory inspection. The unit historically had a bottleneck in the amount of primary air that could be fed to its combustor, and the processing capacity was found to be even lower after the turnaround.

Apart from the valve opening to 100% sooner, and capacity being reduced, DCS alarms did not shed light on the cause of the post turnaround capacity reduction. The burner pressure drop (seen in Fig. 6) was not a parameter that was monitored very closely,



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and was not all that different, speaking in absolute value terms, to pre-turnaround values. Only a graphical comparison against its pre-turnaround behaviour revealed that activities during the turnaround had left a restriction in the burner.

The unit operated at reduced capacity for a month before this problem was detected and it was decided to shut it down again to resolve the problem and restore capacity.

Continuous performance assessment through ClearView<sup>™</sup> builds up a database of expected values where rigorous models are available, and historical parameters where they are not. These baseline values can then be compared for similar operational periods obtained from data reconciliation, and their behaviour over time is tracked, issuing a warning sooner than possible with DCS alarms, as evidenced by the two examples provided. Earlier detection means earlier action, and lower risk of unplanned downtime.

# Benefit to new unit operation

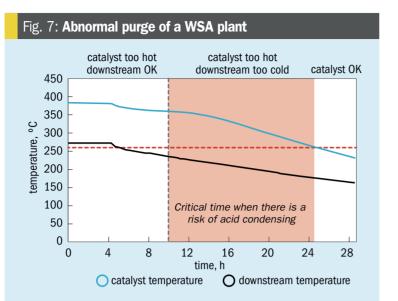
The commissioning of a unit represents a critical period where months, if not years, of planning, engineering, and construction activities come together to achieve the desired outcome of successful start-up of a unit. It seems obvious to say that this is an important period, however, the reasons are not as obvious as one may think. Apart from the successful execution of the project, this period is when:

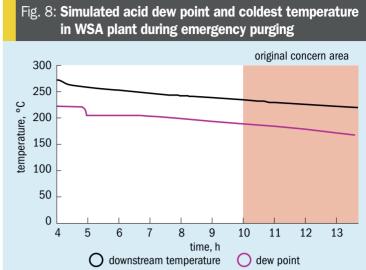
- the design basis and design assumptions of the unit can be verified;
- the detailed standard operating procedures and checklists are adapted to real-life conditions to enable operation of the unit:
- operating habits are formed;

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 a transition between the project execution team and the operational team takes place, often with the loss of knowledge that has been accumulated within the project execution team.

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The culmination of weeks of commissioning is typically the performance/guarantee test run, which takes place after the unit has had time to stabilise. This test run is intended to prove that the unit is able to perform at the desired capacity, produce the guaranteed product quality, and comply with guaranteed emissions. Thereafter there is acceptance of the unit by the plant owner/operator, and the responsibilities of the Engineering, Procurement, and Construction (EPC) contractor and technology licensor are for the most part complete.

In the event that there has been a shortfall in any of the points listed above, operational challenges may only develop after the unit has spent some time in operation (a reminder of the two years a plant spent with a cooler valve fully open, in the example given earlier). Should a unit experience a capacity bottleneck, unplanned downtime, or equipment failure, a plant owner needs to understand whether this was a once-off incident, whether the root-cause was outside of the owner's control, and whether there is a deficiency in design or operation. In troubleshooting such a situation, one typically only looks at the periods of time leading up to an incident, as looking all the way back to the plant's commissioning would involve processing too much data.

ClearView<sup>™</sup> WSA now enables Topsoe, to facilitate a smooth transition between commissioning and commercial operation. ClearView<sup>™</sup> WSA combines the technology-specific knowledge with experience gained from the ongoing support offered to Topsoe clients. It also means that the plant has a complete database of its operation that surpasses the DCS historian, as all reconciliation calculations are also stored, and projections made by calculations can then easily be verified.

ClearView<sup>™</sup> works on a fault-model system in which alerts are triggered in the event that abnormal or sub-optimal operation is detected. The alert is linked to an action panel that describes the deviation, shows trends relating to it, explains the effect that this deviation may have if it is allowed to continue or increase, and also suggests mitigating actions to be taken by operators. In this way, it also facilitates training and knowledge retention, guarding against problems such as high rates of staff turnover.

ClearView<sup>™</sup> presents all data, calculations, and predictions in easy-to-understand dashboards that are available from day one of a new unit's operation, meaning that monitoring tools do not have to be developed on a trial-and-error basis. This also means that, with all the analysis being done automatically, there is more time for customers to be engaged in constructive discussion with Topsoe, rather than spending time compiling data, and being caught up in email or telephonic back-and-forth, as is all too common.

# Using DynSOx<sup>™</sup> to complement ClearView<sup>™</sup>

For wet gas sulphuric acid plants, ensuring that there is no risk of condensation is a crucial part of avoiding unwanted equipment damage and downtime. As a consequence, operating conditions near

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the dewpoint of sulphuric acid is a key consideration during both the design and operation of these plants. Since the acid dewpoint is a result of several different parameters, intricate analysis and knowhow is necessary to determine whether new operating conditions are safe or not. During steady state, such analysis and tools have long been an important consideration for technical service team at Topsoe, and it is also included in the ClearView<sup>™</sup> solution. So far, transient conditions have been much harder to analyse. since it is not only the sulphur content in the feed that plays a role, but the conversion, absorption and desorption capabilities of the SO<sub>2</sub>-oxidation catalyst as well. Plants have of course been able to handle these operating conditions in the past as well, however, it has required the use of large safety margins to avoid potentially unsafe operation. With the addition of Dyn-SOx<sup>™</sup>, the black box that is dynamic conditions is now more transparent, offering the possibility to tailor procedures and operation to achieve both more optimised, and safer, operation.

To illustrate how DynSOx<sup>™</sup> can be used in combination with ClearView<sup>™</sup> to address the specific concern of acid condensation, we look at an example from a WSA plant where the unit tripped due to an upstream upset and was purged with hot air. Due to the desorption of SO<sub>3</sub> from the catalyst, sulphuric acid can form downstream of the catalyst beds hours after the process gas fed to the plant has been replaced with air. Combined with decreasing temperature during the purge, the presence of sulphuric acid is potentially problematic, and where this is not normally a concern, in this particular case there was a fear that

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the allowable operating window was being exceeded. Typically, a guideline is provided to keep a downstream temperature above a threshold value until the catalyst is cooled to 260°C. The potential concern period is illustrated with the plot in Fig. 7, where the critical period when the catalyst is still warm enough to desorb  $SO_3$ , while the downstream temperature of the plant is falling, is highlighted.

Previously there would have been no way of knowing if acid condensation was a risk without waiting to conduct a physical inspection during the next turnaround, but with DynSOx<sup>™</sup>, there is now a faster and much more informative way. The recorded outlet temperatures and simulated acid dewpoint are presented in Fig. 8.

The DynSOx<sup>™</sup> simulation, when compared to the lowest temperature in the plant, shows that the actual temperature was consistently well above the sulphuric acid dewpoint for the entire purge following the plant trip. It was therefore concluded that there was never a risk that sulphuric acid would condense on the equipment downstream of the  $\mathrm{SO}_{\mathrm{2}}$  converter during these conditions. Not only does these results give the plant operator the reassurance that the plant was controlled correctly during the incident, but the operator also knows that in future that the plant can be shut down in a similar fashion without a risk of corrosion

The validity of these results was confirmed at the next turnaround when Topsoe service engineers performed a plant inspection and no corrosion was found.

While DynSOx<sup>™</sup> is not fully integrated with ClearView<sup>™</sup> at this early stage of development, the combination of the two offers important synergies. On the one hand, technical service engineers at Topsoe can use trustworthy reconciled data from ClearView<sup>™</sup> as a basis for Dyn-SOx<sup>™</sup> studies of complex dynamic situations; on the other, results and knowledge from the DynSOx<sup>™</sup> studies can then be fed back to ClearView<sup>™</sup>, resulting in safer and more efficient operation and procedures.

# DynSOx<sup>™</sup> on its own

Although DynSOx<sup>m</sup> can be used very successfully together with ClearView<sup>m</sup>, it can also be used on its own to simulate dynamic conditions in both conventional dry gas sulphuric acid plants and WSA plants. To illustrate how DynSOx<sup>m</sup> can be applied on it is own, an industrial example of how it is used at one acid plant to help address start-up emissions is given.

A large-sized sulphur burning sulphuric acid plant was struggling with its emissions during start-up. The operator considered installing caesium catalyst to try to resolve the situation, but resources were limited, so a large investment in caesium catalyst had to be justified by some evidence of the effect of the catalyst change. To better understand the complex behaviour during start-up, data from one start-up was studied using DynSOx<sup>™</sup>.

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In addition to the current state, where no caesium promoted catalyst was being used, the effect of ignition layers with caesium promoted catalyst in bed 3, bed 4 or a combination of beds 3 and 4 was investigated.

From Fig. 9 it is clear that any ignition layer in either bed 3 or bed 4 would reduce the start-up emission peak significantly, by at least 35% compared to the current catalyst loading. The simulation results also indicate that for this particular plant and set of conditions, the effect of an ignition layer in beds 3 and 4 is similar, but with it being slightly more effective to use the caesium catalyst in bed 4. Finally, the study showed that the improvement of using ignition layers in both beds 3 and 4 was significant over just using a caesium ignition layer in one of the beds. The total emission reduction compared to the current situation would be 70%, while the improvement compared to only having an ignition layer in bed 4 would be 40%

For the operator in this example the improvement in start-up performance offered by a caesium ignition layer in bed 4 was sufficient. Furthermore, since the steady state conversion was acceptable, replacing only 1/3 of the bed was all that was needed. By applying DynSOx<sup>™</sup>, the operator could be confident that their start-up issue could be solved by using caesium catalyst. Not only could it be solved, but by using DynSOx<sup>™</sup> it could also be done while keeping catalyst replacement at a minimum.

# Conclusion

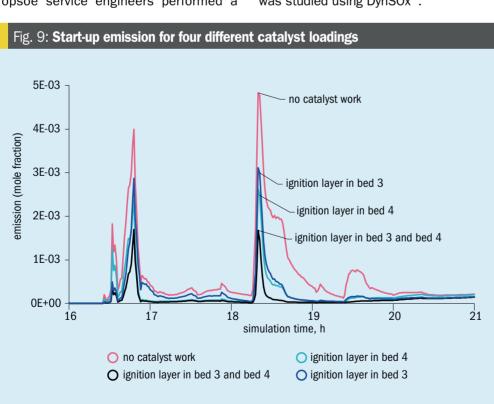
While the sheer amount of data available to an operator of a modern sulphuric acid plant can be daunting, the data, computational capabilities and tools offered by the latest digitalisation trends can also offer significant advantages. ClearView<sup>™</sup> and DynSOx<sup>™</sup> are two examples of the advantages that the latest technology can bring to acid plant operators.

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# **Comprimo Charts a New Path Forward in** Sulphur & Process Technology

As part of Advisian, the global advisory business line of Worley, Comprimo brings more than 65 years of proven experience and expertise in the development, application, and management of sulphur removal technology, with more than 1,200 sulphur recovery units worldwide.

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WorleyParsons and Jacobs Engineering's Energy, Chemicals and Resources division are now one company, operating as Worley. Advisian is the global advisory & technology business line of Worley. All of Jacobs Comprimo Sulfur Solutions and WorleyParsons Sulphur technology are part of Worley and operate under the brand name Comprimo.

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London



# Hydrocarbon removal from sour water systems

Hydrocarbon contamination of sour water streams feeding sour water strippers is a well-known challenge in the refining and gas processing industry. The source of this challenge is the formation of a stable oil emulsion in an aqueous phase that may contain both H<sub>2</sub>S and NH<sub>3</sub>. The typical approach to the problem involves large residence time tanks with the assumption that droplet settling will occur over a long enough time frame. In practice, droplet settling is very slow due to a variety of reasons, and as a result, operators encounter sour water heat exchanger fouling, stripper fouling, hydrocarbon excursions to sulphur recovery units along with other operating challenges. **M. Thundyil, D. Seeger** and **E. McIntosh** of Transcend Solutions present a case study of the TORSEP<sup>™</sup> oil and solids removal system for contamination removal from a sour water feed stream. The case study illustrates the effect on heat exchanger fouling along with the effect of the variation of several system parameters on operating performance and economics.

our water systems can be found in most refineries and gas plants throughout the world. The sour water is generated throughout the facility from many sources and is accumulated in large tanks for treatment in the sour water system. In the sour water system, light hydrocarbons, hydrogen sulphide (H<sub>2</sub>S) and ammonia (NH<sub>3</sub>) are stripped from the sour water and the stripped gas is often sent to the Claus unit reaction furnace for destruction and conversion to nitrogen and sulphur. Examples of sources of sour water from within the facility include<sup>1</sup>:

- hydrotreater or hydrodesulphurisation units where sulphur-containing hydrocarbons are reacted with hydrogen and H<sub>2</sub>S is formed and the temperature of the hot gas from the reactors are quenched with water to reduce the temperature;
- the reflux water from the regenerator in the amine unit can be a source of ammonia;
- steam is used throughout various processes in the refinery where it may contact NH<sub>3</sub> and H<sub>2</sub>S when condensed and recovered, the water may become sour and contain H<sub>2</sub>S and NH<sub>3</sub>;
- wash water used throughout the facility may contact NH<sub>3</sub> and H<sub>2</sub>S and become sour;

• water is recovered in the crude, fluidised catalytic cracker, and coker units, and is also likely sour water.

These and many other sources of sour water are all accumulated from throughout the facility and pumped into feed tanks to be treated in the sour water system. An examination of the various sources of sour water quickly indicates that this water is probably highly contaminated with salts, solid particulates and hydrocarbons. One attempt to handle the contaminants found in the sour water stream is to accumulate the water in large holding tanks in the hope that the solid particulates will settle to the bottom and the hydrocarbons will separate and float on top of the water where it can be skimmed<sup>2</sup>. The solid particles would be removed during turnaround when the tanks may be cleaned. The issue is that the approach does not work well, and solid particulates and hydrocarbon are not separated in the large holding tanks. Instead they are pumped into the sour water system which perpetuates the problems throughout that system and others connected to it. Solving the sour water system contamination problem at its root cause is what inspired the design of TORSEP™ contaminant removal from sour water systems.

# Background

A refiner on the US Gulf Coast was forced to clean the heat exchanger in the sour water system approximately every 3-6 months due to fouling. The operators at the facility had come to accept this problem as the normal routine course of operation. During a meeting where Transcend Solutions were reviewing operations and maintenance, it was discussed that operations did not have to accept heat exchanger cleaning every three months as a routine operation, but rather that the problem could be fixed. It was suspected that the problem was not only solid particulate fouling but also hydrocarbon fouling on the surfaces of the heat exchanger. To better define and understand the issues Transcend Solutions took in situ solids loading samples<sup>3</sup> and bottle samples at the sour water system. The results of that testing determined that both problems were occurring.

This refiner originally took the approach of holding the sour water in large tanks with a long residence time (1-2 days), however, even with that residence time, the solids did not settle, and the hydrocarbons did not fully separate from the sour water. As the unit was operated, the hydrocarbons and solids were pumped with the sour

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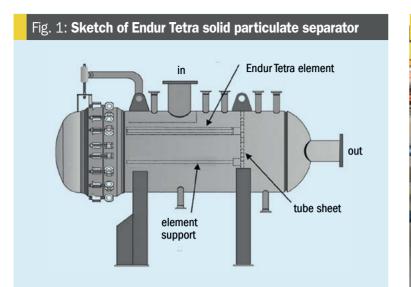
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water from the tanks to the feed/effluent heat exchanger and eventually the stripper column. The heat exchanger fouled with hydrocarbons and solid particulates sticking to the exchanger surface causing reduced heat transfer efficiency and created the need to be cleaned. To perform the cleaning, the system had to be shut down, drained, purged and cleaned followed by reassembly. The cleaning process typically takes about a week. The complete cleaning process caused the refiner to incur significant operating expense. As a result, the refinery staff were very interested in establishing a solution. It was suggested that they remove the solids and separate the hydrocarbon liquid phase from the water. With a simple, cost-effective contaminant removal system, provided on a rental basis, they could evaluate the approach to solving their exchanger fouling problem and, if successful, install a permanent system in the future.

# TORSEP contamination removal system

The system includes the Envision<sup>™</sup> emulsion separator for liquid/liquid coalescing where the oil phase is separated from the bulk sour water phase. Upstream of the emulsion separator is an Endur<sup>™</sup> Tetra<sup>™</sup> separator for removal of solid particulates. The first stage removes solid particulates and protects the downstream emulsion separator from rapid plugging. The two separators are described in more detail in the following sections.

# **Endur Tetra solid separator**

The operating cost of fluid quality management is highly dependent on the choice of element and the vessel size. The vessel

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needs to be large enough and contain enough filter elements so that there is a reasonable time between filter changeouts. However, the larger the vessel the higher the capital cost, therefore the capex of the vessel is weighed against the opex of filter changeout. For this opportunity Transcend Solutions had an available rental unit and the vessel size resulted in an expected changeout frequency of 1-2 weeks which was sufficient to keep opex low. For solid particulate control a suitable media configuration was applied to capture and retain the particulate contaminants in the inlet liquid flow, at a defined level of efficiency. The media is a locked pore configuration of cross-linked fibres that prevents particulate release under higher differential pressure conditions. A sketch of the solid separator vessel is shown in Fig. 1.

The liquid enters the vessel through the inlet nozzle on top, is diverted by the inlet baffle, and passes through the solid particulate filter elements outside-to-in. The particulate is retained by the media and the clean liquid passes through, into the riser, down the centre riser support, through the tubesheet and into the outlet chamber, exiting through the outlet nozzle to the right in the sketch.

Some of the features of the separator and the filter elements include:

- **Preferred flow configuration** The separator elements flow outside-to-in. This is the flow configuration that maximises dirt capture within a given vessel size, thereby allowing the lowest overall operating cost for a given capital expenditure.
- Optimised element configuration The element maximises contamination holding capacity while also maximising packing density within a housing.

Ergonomic – The elements are approximately 40" long and come with an ergonomic handle that allows easy removal and installation. A picture of installing the separator elements is shown in Fig. 2.

 Coreless element configuration – The Tetra element consists of a coreless design, making the element lighter and providing a less strenuous changeout process. The coreless design will also have reduced disposal volume.

# **Envision emulsion separator**

The separator is a single-stage, liquid emulsion separation system. The separator elements can capture and coalesce the small discontinuous phase droplets from a continuous phase that may be aqueous or hydrocarbon in nature. In this case the refiner needed to remove hydrocarbon from the sour water. A sketch of the emulsion separator vessel is shown in Fig. 3.

The liquid enters the vessel through the inlet nozzle located on the right in the sketch. The liquid travels through the tubesheet, down the riser and through the separator element inside-to-out. As the liquid passes through the media of the separator element, the small droplets of the hydrocarbon phase (discontinuous phase) are captured by the tight media where they are retained until they come into contact with additional hydrocarbon droplets and coalesce into larger droplets. Once the droplets coalesce and grow into large enough droplets, they force their way through the media as very large droplets that readily rise through the water phase and collect in the boot on the top of the vessel. The boot is shown at the top left of the sketch in Fig. 3. The hydrocarbon exits through

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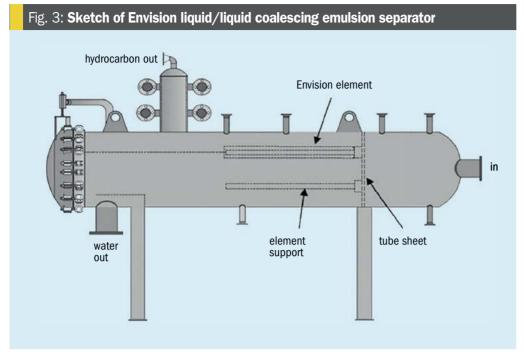
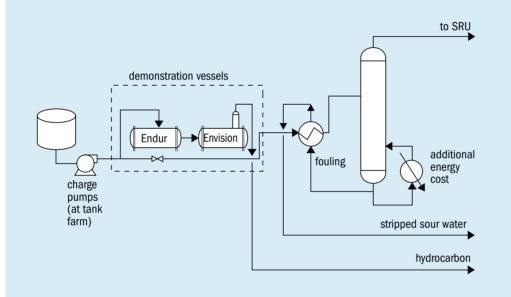
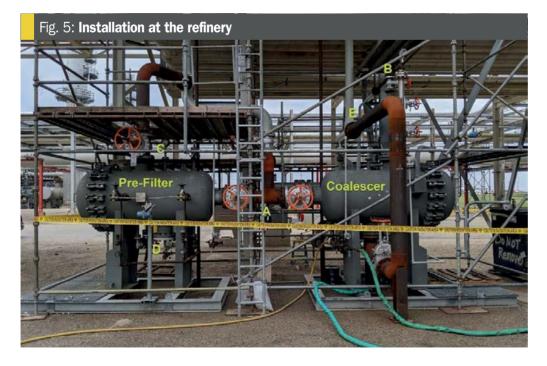


Fig. 4: Simplified PFD of the TORSEP installation







# Table 1: Design parameters

Parameter	Value
Fluid	sour water
Operating flow rate, gpm	440
	(600 max)
Operating temperature	75 – 105
°F (°C)	(24 – 41)
Operating pressure, psig	140
Design viscosity, cP	0.8
Bulk liquid, specific gravity	1.0

the nozzle at the top of the boot and the water exits from the nozzle at the bottom, shown on the bottom left in the sketch. A baffle over the outlet helps ensure the longest possible separation time for the hydrocarbon droplets to rise to the top of the vessel rather than be drawn out with the water flow. The residence time is typically of the order of seconds rather than minutes, and is dependent on the media velocity, and densities and viscosities of the two fluids.

The emulsion separator elements offer the following benefits:

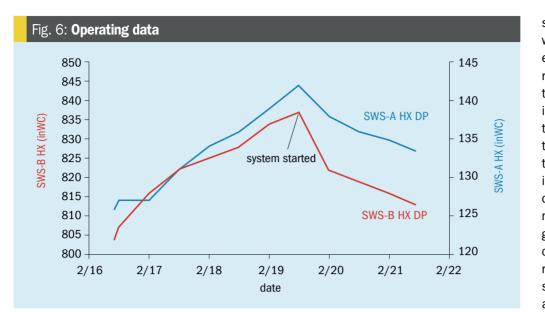
- Applicability The coalescing separator elements will meet a broad range of physical and chemical resistance requirements while allowing very high efficiency separation of aqueous/ hydrocarbon, or hydrocarbon/aqueous dispersions.
- Long online life Without particulate fouling, the elements are merely reclassifying liquid droplets, and will have an extraordinarily long online life.
- Ergonomic The liquid/liquid coalescing vessels are preferentially oriented horizontally, eliminating the need for expensive ladders and platforms, while making it easy for operators to replace elements.
- Lower capital cost Since the coalescer is a single-step process, with liquid disengagement occurring once large droplets are created, the pressure vessel size is reduced by an order of magnitude relative to conventional corrugated plate or other coalescing devices.

With matched particulate removal from solid separators upstream (prefilters), the emulsion separator elements generally will remain in service for six months to one year, possibly longer.

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# **Performance evaluation**

The parameters for the installation are summarised in Table 1. The system was installed on a rental basis to demonstrate the effectiveness to the customer. The system could handle a maximum of 600 gpm inlet flow, however the customer's sour water system only operated at 440 gpm.

A process flow diagram of the system is shown in Fig. 4.

The equipment configuration installed at the refinery is shown in Fig. 5. The system was started in February 2019 and has operated near continuously since that time. The only time the system has been bypassed is for cleaning and element changeout. As shown, the system was installed with one solid separator and one emulsion separator, therefore during change out of the elements in either vessel, both vessels were put into bypass. In an optimised installation it is advised to have two solid separators so that when changing out those filters, the emulsion separator does not have to be put into bypass. The performance evaluation criteria for the system were:

- impact on heat exchanger fouling;
- amount of hydrocarbon recovered;
- filter changeout frequency.

# Impact on heat exchanger fouling.

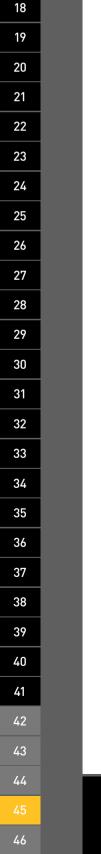
As discussed previously, the pressure drop (dP) across the heat exchanger in the sour water system continuously rises until the operators are forced to shut down and clean the exchanger. The data, provided by the refinery (Fig. 6), shows that the constant upward trend of the sour water exchangers dP stopped within minutes of bringing the system online. Following start-up, the upward trend stopped and even slightly reversed trend. The dP has remained nearly constant since the start-up and the refiner has not had to shut down to clean the heat exchanger.

The dP of the heat exchanger over time is shown in the graph on the left in Fig. 7. After the start-up of the solids and emulsion separation system, the operators were able to raise the flow rate through the exchanger because the dP was no longer rising. When the flow rate is increased the heat exchanger dP will rise due to the increased flow. In addition, there are fluctuations in the flow rate during routine operation. Since differential pressure is related to flow, and the flow through the unit has increased and fluctuated, the true trend in differential pressure is much clearer when normalised for flow, which is shown by the graph on the right in Fig. 7. The graph of the dP normalised negates the effect of the flow rate increase and shows that the dP consistently dropped over the entire time period and eventually leveled out. The system has not experienced heat exchanger fouling or DP increase since the start of the TORSEP solid and emulsion separator operation.

# Hydrocarbon recovery

Hydrocarbon recovery can be determined by plotting a graph of the level of the liquid/liquid interface in the boot, and the valve-percent-open of the boot level control valve (the "dump" valve). These graphs are shown in Fig. 8, with the boot interface level as a line and the valve percent open as a column graph.

In operation, the oil level in the boot builds until it reaches 80%, at which point the valve opens and oil is drained from the top of the boot. The frequency of oil dumping is not consistent. An "upset" condition can be seen around 3/25-3/27 when the valve is fully open and oil level drops below the 80% mark. The refiner has not shared an explanation of that upset. Typical process upsets in sour water systems have been previously noted to be related to level control failures, turnarounds, power failures, and weather among others.



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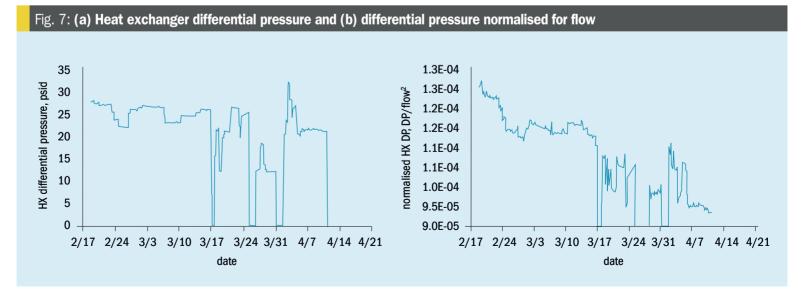
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# Filter changeout frequency

The solid separator elements were changed out every ten days on average since February. The coalescing separator elements were changed out once since start-up. The changeout frequency met the expected target and the customer is satisfied.

# **Recovered hydrocarbon**

A picture of some of the recovered hydrocarbon is shown in Fig. 9. Its boiling range was determined by simulated distillation, illustrated in Fig. 9. The boiling range extends from 80-700°F (27-371°C). The specific gravity was measured at 0.8.

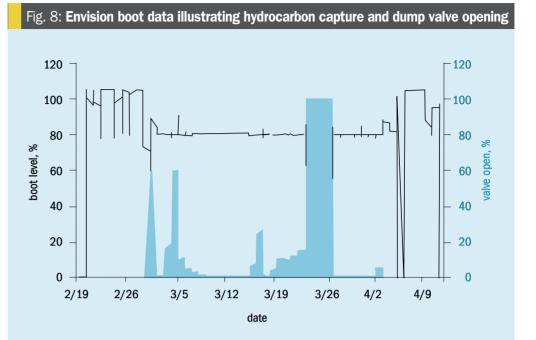
# Summary

In summary, a picture is worth a thousand words. Samples taken from the inlet and outlet of the system are shown in Fig. 10. The picture on the left is a sample of the inlet which has hydrocarbons and solid particulates and the picture on the right is taken from the water outlet and shows only a clear water phase.

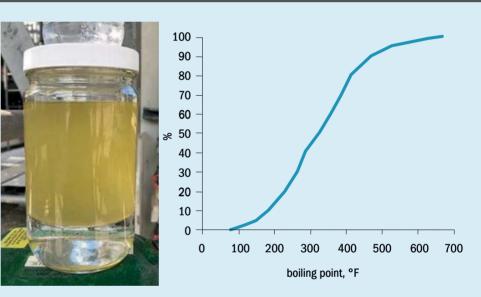
The performance evaluation successfully demonstrated that heat exchanger fouling was mitigated immediately upon start-up of the hydrocarbon and solids removal system. Hydrocarbon recovery was demonstrated, and filter changeout frequency was validated as reasonable and acceptable by the customer, i.e., the solid particulate filters did not have to be changed out more often than expected. The TORSEP system was a success to such an extent that the refiner is purchasing the rental system. In conclusion, this paper illustrates a technique that can allow sour water stripper units to effectively remove solid and hydrocarbon contamination, and thereby allow the stripper columns to operate as designed, without exchanger fouling and likely without hydrocarbon excursions to the sulphur recovery unit.

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# Fig. 9: (Left) Recovered hydrocarbon; and (Right) roiling range



# Fig. 10: (Left) Inlet to system; and (Right) water outlet from system



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# Improve asset integrity by predicting corrosion

Using case studies of a refinery amine unit and a sour water stripper (SWS), **U. M. Sridhar** of Three Ten Initiative Technologies LLP, **N. A. Hatcher** and **R. H. Weiland** of Optimized Gas Treating Inc. demonstrate the capabilities of a mechanistic, chemistry-based, truly predictive model for calculating corrosion rates for various amines and for sour water. At a time when asset integrity is much sought after, the utility of this fully predictive model is to prevent failures before they occur, rationally select materials of construction, enhance plant safety, and mitigate risk.

orrosion is a major concern in gas treating and refinery sour water systems, caused mainly by the acid gases  $CO_2$  and  $H_2S$ . One of the major factors influencing corrosion rates is the chemical activity of the dissolved acid gases themselves and the ions they form when they dissolve into the solvent. Activities depend on temperature, the amine type, its concentration, and acid gas loadings. Flow velocity, pipe roughness, heat stable salts, metallurgy, and suspended solids also affect corrosion rates.

This article highlights a mechanistic, chemistry-based, truly predictive model built using both proprietary and public corrosion rate data that can be reliably interpolated and extrapolated within and outside the measured ranges of the data. The model uses detailed speciation of dissolved acid gases, sheer stress at the pipe wall, metallurgy, and temperature to calculate corrosion rates for various amines (primary, secondary, tertiary) and for sour water over a range of temperatures, flow velocities, and loadings.

# Acid gases and corrosion

The basic corrosion reactions of iron with  $H_2S$  and  $CO_2$  dissolved in water are:

# H<sub>2</sub>S:

$H_2S$ (aq) + Fe (s) $\rightarrow$ FeS (s) + $H_2$ (g)	(1)
$2\text{HS}^{\cdot}(\text{aq}) + \text{Fe}(\text{s}) \rightarrow \text{FeS}(\text{s}) + \text{H}_2(\text{g}) + \text{S}^{2 \cdot}(\text{aq})$	(2)

# CO<sub>2</sub>:

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Bisulphide ion (HS<sup>-</sup>), free physically-dissolved  $H_2S$ , bicarbonate ion (HCO<sub>3</sub>), and free physically-dissolved CO<sub>2</sub> are protonic acids. They are oxidising agents because during the oxidation of iron, they can either give up or produce a hydrogen ion. However, the final ionic reaction products, sulphide (S<sup>2-</sup>) and carbonate (CO $_3^{2-}$ ) cannot produce the hydrogen ion necessary for oxidation. At the modest temperatures in most solvent treating and sour water systems, molecular H<sub>2</sub>S and CO<sub>2</sub> react with iron at appreciable rates only in the presence of water. "Speciation" refers to the equilibrium ionic and molecular species concentrations found by solving the chemical reaction equilibrium equations, atom balances, and a charge balance. Speciation of the solution is necessary in order to make sense of corrosion rates. However, the corrosion products themselves (i.e., solids) do not alter the speciation.

The concentration of free molecular  $H_2S$  and  $CO_2$  are pH dependent. In turn, pH is a function of total dissolved acid gases, amine type and strength, and temperature.

In general, free  $H_2S$  and  $CO_2$  oxidise iron faster than bisulphide and bicarbonate ions; however, their concentrations are usually very much lower.

Oxidation occurs in four steps (see Cummings et  $al^1$ ):

- transportation of dissolved free acid gases and their ions (collectively acid gases) from the bulk solution to the metal surface;
- adsorption of the acid gases onto the metal surface;
- reaction of the acid gases with the metal;
- transportation of the reaction products back into the bulk solution.

Corrosion is ongoing because the reaction products FeS and FeCO<sub>3</sub> are always removed as solids, which drives the corrosion reactions forward. The results can be extreme (Fig. 1). The amount of unreacted iron and the concentrations of the reacting species (H<sub>2</sub>S, CO<sub>2</sub>, bisulphide and bicarbonate) are limiting reagents for the corrosion reaction. Metallic iron itself can be a limiting reagent because FeS and FeCO<sub>3</sub> deposited on the surface of the metal can shield it from contact with the oxidising agents. In practice, solution loading is generally limited to 0.4-0.5 mole per mole of amine in mild steel metallurgies because higher values cause more extreme corrosion rates.

In a newly built amine unit or one that has undergone a turnaround and been completely cleaned, initial corrosion rates will be very high because all metal surfaces are fully exposed to the corrosive solution. Over time corrosion levels off,

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then starts to drop as an iron sulphide layer occludes more and more of the surface, preventing contact between iron and the corrosive components. Once the iron sulphide layer is completely formed, the corrosion settles down to a nominal, hopefully manageable, rate, determined by the rate at which FeS is removed from the surfaces chemically and via scouring by suspended particulates. The solution changes colour through the different stages of corrosion from pale amber, through light and dark green, to nearly black. This is different from corrosion by CO<sub>2</sub> because CO<sub>2</sub> forms a more fragile iron carbonate layer that does not adhere well to the metal surface and is more easily sloughed off.

Fluid velocity also affects corrosion rates by creating shear stress that tears away the sulphide or carbonate layers, exposing fresh iron surface to further corrosion. In practice, the rich amine velocity is limited to below 3-5 ft/s and lean amine velocity to below about 7 ft/s.

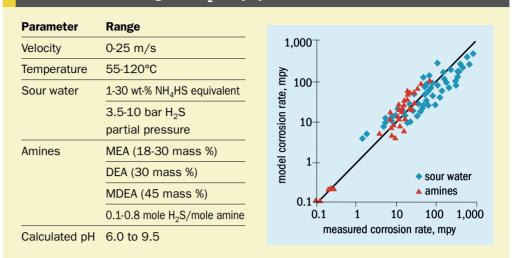
# **Basis for a predictive corrosion** model

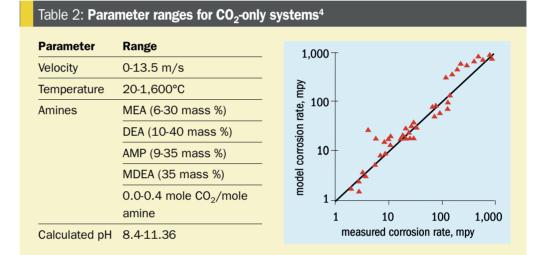
Fundamental or first-principles models are based on physical and chemical principles and obey nature's laws of chemistry, physics, and thermodynamics. While harder to develop than empirical models, they are rooted in science and so tend to apply over much broader ranges. Fundamental models are also much more predictive.

This phenomenological approach has been used to create a best-in-class predictive corrosion model. Experimental corrosion rate data collected in a Joint Industry Program (JIP) were studied to quantify dependence on a variety of parameters, then integrated into a comprehensive corrosion module and married with the abilities of the ProTreat® simulator, itself a fundamental process simulation tool. The result is a corrosion module that allows corrosion coupons to be placed at multiple locations within an acid gas removal (AGR) or sour water stripping (SWS) simulation to predict the effects of operational and design decisions on corrosion virtually anywhere in a unit. Linking empirical data to a fundamental model and embedding it into the ProTreat® gas treating and SulphurPro<sup>®</sup> sulphur recovery simulators gives the industry a powerful new tool that is reliable and extremely easy to use.

The corrosion rate model has been implemented within ProTreat via a Vir-

# Table 1: Parameter ranges for H<sub>2</sub>S-only systems<sup>4</sup>





tual Corrosion Coupon, which can be inserted anywhere in a ProTreat simulation flowsheet. Recognising the four-step oxidation process, model parameters were regressed to a large amount of H<sub>2</sub>S and CO<sub>2</sub> corrosion data collected in JIPs for both rich amine and sour water systems in a variety of metallurgies. Corrosion rate is a function of the activities (ai) of free molecular  $H_2S$  and  $CO_2$ , bicarbonate and bisulphide ions, temperature (T), and fluid velocity (v).

#### Corrosion Rate

 $= f (a_{H2S}, a_{HS}, a_{CO2}, a_{HCO3}, v, T)$ 

Tables 1 and 2 show the data ranges used for H<sub>2</sub>S- and CO<sub>2</sub>-only systems, respectively, together with parity plots showing predicted vs. measured corrosion rates over nearly four orders of magnitude. (Note: mpy means mils per year and 1 mil = 0.001 inch.)

Component activities rather than concentrations produced a better fit to the data. Note that although the amine type, strength

and concentration are parameters that do not directly affect corrosion rates<sup>3</sup> (hence, they do not appear explicitly in the correlations) they certainly affect the activity of the acid gas species. In that sense, their effect is indirect. The model calculates corrosion for a straight pipe as well as for a variety of fittings and, being mechanistic, it can be reliably extrapolated to conditions outside measured ranges. The model is within a factor of two or so of the measured data. This may seem like a wide uncertainty: however. practitioners will recognise just how difficult it is to achieve great reproducibility of corrosion rate measurements, especially in commercial settings.

# Case Study 1:

Treating refinery fuel gas in an amine unit The case centres on an amine-based refinery fuel gas treater in India. The refiner wanted to reduce energy consumption and increase unit capacity by replacing DEA with MDEA. With the recent changes

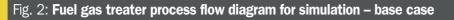
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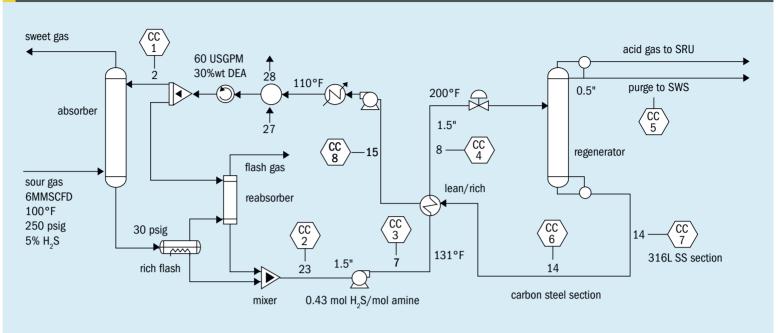
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to BS-VI standards mandating significantly lower sulphur specifications in fuels, there was a keen desire to avoid higher H<sub>2</sub>S slip under increased sulphur load contributing to total sulphur emissions. The hope was that MDEA would achieve better H<sub>2</sub>S selectivity at lower circulation. However, there was concern that corrosion might increase so the question was whether some carbon steel piping might need to be replaced with stainless-steel or other exotic metallurgy. The case study was built in ProTreat®.

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Fig. 2 is a flow diagram of the refinery fuel gas treating system. Corrosion coupons are shown by the hexagonal symbols labeled CC attached to various streams. Fig. 3 shows typical corrosion coupon information that is fed into the flowsheet (left-hand side) and the corrosion rate information (right-hand side) generated as part of the general process flowsheet simulation.

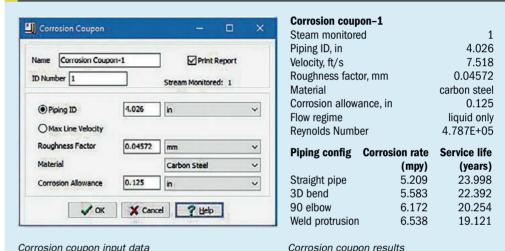
Eight corrosion coupons were inserted in various pipe sections. Three cases were considered:

- 30 mass % DEA and 60 gal/min circula-• tion (base case)
- Case (a) switched to 45 mass % MDEA
- Case (b) with 45 mass % MDEA and 45 gal/min circulation (reboiler duty scaled to the same duty per volume of solvent as base case)

Fig. 4 compares predicted corrosion rates in various parts of the plant for the (a) 30% DEA, (b) 30% MDEA and (c) 45% MDEA cases. Note that the reboiler duty in Cases (b) and (c) was scaled to the same heat load per unit volume of solvent as Case (a),

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#### Fig. 3: Typical input data and results for corrosion coupon



Corrosion coupon input data

and the circulation rate of 45 US gal/min for Case (c) was designed to produce the same treated gas composition as in Case (a). The high corrosion rates experienced by Coupon 4 show the greatest sensitivity to amine type, strength, and circulation rate. Coupon 4 is in the hot rich amine line entering the regenerator. Increasing corrosion rates for Coupon 4 result from increasing concentrations of both H<sub>2</sub>S and HS- ion, directly caused by different amine alkalinities and strengths. Corrosion rate does not directly track with pH or solvent loading for this case study.

Based on this case study, upgrading the entire metallurgy to stainless steel was obviously unnecessary. However, the corrosion rate of the hot rich line with MDEA at 45 mass % is quite a bit higher

than the base case. When the circulation of MDEA at higher strength is reduced, corrosion increases even further to the point where the service life of the piping in that area is only about four years with a corrosion allowance of 1/8th inch. Thus, a more exotic metallurgy was recommended. The piping for the hot rich and hot lean flows are always areas of concern, and the industry has migrated towards the use of austenitic stainless steel in these locations. The model supports these observations.

The corrosion coupon model can be used on sour water stripper systems as well. Similar observations have been drawn from various design and operating sour water stripper scenarios. Pertinently, the ammonia content in sour water stripper systems

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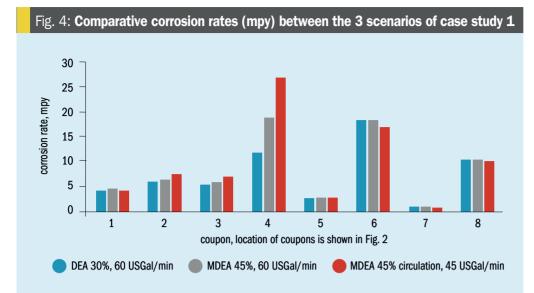
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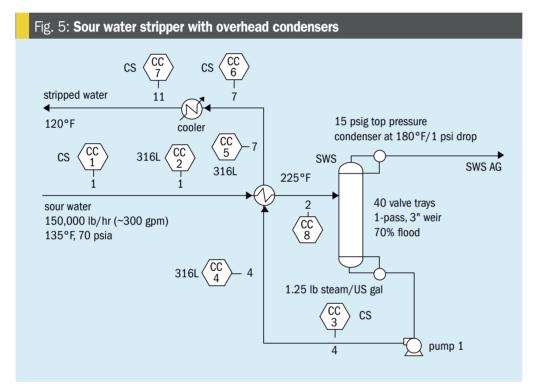
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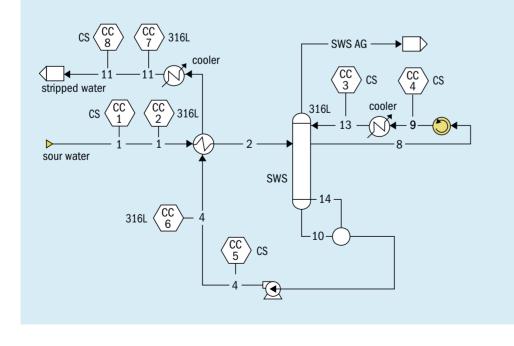
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# Fig. 6: Sour water stripper with pumparound condenser



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does not influence the corrosion. However, the ammonia content affects the speciation which in turn affects the corrosion.

# Case study 2:

#### SWS corrosion

Two cases were considered: a conventional overhead condenser system (Fig. 5), and a pumparound condenser configuration (Fig. 6). It is not uncommon to hear in the industry that pumparound type systems are less corrosive, so this type of system was of interest to contrast and challenge the statement. For this case study, the feed sour water contained 4 wt-% equivalent  $NH_4HS$ . Table 3 summarises predicted corrosion rates.

The hot sour water (Stream 2) shows a high corrosion rate as one might expect. The high temperature combined with the fact that the tower feed is partially vaporised leading to quite high velocity of a stream in slug flow will no doubt cause the corrosion rate in this line to be even higher than predicted by the model. Therefore, stainless steel (304 or 316) metallurgy would normally be recommended in this service.

Perhaps the greatest surprise is the corrosiveness of the hot stripped water. A service life of just over three years is unacceptable. The stripped water is predicted to contain 26 ppmw ammonia with 0.33 ppmw  $H_2S$  and 0.1 ppmw  $CO_2$ . There is not enough  $H_2S$  to passivate the carbon steel pipe, but there is enough for unimpeded corrosion of the metal surface. At a flow velocity of 7.5 ft/s in the pipe, the very high temperature (260°F) almost guarantees maximum corrosion rate.

In the pumparound condenser configuration, the pumparound flow itself contains 7.3 wt-% ammonia with 4 wt-%  $H_2S$  and 0.7 wt-% CO<sub>2</sub>. This is enough  $H_2S$  to provide good passivation; however, high temperature causes a rather low service life of only ten years, suggesting higher metallurgy would be advantageous.

# Conclusions

Neither amine type, nor amine strength, nor ammonia content have a direct effect on corrosion rate but they do have an indirect effect because of their role in the speciation of the acid gases that cause corrosion. This mechanistic, chemistrybased model built using both proprietary JIP and public corrosion rate data predicts corrosion rates. It has the added

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# Table 3: Corrosion rate summary

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	SWS with overhead condenser					SWS with pumparound condenser						
Stream description	Stream No.	Coupon	Metal	Temp, °F	Corrosion rate, m/a	Service life, yrs	Stream No.	Coupon	Metal	Temp, °F	Corrosion rate, m/a	Service life, yrs
Sour water	1	1	CS	135	5	24	1	1	CS	135	5	24
Sour water	1	2	316L	135	0.2	660	1	2	316L	135	0.2	660
Cold pumparound	-	-	-	-	-	-	13	3	CS	110	3.2	40
Hot pumparound	-	-	-	-	-	-	9	4	CS	205	10	12
Hot stripped water	4	3	CS	260	34	3.6	4	5	CS	260	34	3.6
Hot stripped water	4	4	316L	260	1.2	100	4	6	316L	260	1.2	100
Warm stripped water	7	5	316L	156	0.4	300	-	-	-	-	-	-
Warm stripped water	7	6	CS	156	10	12	-	-	-	-	-	-
Cold stripped water	-	-	-	-	-	-	11	7	316L	120	0.2	660
Cold stripped water	11	7	CS	120	5	24	11	8	CS	120	5	24
Hot sour water*	2	8	CS	225	22	5.6	2	9	CS	225	22	5.6

\*Stream is in slug flow so corrosion rate is likely much higher

advantage of being useable directly within a process flowsheet simulation. And the model's scientific foundation permits it to be extrapolated outside the known data ranges. Corrosion can now be assessed reliably and conveniently as an integral part of every simulation.

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# **Refinery green fuel integration with a sulphur complex**

**M. van Son** and **S. Sreejit** of Comprimo present a case study involving the design and potential integration of the sour water and acid gas treatment units for a renewable diesel facility with an existing refinery sulphur complex. The case study evaluates the potential for operating cost reduction by integrating an enrichment loop in the acid gas treatment plant as well as for using the existing infrastructure of the refinery to limit emissions.

he renewable diesel market has been growing and is driven by fluctuating oil prices, the mandates of governmental agencies to use renewable fuels and greenhouse gas reduction initiatives. In recent years, the integration of renewable diesel facilities with the existing infrastructure in refineries has proven lucrative and there are a number of projects in various phases of operation, engineering or construction. One common renewable diesel production process is via the hydrotreating of vegetable oils and/or grease, which produces a diesel product that can be blended with conventional diesel products from crude oils. In order to achieve this, the hydrotreaters are operated with sulphided catalysts which limit the formation of Fatty Acid Methyl Ester (FAME), which can lead to problems with corrosion, blending with other diesel pools as well as stability and decomposition issues. As a result, many car manufacturers have limited the amount of FAME that can be present in the diesel used in automobiles

In order to overcome the issues associated with FAME produced in transesterification technologies, new options have been developed to work with sulphided hydrotreating catalysts, which have proven to be able to produce higher quality diesel product that can be blended directly with the refining diesel pool. As typical green fuel feed stocks, such as rapeseed oil, soybean oil, vegetable oils or tallow contain very low concentrations of sulphur, it is essential to keep the hydrotreating catalyst sulphided and activated by supplying the unit with a sulphiding agent. This results in the formation of  $H_2S$  as a product from the hydrotreating unit. In the scenario of the case study in this article, the original basis consisted of using DMDS as the sulphiding agent. However, upon further review, the potential to recycle the produced  $H_2S$  was further considered as a means to reduce the DMDS consumption.

# **Project background**

A green diesel facility is currently in design for a refinery in North America. The existing refinery has a sulphur complex that is used to process the sour water and rich amine streams that are produced in the refinery due to the processing of sour crudes which contain varying levels of nitrogen and sulphur. With the current typical limitations for the refinery products such as gasoline, jet fuel and diesel and the expected future limitations for bunker fuel after IMO 2020. these units typically are operated close to capacity with the final product being a waste water stream from the sour water stripper and elemental sulphur from the sulphur recovery unit. The scheme will typically include some kind of tail gas technology for the sulphur recovery unit to limit the SO<sub>2</sub> emissions from the stack.

During the initial phase of the project, the technology licensor had proposed a conventional sulphiding route for the sulphiding of the hydrotreating catalyst but offered an option to consider the installation of an acid gas enrichment scheme to be able to recycle produced  $H_2S$  back to the hydrotreater. By employing this scheme, the consumption of sulphiding agent could be reduced substantially with a very short payout time of the additional investment cost associated with the enrichment of the acid gas and acid gas compressor.

A standalone sour water system was proposed as well, which handled the sour water from the hydrotreater. The sour water acid gas, which contained both ammonia and  $H_2S$  was proposed to be processed in the new thermal oxidiser with a caustic scrubber installed downstream to meet the environmental regulatory requirements.

# **Initial design**

The initial basis for the project was to have a fully standalone installation for the green fuel facility, consisting of an acid gas enrichment scheme followed by an acid gas compressor with a sour water stripper to process the sour water. The proposed scheme had no interconnection with the existing sulphur complex. This appeared to simplify the design on paper, as there was no need for long piping crossing the boundaries of the facility as well as no requirement to evaluate the ability of the existing units to process the additional streams produced by the green fuel facility. In this scheme, a thermal oxidiser had to

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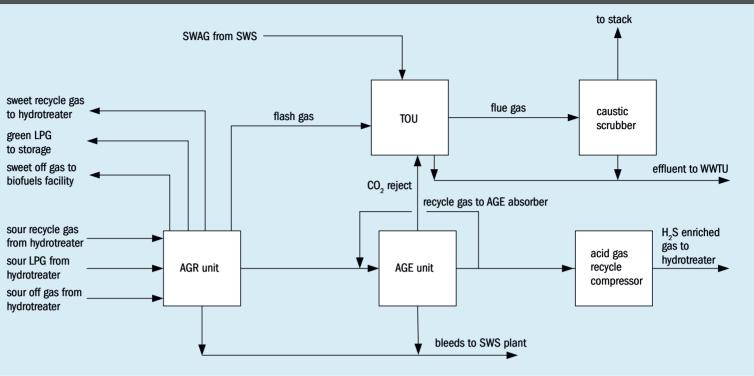
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be installed to process the flash gas from the acid gas removal (AGR) unit,  $CO_2$  gas from the enrichment unit as well as the sour water acid gas (SWAG) from the sour water stripper, where the H<sub>2</sub>S from these streams was converted to SO<sub>2</sub>.

Due to the concentration of  $H_2S$  in the  $CO_2$  reject stream from the enrichment unit as well as in the sour water stripper acid gas, a caustic scrubber was considered for the flue gas from the thermal oxidiser to meet the environmental regulations.

Fig. 1 shows the original proposed lineup for acid gas treatment in the green fuel facility.

In order to recycle the acid gas into the hydrogen recycle loop of the hydrotreater, the acid gas, which was to be enriched to 60%  $H_2$ S, will need to be compressed from about 12 psig (85 kPag) to 1100 psig (7590 kPag). Due to the very small volume of acid gas for this facility, a diaphragm compressor was selected.

Stripped water and spent caustic were intended to be routed to the existing waste water treatment facility associated with the site where the green fuel facility was to be installed, which was not directly connected to the refinery and sulphur complex.

# **Project hazard analysis**

During the preliminary hazard analysis (PHA), the hazards of loss of containment on the high-pressure side of the compressor with a release of an acid gas stream

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containing 60%  $H_2S$  was highlighted as a very high risk with a potential for a Level 6 event. As a result, the decision was made by the project team to re-assess the options for the project to limit the potential exposure to  $H_2S$  as a result of the installation of an enrichment scheme with an acid gas compressor. This evaluation included the use of Process Hazard Analysis Software Tool (PHAST) software to determine the potential impact of a loss of containment associated with the acid gas enrichment unit as well as the installation of an acid gas compressor.

# **Configuration study**

To determine the potential alternatives for the base case configuration, an evaluation of the options for handling the  $H_2S$  produced by the green fuel facility was done. This included options to handle the sour water produced by the green fuel facility, as the base case considered the installation of an incinerator followed by a caustic scrubber to limit the environmental impact due to the presence of  $H_2S$  and ammonia in the sour water stripper off gas.

Alternative configurations were evaluated based on the following considerations:

 Options with sour gas streams crossing over roads on public land were deemed unacceptable from past projects. Therefore, options with acid gas lines between the green fuel facility and the existing sul-

phur complex were eliminated

- The option to use the existing amine system of the existing refinery sulphur complex was eliminated due to issues with  $NH_3$  and  $CO_2$  forming salts in the lean amine, with potential for impacting the sweet gas specifications in the other absorbers. As well the existing amine regeneration system was already limited in capacity.
- The SWS location was deemed to be a cost optimisation potential and not technically limiting the evaluation of the risks associated with the acid gas recycle compressor and the alternative options for handling the sour gas streams.

# Acid gas treatment

The purpose of the acid gas treatment (AGT) plant was to sweeten the recycle gas from the green fuel facility as well as the LPG and fuel gas streams produced in the associated gas plant. In the base case design, this was done by installing three absorbers in an acid gas recovery (AGR) system which used a primary amine selected to meet the required specifications for the recycle hydrogen, LPG and fuel gas. The acid gas produced in the regenerator of the AGR, which contained about 3.5%  $H_2S$ , was then sent to an acid gas enrichment (AGE) unit, where with a proprietary amine, the acid gas was enriched to a concentration of 60% H<sub>2</sub>S.

This enrichment level minimised the recycle of  $\mathrm{CO}_2$  to the hydrotreater reactors and

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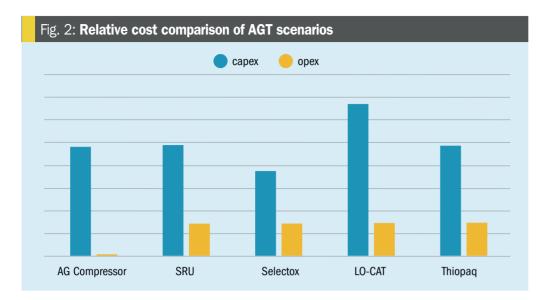
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minimised the impact of recycling acid gas to the hydrotreater. As indicated above, the installation of a high-pressure acid gas line was deemed to have an elevated risk and other design schemes were considered.

# **Evaluation of SRU options**

The alternative options to be considered were narrowed down to the following:

- Installation of an AGR/AGE option followed by a sulphur recovery unit:
- For this project a two-stage Claus unit with co-firing and split flow was considered to treat the sour water acid gas from the sour water stripper and the acid gas from the AGT unit. AGE is required to concentrate the feed to acceptable levels of H<sub>2</sub>S concentration for the Claus unit.
- Installation of an AGE unit followed by a low sulphur removal technology:
  - Selectox is a catalytic process which is similar to a conventional sulphur recovery unit, however does not have thermal stage due to the low  $H_2S$  concentrations in the acid gas. The Selectox reactor, which contains an oxidation catalyst is followed by two conventional Claus stages. This process can operate with low concentration acid gases as no combustion has to be maintained in a thermal reactor.
  - LO-CAT employs a liquid reductionoxidation (redox) process that converts H<sub>2</sub>S to solid elemental sulphur, utilising an aqueous solution with proprietary blend of chemicals. Sulphur is recovered in a cake form with 60% solids content that can be disposed of in landfills. LO-CAT technology has the ability to process lean acid gas streams and

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has several installations worldwide in similar applications.

○ Thiopaq is a biological process for removal of  $H_2S$  and is well suited to low tonnage low concentration acid gas streams. Sulphur is recovered in a cake form with 60% solids content that can be used in fertilizers or disposed of in landfills.

# **Comparison of the AGT options**

The four options that were selected for further evaluation in comparison with the base case, were evaluated for the following parameters:

- operability;
- maintainability;
- reliability;
- capex;
- opex;
- process safety;
- $SO_2$  emissions;
- plot plan requirements;
- requirements for buildings;
- references for installation and consideration of technical feasibility.

In addition, the impact on the overall configuration of the AGT selection with respect to being able to meet environmental requirements needed to be considered together with the base case scenario where the sour water stripper unit was also installed in the green fuel area. With the installation of the sour water stripper, a small sour water acid gas stream containing  $NH_3$ ,  $CO_2$  and  $H_2S$  needed to be processed as well.

The economics of the base case configuration and the four alternatives were evaluated to determine both the capex and opex for each scenario. The relative cost comparison for the five options are provided in Fig. 2. As in the four alternative scenarios, the bulk of the operating cost was resulting from the DMDS supply that needed to replace the acid gas recycle, there was a very large premium in operating cost in the base case.

# **Selection of alternative AGT option**

The installation of a sulphur recovery unit requires acid gas enrichment and therefore still has the risk associated with the high concentration acid gas stream. This process can handle SWAG, however due to the low sulphur recovery associated with a two-stage Claus unit will still require a caustic scrubber in the facility to meet the environmental requirements. It is also not efficient for low sulphur tonnages, particularly from a heat loss perspective.

The Selectox process will not require acid gas enrichment. This process cannot handle SWAG and therefore, this option would require a thermal oxidiser unit able to process ammonia from the sour water acid gas stream as well as a caustic scrubber. Similar to the Claus process, it is not preferred for its low efficiency for low sulphur tonnages.

The Thiopaq process does not require acid gas enrichment. This process cannot handle SWAG and therefore, this option would require a thermal oxidiser unit able to process ammonia from the sour water acid gas stream as well as a caustic scrubber. However, it is not as well established compared to the other processes and has very few installed units in similar applications.

The LO-CAT process was developed to treat low tonnage low concentration acid gases and has approximately 200 units worldwide. The process does not require the installation of acid gas enrichment and it has the capability to treat SWAG, even though the  $NH_3$  will be present in the treated gas and will have to be routed to the thermal oxidiser unit. A caustic scrubber however may not be needed.

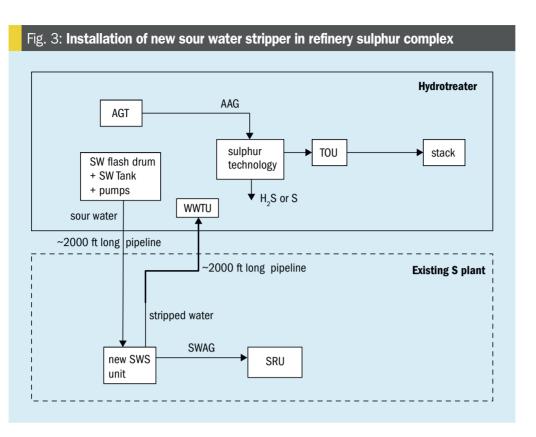
Based on evaluation and comparison of the four AGT configurations, the LO-CAT process, which is also the established industry leader for low sulphur tonnage processing with low concentration  $H_2S$ feeds, was recommended as an alternative, if the acid gas recycle compressor option was not being pursued. Even though the capex was deemed to be the highest, all three other options evaluated were either deemed technically inferior for the low capacity of sulphur or insufficiently proven for requirements for this project.

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# Sour water stripping

# **Evaluation of SWS options**

The sour water stripper has no impact on the selection of the acid gas treatment technology and was therefore initially excluded from the configuration study. The sour water stripper however does have an impact on the design of the thermal oxidiser unit (TOU) and as such the sour water stripper technology as well as the location of the sour water stripper and destination of the sour water stripper off gas were studied.

The sour water stripper options could be broken down into the following options:

- Locate a new sour water stripper in the green fuel facility and route the sour water stripper off gas to the thermal oxidiser (base case).
- Locate a new sour water stripper in the green fuel facility and route the sour water stripper off gas to the existing SRU of the refinery in the sulphur complex.
- Route the sour water from the green fuel facility to the existing sulphur complex and install a new sour water stripper there to process the existing sour water load from the refinery and the additional sour water from the green fuel facility. For this scenario, the collection of the sour water would still take place in the green fuel facility area.
- Install a new sour water concentrator in the green fuel facility and route the

concentrated sour water to the existing sour water stripper in the existing sulphur complex, where it can be treated with the refinery sour water and the sour water acid gas processed in the existing SRU.

Due to past experience with requesting regulatory approval for routing long acid gas lines between facilities, the option to route the SWAG to the existing sulphur complex was quickly eliminated. This left only two options – to install a new sour water stripper in the existing sulphur complex or install a sour water concentrator in the green fuel facility as options for further evaluation.

The existing sour water stripper in the sulphur complex had a design capacity that was insufficient to handle the additional water from the green fuel facility. In order to overcome this limitation, two options were considered. A new sour water stripper could be constructed in the sulphur complex that would be designed for the existing sour water capacity of the sulphur complex currently plus the green fuel facility sour water capacity with capacity built in to run off any built-up sour water storage. Alternatively, to be able to use the capacity of the existing sour water stripper, the sour water produced in the green fuel facility could be concentrated in a socalled sour water concentrator, resulting in approximately 90% reduction of the sour water routed to the sulphur complex.

In both scenarios, sour water piping with an estimate length of 600 m needed to be taken into account to be able to transport the sour water from the site where the green fuel facility was intended to be built and the existing sulphur complex. As the sulphur complex did not have a waste water treatment facility to process the stripped water, a return line was also required for the stripped water to the green fuel facility.

#### New sour water stripper

For the new sour water stripper, a similar design as opposed to the standalone green fuel area was considered with a higher capacity to be able to process the existing water produced in the refinery sulphur complex. The unit proposed was a single-stage sour water stripper with a pumparound system.

The installation of a new sour water stripper provided the following benefits to the project:

- Replacement of an old sour water stripper which was near to end of life.
- All sour water acid gas produced can be processed in the existing sulphur recovery unit.
- No sour water acid gas processing in the new green fuel area thermal oxidiser.
- No requirement for the installation of a caustic scrubber associated with the thermal oxidiser to meet emissions regulations.
- Elimination of additional waste stream due to elimination of caustic scrubber.

The following disadvantages for the installation of a new sour water stripper were determined:

- Limited plot space available to install the new sour water stripper.
- Demolition scope to remove existing sour water stripper.
- Limited ability to shut down the existing sour water stripper, resulting in potential difficulty to make tie-ins.
- Additional tie-ins are required to connect the existing sour water system with the new sour water stripper as well as with the acid gas lines to the SRU.
- Long sour water and stripped water lines crossing the battery limits of the sulphur complex and the green fuel area.

Fig. 3 shows the proposed configuration for the installation of a new sour water stripper in the existing refinery sulphur complex.

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# Sour water concentrator

A sour water concentrator is a non-refluxed tower in which most of the overhead from the stripping tower is condensed so that a small sour water stream remains that can be processed in an existing sour water stripper. As indicated earlier, it is typically possible to reduce the sour water rate to be processed by about 90%. Due to the presence of  $CO_2$  in the sour water of a green fuel facility, a small off gas stream typically still remains which contains some  $H_2S$  as well. This stream still requires processing in a thermal oxidiser.

The installation of a sour water concentrator provided the following benefits to the project:

- No replacement of the existing refinery sour water stripper required.
- All sour water acid gas produced can be processed in the existing sulphur recoverv unit.
- No sour water acid gas processing in the thermal oxidiser

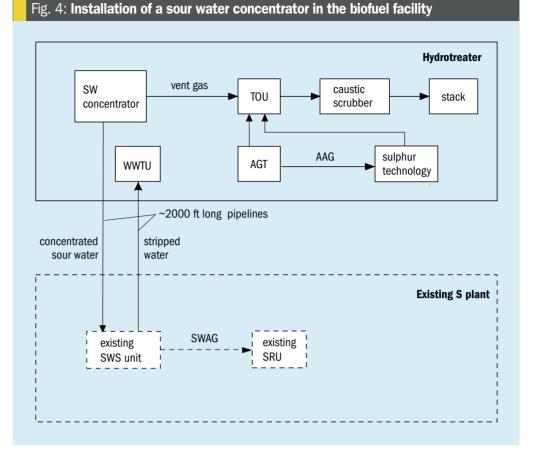
The following disadvantages for the installation of a new sour water stripper were determined.

- Similar plot space requirement as a new sour water stripper in the green fuel facility
- Additional tie-ins are required to connect the existing sour water system with the new sour water concentrator as well as with the acid gas lines to the SRU.
- Long sour water and stripped water lines crossing the battery limits of the sulphur complex and the green fuel facility areas.

Fig. 4 shows the propo sed configuration for the installation of a sour water concentrator in the green fuel facility, with the concentrated water processed in the existing refinery sour water

The option to process sour water acid gas in the thermal oxidiser requires the installation of special thermal oxidiser technology to handle the ammonia that is present in the gas. Ammonia destruction in a thermal oxidiser is typically considered difficult and requires special configurations to ensure that the ammonia is destroyed as well as the NOx formation is kept low. This can be achieved with higher than normal thermal oxidiser temperatures and implementation of staged combustion schemes for the introduction of the ammonia rich streams. In addition, there is a greater risk of the formation of  $SO_3$  in these thermal oxidisers due to the higher temperatures and additional oxy-

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gen required for the combustion. Due to the environmental limitations of the location of the refinery, a caustic scrubber was required in all scenarios where sour water acid gas or even the vent stream from the sour water concentrator had to be sent to the thermal oxidiser

Only in the scenario where the sour water was routed to a new sour water stripper located in the sulphur complex was it possible to eliminate the need for a caustic scrubber as the existing SRU had both capacity and tail gas technology that eliminated any additional SO2 emissions associated with the green fuel facility installation.

# **Comparison of the SWS options**

The relative capital costs associated with installing either a new SWS or a sour water concentrator in the green fuel facility or installing a new sour water stripper in the existing refinery sulphur complex are provided in Fig. 5. The relative cost includes the capital cost benefits of the elimination of the caustic scrubber.

# **Selection of SWS option**

All three SWS options considered are workable solutions. Even though installing a new SWS in the existing sulphur complex is approximately 30% higher in capex, it was recommended over the new sour water stripper or the concentrator option

Fig. 5: Relative capex for SWS options capex SW SWS in base concentrator sulphur complex

in the green fuel facility for the following main reasons:

- Better overall reliability, availability and maintainability due to a single processing unit versus a concentrator and SWS.
- Concentrator unit option will necessi-• tate a caustic scrubber to be installed downstream of the thermal oxidiser unit for residual SO<sub>2</sub> removal, therefore also including a waste heat boiler.
- Requirement for a thermal oxidiser unit that is capable of destroying ammonia. The existing sulphur complex has had severe fouling issues with the processing of ammonia in the thermal oxidiser in the past.
- Concentrators are not commonly used for high CO<sub>2</sub> applications, due to vent gas which requires further treating for residual H<sub>2</sub>S removal.

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• Lower overall opex for processing the sour water in the existing refinery sulphur complex.

By integrating the consequences of the presence of ammonia in the sour water acid gas with the options available for the acid gas treatment unit, it was concluded that substantial benefits could be expected by using the available SRU in the refinery sulphur complex. This resulted in simplification of the design of the thermal oxidiser as well as the need for a caustic scrubber to meet environmental requirements.

# PHAST study

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A PHAST (Process Hazard Analysis Software Tool) study was carried out to determine the dispersion scenarios in the event of loss of containment for pipe rupture scenarios for both the AGR as well as the AGR + AGE configurations. This also included the evaluation of the difference in consequence from the installation of an acid gas compressor and the potential risk that could be resulting from a leak.

The study was based on vulnerability, which includes factors like inventory,

dynamics of the dispersion and duration of exposure for a leakage arising out of a 2" hole in the pipe.

The PHAST study indicated potential for exceeding H<sub>2</sub>S risks outside of an acceptable distance from the source of a leak. However, on further analysis, based on vendor information for the compressor, the risks associated with the installation of an acid gas compressor were better understood and the realistic risk was considered mitigable by appropriate design. The operating cost reduction due to the significantly lower sulphiding agent consumption was deemed sufficient incentive to improve the piping design as well as implement safeguards for the installation of the acid gas diaphragm compressor. The resulting reduction of sulphiding unloading frequency at the plant site was also a significant advantage to operations. Therefore, the project decided to proceed with the acid gas enrichment and acid gas compressor scheme.

# **Final recommendations**

The project decided to proceed with the acid gas enrichment and acid gas compressor

scheme. As for the installation of the sour water stripper, the recommendation was made to install a new sour water stripper in the existing sulphur complex with a capacity that was sufficient to handle the produced water in the sulphur complex as well as the additional water produced in the green fuel facility.

The benefit of being able to process the sour water acid gas in the existing sulphur recovery unit which was designed already to process this gas far outweighed the potential risks associated with handling SWAG in a thermal oxidiser.

By combining the selected option for the acid gas treatment with the installation of a new sour water stripper in the existing sulphur complex, the need for a caustic scrubber could be eliminated. This allows for the reduction of caustic consumption in the facility as well as reduced the impact on the waste water treatment.

By eliminating the caustic scrubber, a simple natural draft thermal oxidiser can be installed instead with no need for waste heat recovery, which was necessary for the caustic scrubber to reduce the inlet temperature into the scrubber.



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# Next issue: March/April 2020

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Subscription rates: GBP 440; USD 880; EUR 680

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ISSN: 0039-4890

**Design and production:** JOHN CREEK, DANI HART

# Mixed Sources FSC www.fsc.org Cert no. SA

**Printed in England by:** Buxton Press Ltd Palace Road, Buxton, Derbyshire, SK17 6AE © 2020 – BCInsight Ltd

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#### Published by: BCInsight Ltd China Works, Unit 102,

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