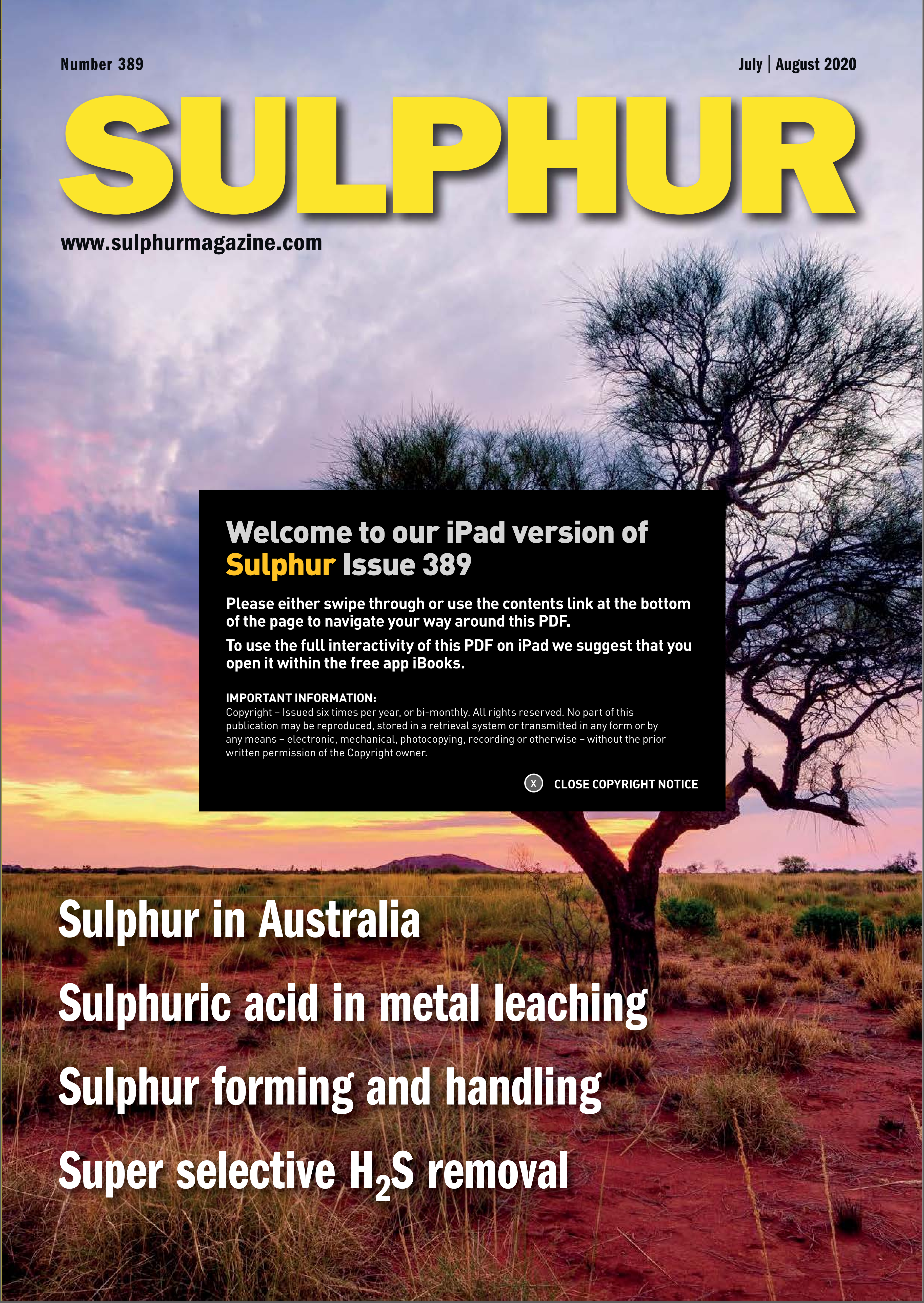
1 47 2 48 3 49 4 50 5 51 6 52 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46

Number 389

July | August 2020

SULPHUR

www.sulphurmagazine.com



Welcome to our iPad version of Sulphur Issue 389

Please either swipe through or use the contents link at the bottom of the page to navigate your way around this PDF.

To use the full interactivity of this PDF on iPad we suggest that you open it within the free app iBooks.

(X) CLOSE COPYRIGHT NOTICE

Sulphur in Australia

Sulphuric acid in metal leaching

Sulphur forming and handling

Super selective H_2S removal

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52

SULPHUR

www.sulphurmagazine.com

NUMBER 389

JULY | AUGUST 2020

Cover: *Hakea tree in the outback, Pilbara region, Western Australia. Image: bmphotographer/ Shutterstock.com*

CONTENTS

Sulphuric acid leaching

Renewed demand for acid in metals processing.

Drum granulation

IPCO's first drum granulation project in Europe still on track.

REGULARS

Read this issue online at: www.sulphurmagazine.com

Published by: BCInsight

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52

Damned lies and statistics

"There are," Mark Twain once remarked, "three kinds of lies: lies, damned lies, and statistics." It's certainly difficult to know what to make of economic statistics and indicators at the moment, in the world turned upside down that the Covid-19 pandemic has delivered. Here in the UK, we are told that April and May saw the national economy contract by 25%, the largest fall in 300 years of the Bank of England's economic record keeping, and the situation is very similar across much of the developed world. But how real is that figure? After all, we were all sent home in March, to 'lock down' and prevent the spread of the virus, and we are only now starting to move back towards some semblance of normality. Some of us, fortunately or not, have still been able to work from home, but for much of the economy, especially for much of the service sector; tourism, travel, restaurants and hotels, theatres and cinemas – there has been zero activity. Remove half of the largest sector of the economy for three months and surely a 25% fall in output is exactly what you'd expect? But is that real, or just a number? Has that activity gone for good, or, now that we are emerging, blinking into the sunlight again, can we switch the economy back on again as easily as we switched it off?

> "Can we switch the economy back on again as easily as we switched it off?"

The International Monetary Fund seems to think so. Its forecasts for economic contractions this year – 4.9% overall for the world, 8% in the US, 10% in UK and the Eurozone, are mirrored by equally optimistic growth figures for 2021; 5.4% globally, 4.5% for the US and 6% for Europe. China is expected to rebound from 1% growth this year to 8.2% next – a figure that the country, in a demographic trough and with an over capacity manufacturing sector, has not seen for several years. The IMF acknowledges some 'lost activity' and rises in unemployment, and assumes some government stimulus packages, but thinks that we will by and large go back to spending much as we did before – the so-called 'V-shaped' recovery.

Others are not so sure. In the absence of a vaccine, social distancing measures will affect incomes from that service sector for months to come. The risk of a second wave of infections remains, and in some places around the world, such as Brazil and Mexico and parts of the US, cases are still rising. Paying workers through periods of inactivity has placed strains on government finances, but removing those protections too soon will create a tidal wave of unemployed. Changed living and working practices mean that we may never return to going out and travelling quite as much as we did before. Interest rates are already at historic lows, and the room for more government stimulus is limited. Beyond the 'V-shaped' recovery, you can find an alphabet soup of predictions to suit your taste, from 'U-shaped' to 'W-shaped', and even an 'L-shaped' recovery, where effects linger for years, and possibly even turn a recession into a depression. Even the IMF has downgraded its 2020 forecast by 2% in between April and June, though it warns of "a higher-than-usual degree of uncertainty" attached to the forecast. No kidding.

Indeed, major world events can sometimes seem like one of those Rorschach ink blot tests that psychologists once used: optimists might see a butterfly unfurling its wings, pessimists see a shark's mouth gaping wide. The sulphur and sulphuric acid industries, part of the rather more solid and measurable manufacturing sector, can sometimes seem isolated from the concerns of the service economy and perhaps on the face of it more predictable. Fertilizer will still be needed for crops, after all, oil and gas will still be burned and smelters will still produce copper, zinc and nickel, come what may. But beyond the short term supply dislocations that global lockdown has caused, which have led to volatile prices this year, the long term knock-on effects of this crisis are likely to be far more profound than we can foresee from where we are now. We really may still be just at the beginning of understanding where we are headed, and at the moment, the numbers are not much help.

Richard Hands, Editor

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52

Price Trends

MARKET INSIGHT

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

SULPHUR

Supply side tightness in the second quarter supported the global sulphur market, leading to reduced liquidity in the spot market. End users were heard holding healthy inventories and the macroeconomic uncertainty weighed on sentiment heading into Q3 contract negotiations. The global pandemic continues to impact the supply demand balance for the year. There are substantial risks of a further Covid-19 flare ups as lockdowns are eased in many countries. The third quarter is usually a period for an upturn in the price cycle with increases still anticipated this year. Limitations on price increases are expected however with a muted market sentiment from downstream markets including processed phosphates and metals.

Uncertainty prevails over how the various containment measures put in place to overcome Covid-19 will impact sulphur end-use markets over the short and long-term. Argus has studied the impact of previous pandemics in order to form a view on possible consequences such an event could have on fertilizer demand. The impact of a pandemic on the agricultural markets and in turn sulphur demand is dependent on the various government responses. Containment measures may be disruptive to the flow of goods and labour or could impact farmers' costs and revenues. Reduced purchasing power means farmers are less able to bear fertilizers costs. Travel restrictions mean that inputs can be more difficult to access, resulting in lower fertilizer demand, ultimately impacting the consumption of raw materials including sulphur. This was the case during MERS in 2012 and Ebola in 2014. Sulphur consumption for phosphoric acid production decreased in 2012 and in 2014. Argus expects a drop in sulphur demand in the sector in 2020.

In other end use markets, Nickel remains the leading metals demand sector for sulphur. Australian sulphur demand is expected to see a boost from 2020 with the restart of the FQM Ravensthorpe nickel project. Australian sulphur imports have been increasing with January-April trade data showing a 116% rise to 442,000t. Meanwhile the Ambatovy nickel project in Madagascar temporarily halted operations, reducing sulphur consumption. Further downward revisions on demand are possible as fresh waves of Covid-19 emerge.

Sulphur demand losses for copper appear to have been far more muted than for sulphuric acid as elemental sulphur forms a small percentage of demand vs direct acid from smelters at copper mines. The macroeconomic outlook remains uncertain with volatility in copper prices leading to questions around investment and future trends. Some mining companies have announced cuts in capex guidance for 2020, influencing the near-term view. Flaring tensions between the US and China have weighed on copper prices but signs of cautious optimism emerged in June.

Mining company MM Boleo suspended operations at its copper, cobalt, zinc and manganese sites in April, following government coronavirus measures to shutter non-essential activities until 30 April. The company restarted operations on 1 June at its various sites and was back in the market for sulphur. Coronavirus is set to test the Mexican economy this year. The country's confirmed cumulative coronavirus cases rose to over 203,000 and over 25,000 deaths in June.

On the supply side, production cuts on the back of Opec+ agreements have resulted in a subsequent decline in oil-based sulphur output in recent months. In its Q1 2020 financial results Saudi Aramco reported its Fadhili Gas plant increased processing capacity to 2.0 scf/d from 1.5 scf/d. Operations at Saudi Aramco facilities are a combination of oil and gas. A significant portion is from associated gas, so reductions in sulphur output are possible given the country is the worst hit in the region by Covid-19.

State-owned refiner KNPC remains on track to complete its long delayed $16 billion Clean Fuels Project (CFP) in the fourth quarter after commissioning a water-cooling unit and the main fuel gas line at its 265,000 bbl/d Mina Abdullah refinery. Kuwait's CFP involves the integration of the Mina Abdullah and Mina al-Ahmadi refineries, raising their combined crude processing capacity to 800,000 bbl/d. The 615,000 bll/d Al-Zour refinery in the south of the country is also expected to come online by the end of the year. The Clean Fuels project and Al Zour combined are set to add 2.3 million t/a of sulphur capacity.

Middle East producer pricing for June reflected increases in line with reduced liquidity in the market. In the UAE, ADNOC set its June monthly price at $58/t f.o.b. Ruwais, up by $2/t on May, for shipments to the Indian market. KPC/Kuwait set its price for June at $57.5/t f.o.b. Shuaiba, up by $4.50/t on the previous month. State-owned marketer Muntajat set its June Qatar Sulphur Price (QSP) at $57/t f.o.b. Ras Laffan/Mesaieed. This was $4/t above the May. Muntajat issued its first spot tender in nine-months in June. It was awarded towards the mid-$60s/t fob.

Chinese supply is not expected to be negatively impacted by the Covid-19 pandemic in 2020. Total production is set to breach the 7 million t/a level in 2020 for the first time, driven by capacity additions in the refining sector. The initial lockdown and strict quarantine measures introduced to contain the spread of the disease in China placed significant uncertainty on sulphur demand. Argus expects a downturn in total demand down for 2020, concentrated in the phosphoric acid and industrial sectors. Whilst many of the country's industries are back up and running, fears of a second wave of infections have not yet entirely been ruled out as authorities in Beijing reintroduced lockdown measures once again in June. There is potential for further downward revisions for supply and demand with outbreaks remaining a risk to the market. Demand recovery is expected from 2021, across most end uses. The rise in local supply, the slowdown in demand and healthy stocks have been eroding China's import requirement. China imported 2.6 million tonnes from January-April, down by around 26% on a year earlier. The UAE remained the leading supplier and delivered around 719,000 tonnes, up by around 97%. Deliveries from other Middle East suppliers fell. Iran supplied 15% less, at 408,000 t. Saudi Arabia supplied 59% less, at 232,000 t and Qatar supplied 77% less, at 122,000 t. India supplied 225,000 t, up by 43%, reflecting improved production capacity in the Indian market on the year as well as increased exports because of the impact of the pandemic in India.

SULPHURIC ACID

Global sulphuric acid market prices saw gains over the last few months, with prices ticking up in some regions on the back of spot demand. The pandemic is weighing on major demand sectors including copper, with disruption from Covid-19 containment measures taking its toll on the market. In NW Europe, average prices for export rebounded from $-10/t f.o.b. in April back into positive territory at $4/t f.o.b. at the start of July. Following significant shipments to Morocco, reduced availability supported the tick up in prices out of Europe. Contract negotiations were underway in the region for the third quarter. Some settlements for sulphur-based acid were reported at a rollover on the previous quarter, but negotiations were ongoing at the start of July for others. Softer prices were indicated for smelter acid. Impact from slow industrial demand and squeezed end product margins weighed on price discussions.

Demand for sulphuric acid for the copper sector is forecast to drop significantly in 2020 vs 2019. Some uncertainty remains on the short-term outlook due to ongoing economic disruption as lockdowns continue in many regions. The shifting macroeconomic conditions raise questions on how the remainder of the year will unfold. Some mining companies have announced cuts in capex guidance for 2020, influencing the near-term view. Flaring tensions between the US and China weighed on copper prices in May with cautious optimism returning in June. Mining projects in Arizona and the Central African copper belt add to prospects for consumption growth for leaching in the forecast. The view for Chile in 2020 is to see a drop in demand, recovering in the medium-term before seeing significant drops from 2025 as copper oxide ores erode. Coronavirus cases in Chile were over 282,000 at the start of July and further disruption to the mining sector was expected due to the escalation in cases.

In project news, Freeport McMoRan expects its Lone Star copper leach plant in Arizona to begin copper production during the second half of the year, completing the remaining $100 million investment in the venture in 2020. Sulphuric acid consumption for the project is expected to mostly be sourced from the company's own production. Copper output is estimated at 91,000 t/a and was close to 90% complete at the end of April 2020.

Excelsior Mining copper mining operations were temporarily suspended at the Gunnison project in Southern Arizona in response to the Covid-19 outbreak. The duration of the suspension is unknown according to the company. The project was under care and maintenance in order to remain flexible for a restart once the issues surrounding the pandemic are resolved.

India has taken most significant Covid-19 related demand hit, with 1.6 million t/a of phosphate based sulphuric acid demand forecast to be lost in 2020. A snap decision in India to stall customs clearances on Chinese product had localised impact on throughput, but a lack of clarity on the nature and duration of the rules added uncertainty. India imported nearly 250,000 tonnes of Chinese acid in the first half of the year. Lower acid prices have supported trade from a range of suppliers so far this year. Prices for spot range $6-19/t c.fr at the start of July, according to Argus assessment of the market.

One of the main bright spots for demand this year is Morocco. Despite all the disruption to phosphoric acid demand in other regions, Morocco is expected to see growth as OCP continues to ramp up at the Jorf Lasfar processed phosphates hub. Imports were expected to remain strong through July with OCP continuing to be active in the spot market in Europe and Asia. Argus analysis shows sulphuric acid June arrivals at Jorf Lasfar reflect the highest ever monthly volume at 271,000 tonnes. Imports are expected to remain strong through the remainder of the year. Supply is led by China – around 361,000 tonnes were shipped in the first half of the year. European trade has seen a significant increase on a year earlier.

Sulphuric acid production is expected to decrease in almost every region in 2020. Significant losses have been noted at captive production sites for the processed phosphates sector and metals leaching projects. A major drop is forecast in India as lockdowns led to temporary closures at several fertilizer plants with associated sulphur burners. Disruption is also noted at the Mopani smelter in Zambia.

Exports from Japan totalled 1.3 million t in January-May 2020, up by 100,000 t on a year earlier. The leading market was the Philippines at 499,000 tonnes, followed by India at 239,000 tonnes. The outlook for trade volumes for the year is stable. Price pressure remained into the start of July, with product available for prompt loading. Markets including southeast Asia have seen offers for Japanese tonnes, but little interested was noted.

Price Indications

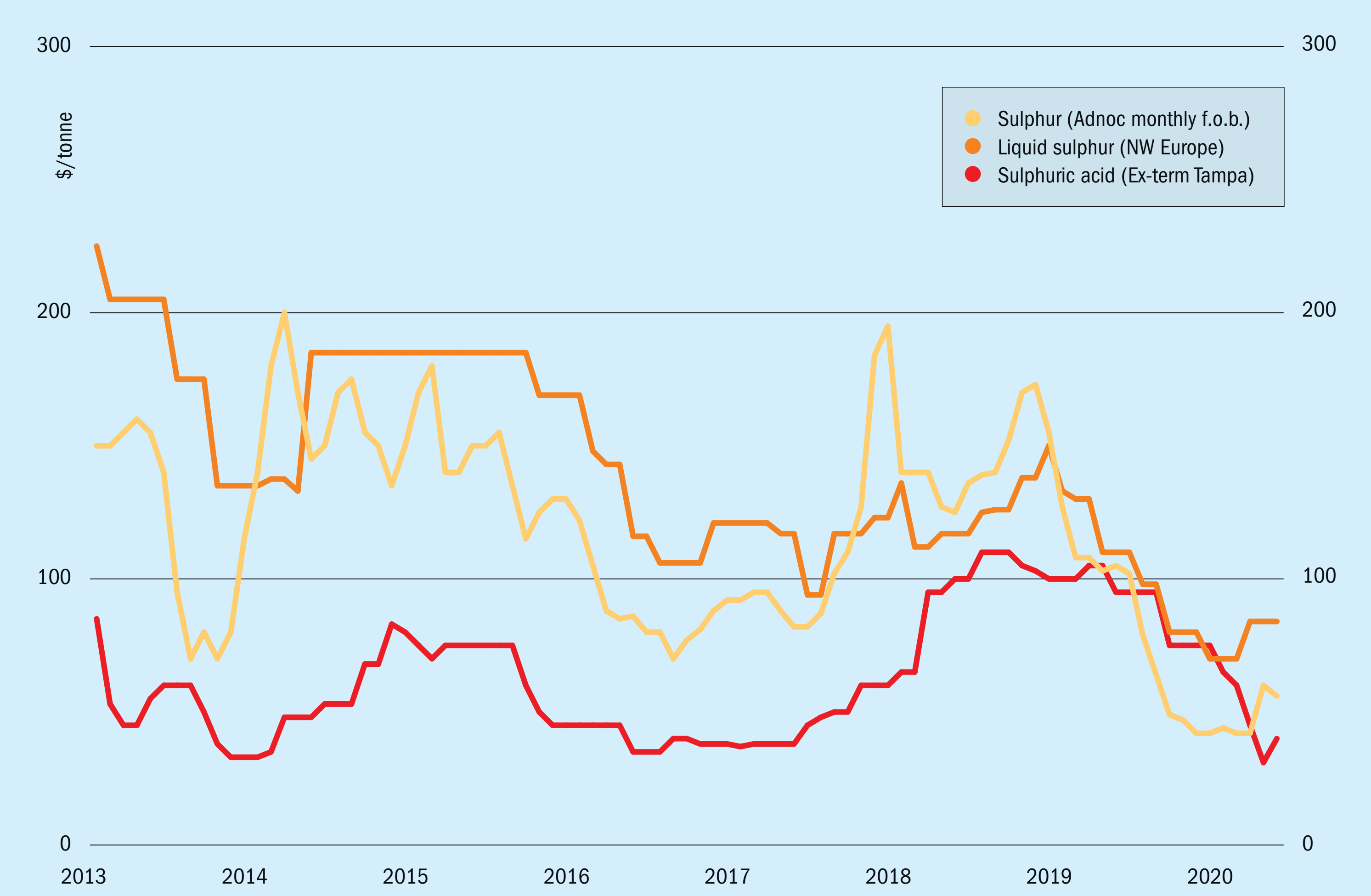
Table 1: **Recent sulphur prices, major markets**

Cash equivalent	January	February	March	April	May
Sulphur, bulk ($/t)					
Adnoc monthly contract	44	42	42	60	56
China c.fr spot	64	64	71	49	46
Liquid sulphur ($/t)					
Tampa f.o.b. contract	36	36	54	54	54
NW Europe c.fr	70	70	84	84	84
Sulphuric acid ($/t)					
US Gulf spot	74	60	45	31	40

Source: various

Market Outlook

Historical price trends $/tonne



Source: BCInsight

SULPHUR

- Sulphur demand losses for production of phosphoric acid are forecast at 2.2 million t/a in 2020. Factoring in demand gains in markets such as Morocco, the sector is expected to see a drop of 800,000 t/a in 2020. Recovery is forecast from 2021 with a 2 million t/a increase forecast.
- Oil price erosion and numerous lockdowns have led to a major downturn for fuel demand. Sulphur supply has seen significant erosion, reducing availability in markets including the US.
- Indian import demand will see a drop in consumption for phosphoric acid. The initial lockdown led to fertilizer operations being disrupted. We forecast imports at below 600,000 t/a.
- Morocco remains a bright spot for sulphur and sulphuric acid trade and one of the few exceptions for demand growth this year. Import demand is expected to rise 300,000 t/a to 7 million t/a in 2020.
- **Outlook:** Covid-19 demand losses will tally over 1 million t/a in 2020 with further revisions likely as investment is cut in light of economic uncertainty. This has led to a revision of project timelines but the short term outlook remains robust. Chinese stocks at over 2.6 million t have left buyers on the sidelines to a degree. High stocks appear to be the new norm, reverting back to historical behaviour, having reduced impact on price direction. Prices in the second half of the year are expected to be stable to firm. Third quarter prices are forecast to tick up – with contracts expected to yield increases on the second quarter.

SULPHURIC ACID

- Copper leaching projects in the US including Excelsior Mining's Gunnison project and Freeport McMoRan's Lone Star project, are set to add around 850,000 t/a of sulphuric acid demand by 2024.
- Uranium prices surged 24% between March and June due to tightening supply from Covid-19 disruption and the suspension of operations at Cameco. Demand from the power sector remained strong over the period.
- A drop in sulphur-based acid production and reduced netbacks for Chinese acid exports will likely see producers more focussed on the domestic market – resulting in drop in 2020 exports. Exports to May fell by 16% on a year earlier to 834,000 tonnes.
- A weak economic outlook has led to the cancellation or suspension of several large smelter based sulphuric acid capacity projects in China. Despite this, the Argus forecast remains robust for China smelter projects in the short term.
- Acid consumption for the industrial sector for 2020 will see a decrease on 2019 levels but has been stable in most regions in recent weeks. Further disruption is a possibility, but a major medium-term growth area remains acidification of slurry in Europe.
- **Outlook:** The price outlook is stable to soft with limited upside anticipated in the short term. Reduced consumption at some mine sites is impacting demand. The broader macroeconomic sentiment also points to challenges in consumption of sulphuric acid.

Sulphur Industry News

UNITED STATES

US oil and gas bottoms out, but may take time to recover

US crude production dropped rapidly during April and May, but figures released by the Energy Information Administration (EIA) showed that this had plateaued and there have been some well reactivations and drawdowns from crude stocks. Total production curtailments in North America were more than 2.5 million bbl/d in May. ConocoPhillips Chairman and CEO Ryan Lance said in remarks to the media that a return to pre-outbreak production levels of 13 million bbl/d looked "pretty difficult", although a recovery to 11 million bbl/d or possibly as high as 12 million bbl/d would be possible, depending upon OPEC moves. About one third of the company's production was shut in as of the start of June – some 400,000 bbl/d. Lance argued that low cost shale oil resources still exist in the US, but there will be pressure on companies to reduce capital spending. The Covid-19 outbreak has had a major impact in investment announcements, with a large number of project delays in the US due to uncertainty over future demand levels. Planned US exploration and production expenditure is down by 50% for the second half of 2020, while the rig count was down 60% on February.

Refinery utilisation is still lower than normal but saw a small increase in June, with gasoline production reaching 7.5 million bbl/d by the start of June and demand back to 78% of normal. The recovery in economic activity is leading to more use of private transportation and demand for gasoline, whereas manufacturing and freight activity where distillate fuel is used are recovering at a slower pace. Gasoline consumption in April 2020 was only 50% of the figure for April 2019. However, rising Covid cases in southern states and Latin America – the latter a destination for US refined product exports – will affect demand for the second half of 2020.

CHINA

Chinese oil demand back to 90% of pre-crisis levels

China's oil demand has continued a sharp rising trend since falling by 40% to reach a low point in February 2020. IHS Markit reports that Chinese oil demand for April reached 89% of the April 2019 level (approximately 12.7 million bbl/d as compared to 14.3 million bbl/d for the previous year) as lockdown measures were lifted and personal mobility and economic activities resume. IHS forecast that it would reach 92% of the prior year level in May. Positive indicators included new car sales, the resumption of work at large industrial enterprises and freight turnover all returning to near-or-at prior year levels. Weekday road traffic is also back to pre-lockdown levels, although use of public transportation remains depressed. China's real GDP growth for 2020 is now forecast at 0.45%, compared with 6.2% predicted prior to the Covid-19 outbreak. Overall 2020 oil demand is expected to be down by 1.2 million bbl/d (8%).

ECUADOR

Restart for refinery sulphur plant

Petroecuador says that it has re-started the sulphur plant at its Esmereldas refinery, following a shutdown on April 7th due to "mechanical damage" resulting from power failures in the National Interconnected System (SIN) – Ecuador's national electricity grid. EP Petroecuador's general manager, Pablo Flores, said that a team made up of 30 technicians carried out the necessary remedial work to return the sulphur plant to operation during extended days, after repairing mechanical damage. Engineers built a new tube and casing bundle, installed refractory cement inside, and completed assembly and final welding. Welding and hydrostatic tests were also carried out, and technicians confirmed the quality of pressure sealing of the valves, to avoid gas leaks.

SAUDI ARABIA

Aramco completes its acquisition of stake in Sabic

Saudi Aramco has completed its acquisition of a 70% stake in the Saudi Basic Industries Corporation (Sabic) from the country's Public Investment Fund (PIF); the sovereign wealth fund of Saudi Arabia. The acquition was completed at a total price of $69.1 billion, as part of Aramco's long-term downstream strategy to grow its integrated refining and petrochemicals capacity and create value from integration across the hydrocarbon chain. It makes Aramco one of the major global petrochemicals players; integrating upstream production with Sabic feedstock, expanding capabilities in procurement, supply chain, manufacturing, marketing and sales; and increasing the resilience of cash flow generation. Sabic says it expects to benefit from Aramco's downstream chemicals feedstock production, and ability to invest in and execute major growth projects at a very large scale. In 2019 Aramco and Sabic recorded combined petrochemicals production volume of nearly 90 million t/a, including agri-nutrient and specialty products.

Yasir Othman Al-Rumayyan, governor of the PIF said: "This is a significant milestone for three of Saudi Arabia's most important entities. It provides capital for PIF's long-term investment strategy as it drives the economic transformation and growth of Saudi Arabia, further benefitting the people of our country; it supports Aramco's continued growth in Downstream and enhances its international footprint; and, it provides Sabic a new strategic energy industry focused shareholder with the ability to support growth projects."

KUWAIT

Kuwait completes sulphur project at Al Ahmadi refinery

Kuwait National Petroleum Company (KNPC) says that it has completed its acid gas recyling plant at its Mina Al-Ahmadi refinery, which will recycle acid gas and condensates produced by the Kuwait Oil Company from its fields in the west of the country. KNPC Deputy CEO for Projects Abdullah Al Ajmi, said the volume of gas processed could reach 231 million cfd based on a 2.5% hydrogen sulphide content of the acid gas, down to 146 million cfd when the H_2S content is 5%. The plant can also process 39,000 bbl/d of condensate. He added that the project will contribute to reducing greenhouse gas emissions to less than 1%, as well as reducing emissions of sulphur dioxide to permissible levels, and generating additional sulphur for export. Mina Al Ahmadi currently produces 1,330 t/d of sulphur.

PHOTO: UWC

UWC's molten sulphur rail tank car.

UNITED ARAB EMIRATES

Adnoc celebrates progress at Ruwais

Adnoc's chief executive Sultan al-Jaber hosted Abu Dhabi's Crown Prince Mohammed bin Zayed al-Nahyan at the firm's Ruwais refinery in mid-June to celebrate progress at the site, already home to a refinery and petrochemicals complex, and now part of a $45 downstream diversification project into a petrochemical and industrial hub. The visit marked four years of transformation of the company following a strategy launched in November 2016 which has seen the state-owned giant become more market focused and develop collaborations with overseas companies such as Baker Hughes, as well as the part privatisation of some assets. Last year Adnoc sold a 40% stake in its domestic oil pipeline network for $4 billion, and a 35% share in its refining business, bought by Eni and Total for $5.8 billion. This year, it has sold a 49% stake in its gas pipelines in a deal worth $10 billion to a consortium including Global Infrastructure Partners, Brookfield Asset Management, Singapore's sovereign wealth fund GIC, Ontario Teachers' Pension Plan Board, South Korea's NH Investment & Securities and Italy's Snam.

However, although the company's oil production reached a record 4.2 million bbl/d in April, falling oil prices have seen margins squeezed and delays to construction phases on some larger projects, especially expensive offshore sour gas development. In April Adnoc terminated $1.65 billion worth of contracts awarded in February to a Petrofac-led group for the ultra-sour Dalma Gas Development project. The company is also having to throttle back oil production by 1.7 million bbl/d until early 2022 to meet new OPEC production targets. Some expansion is still occurring, even so – bids are due by the end of June on an estimated $400 million engineering, procurement and construction contract to raise capacity at the offshore Umm Shaif field by 75,000bl/d to around 475,000bl/d.

RUSSIA

Molten sulphur rail cars delivered

United Wagon Company (UWC), one of Russia's largest producers of rail cars, says that Ivanomorsk TPK has taken delivery of a batch of TikhvinChemMash molten sulphur rail cars for use by Norilsk Nickel. This follows the delivery last year of rail cars for sulphuric acid transport. In a press statement, UWC said the Type 15-6913 molten sulphur wagon featured thermal insulation, a double casing of stainless steel, and an air gap outside the tank shell to enable uniform heating of the load with hot air generated by tubular heating elements. The 25 tonne axle load bogies provide the wagons with a capacity of 72 tonnes or 44 m^3; they are designed for maintenance intervals of up to 1 million km or eight years and a life of 32 years.

KAZAKHSTAN

Sulphur output up

Kazakhstan's Statistics Committee reports that the country's sulphur output for the first five months of 2020 reached 1.7 million t/a. This figure was up 6.4% on the same period for 2019.

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52

FINLAND

Outotec merger with Metso Minerals

On June 30th, following clearance from the European Commission, Outotec completed the year-long merger of Metso's Minerals business with Outotec via a partial demerger of Metso. The newly formed company, Metso Outotec, will focus on leadership in sustainable minerals and metals processing and recycling technologies. Headquartered in Finland, Metso Outotec employs over 15,000 professionals in more than 50 countries and its combined sales for 2019 were €4.2 billion.

The company will provide crushing and screening equipment for the production of aggregates as well as equipment and solutions for minerals processing, metals refining, chemical processing, and metal and waste recycling. Growing interest in the environment and the impact of climate change, urbanisation, decreasing ore grades and electrification are forcing traditional industries like aggregates, minerals processing and metals refining to redefine their license to operate, Metso Outotec said.

"It is our core expertise to help our customers transform the industry. We offer sustainable technologies and services that reduce the consumption of energy and water by increasing process efficiency, recycling and reprocessing of tailings and waste," president and CEO Pekka Vauramo said in a press release. ■

SAUDI ARABIA

Ma'aden completes refinancing of Wa'ad Al Shamal

The Saudi Arabian Mining Company (Ma'aden) says that its subsidiary Ma'aden Wa'ad Al Shamal Phosphate Company (MWSPC) has signed new financing agreements for $2.3 billion with leading local and regional financial institutions. The proceeds from these agreements will be used to pay down existing loans. The new financing facilities replace the more restrictive project financing terms and conditions originally put in place, and are, says the company, "a step towards significantly strengthening the long term cash flow position for Ma'aden as part of its strategy to pursue new growth and development projects".

Commenting on the announcement, Ma'aden's CEO, Mosaed Al Ohali, said: "We are proud of the strong appetite from banks to lend to Ma'aden MWSPC during the current challenging market conditions. This is a reflection of our financial strength and growth prospects and the durability of our assets. With abundant phosphate deposits in the north of Saudi Arabia, Ma'aden is well placed to build on its position as a leader in the global phosphates market and make Saudi Arabia a major contributor to global food security."

The MWSPC integrated phosphate fertilizer production complex at Wa'ad Al Shamal is one of the largest in the world, including a $8 billion joint venture between Ma'aden (60%), Sabic (15%), and Mosaic (25%).

THAILAND

Thailand approves large scale green projects

The Thailand Board of Investment has approved five large-scale projects with a total investment value of $1.35 billion to strengthen the country's agricultural sector in line with a stated 'bioeconomy, circular economy, and green economy' model. Among the projects, Thai Oil PCL received approval for a power project which will form part of the Sriracha Refinery Clean Fuel Project. The power plant will burn refinery residues to produce 250 MW of electricity. Sulphur dioxide recovered from flue gas will then be converted into 80,300 t/a of sulphuric acid using Haldor Topsoe's SNOX process (see Sulphur Industry News, *Sulphur* 388, May-Jun 2020, p11).

DEMOCRATIC REPUBLIC OF CONGO

Outotec to supply SX/EW technology

Outotec has been awarded a contract by La Sino-Congolaise Des Mines SA (Sicomines) for the delivery of copper solvent extraction technology to Sicomines' project near Kolwezi in the Democratic Republic of Congo (DRC). The order value, approximately €20 million, has been booked in Outotec's 2020 second quarter order intake. Sicomines is a joint-venture formed by companies from China and the DRC.

Outotec's scope includes basic engineering, technology and equipment deliveries and advisory services for mechanical installation as well as commissioning and start-up of the modular VSF®X copper solvent extraction plant.

"The Sicomines project will be a great reference for Outotec in the active African copper/cobalt market," said Kalle Härkki, head of Outotec's Metals Refining business.

CHILE

Chuquicamata smelter shut down by Covid outbreak

Chile's state copper company Codelco has decided to shut down its Chuquicamata copper smelter and refinery in the Antofagasta region of northern Chile as a preventative measure against the spread of the Covid-19 virus. The smelter produced 321,000 tonnes of copper in 2018. In addition to reducing copper production, the decision will also reduce the production of sulphuric acid which is used to leach copper at other operations.

RUSSIA

Acid tank wagon contract

Freight wagon manufacturer United Wagon Company (UWC) has delivered a batch of 77 tonne, $44 m^3$ capacity Type 15-9545 sulphuric acid tank wagons to the Transport Logistics Systems (TLS) rail operator. This is the first supply agreement between the companies, and the first acquisition of specialised new-generation cars by the Siberian operator.

"The Siberian region serves as one of Russia's largest transport and transit hubs," says Mr Oleg Balakirev, CEO at Transport Logistics Systems. "In order to work effectively in this highly competitive environment, companies require not only efficiency and high professional standards from their teams, but also modern rolling stock. The rolling stock we have acquired will allow us to ensure the uninterrupted export of our clients' products, while reducing transportation costs per tonne of transported product."

Norilsk under fire for waste water dumping

Norilsk Nickel says that it has suspended staff for pumping waste water from one of its processing plants into nearby countryside. Local press allege that the waste water contained nickel, cobalt, copper and sulphuric acid, which the firm has denied. In a statement, Norilsk Nickel (Nornickel) said "those responsible at the plant have been suspended" for "allowing a flagrant violation of the operational rules at the plant's tail-

Foskor's site at Richard's Bay, South Africa.

PHOTO: FOSKOR

ings reservoir. Nornickel has launched an investigation into what happened, and the firm is working with the ministry of natural resources and the emergencies ministry." According to Norilsk, the waste water does not contain toxic tailings from its mining operation. The firm says the purified water had been pumped away from the reservoir to prevent overspill, while admitting that it was not acceptable practice.

SOUTH AFRICA

Fire at Foskor's sulphuric acid plant

Phosphate producer Foskor says that a fire at its acid plant in Richards Bay will not impact production and supply. The fire broke out at a rock phosphate transfer tower where phosphate rock and sulphur are conveyed into stores, Foskor said in a statement. It was extinguished before any severe damage could occur to the conveyor structure, and no employees or contractors were hurt, said Musa Xulu, general manager of logistics, shipping and materials handling at Foskor.

"The fire outbreak will have no impact on our production nor on the ability of Foskor to supply our products to the customers," Xulu said. "The damaged conveyors are expected to be operational by end of June, 2020."

UNITED STATES

Mosaic instigates anti-dumping investigations

US fertilizer producer Mosaic has filed with the US Department of Commerce and the US International Trade Commission to request an investigation into "countervailing duty" on imports of phosphate fertilizers from Morocco and Russia. Mosaic says that, as the largest US producer of phosphate fertilizers, with an annual output of 16 million t/a, it is taking this action because "large volumes of unfairly subsidized imports from Morocco and Russia are causing significant harm to Mosaic's operations". Mosaic's phosphate fertilizer business employs approximately 3,500 workers and operates mines and production facilities in Florida and processing plants in Louisiana.

The company added that the purpose of the petitions is to "remedy the distortions that foreign subsidies are causing in the US market for phosphate fertilizers, and thereby restore fair competition". "Mosaic believes in free trade and vigorous competition, and we believe we should compete on a level playing field," said Mosaic President and CEO Joc O'Rourke. "The duties we are seeking will help ensure that North American farmers can rely on the American phosphate industry to supply critical fertilizers for the long term."

The US Department of Commerce and International Trade Commission will consider the petitions and determine the next steps, which typically involve lengthy investigations.

EGYPT

Loan for Abu Tartur phosphate project in Egypt

The National Bank of Egypt (NBE) and the Arab African International Bank (AAIB) are considering a $750 million loan for Al Wady for Phosphate Industries and Fertilizers. The loan would cover the construction of a new phosphoric acid plant at Abu Tartur. The expected cost of the project is $1.2 million, of which 35% will be self-financed and 65% via external loans. The project's implementation is likely to start during the fourth quarter (4Q) of 2020, and its completion is expected in 30 months.

INDIA

Recovery in Indian DAP production

India diammonium phosphate (DAP) production is recovering, rising to 325,000 tonnes in May after a fall to 260,000 tonnes in April due to the country's nationwide lockdown because of the Covid-19 pandemic. Indian fertilizer demand has remained fairly strong in spite of the pandemic, with forecasts for a good rice crop and plentiful rainfall during the June-September monsoon season leading to increased buying by farmers. Producers in turn have sought to return production to maximum rates ahead of the kharif application season.

SERBIA

July completion for SO_2 capture system

Zijin Bor Copper, the Serbian unit of China's Zijin Mining Group, says that it will complete the construction of a sulphur dioxide capture system at its Serbian copper smelter in July. Zijin Bor Copper was renamed after RTB Bor was bought by the Chinese mining company in December 2018, following a $350 million capital injection. Zijin Bor Copper is aiming to invest $800 million during 2020 and 2021 in expanding capacity at the site, via the revamping of existing and opening of new mines, increasing the capacity of the copper smelter in Bor, as well as in environment protection activities.

Company director Jian Ximing said: "We plan to solve the SO_2 air pollution problem in Bor permanently, by making a system for capturing fugitive gases, so that we will redirect all the gases to the sulphuric acid plant." The company plans to process 440,000 t/a of copper concentrate in 2020 to produce 200,000 t/a of copper cathodes and anodes, and 370,000 t/a of sulphuric acid. ■

People

The Sulphur Institute (TSI) has announced the selection of **Ron Olson** as its agronomist. Olson has over 30 years of experience as an independent consulting agronomist as well as 15 years with Cargill and The Mosaic Company. His agronomic consulting company worked directly with farmers and agricultural retailers offering custom soil sampling and soil analysis, and crop management expertise. The company pioneered the implementation of using precision agriculture tools for taking soil samples on a 2.5 acre grid, converting that data to computer maps and linking that data to GPS/GIS technology to develop crop management programs to achieve maximum economic yields. With Cargill and Mosaic he served as Research and Development Manager and led the team that developed the *MicroEssentials*™ suite of products., which has grown to become the leading commercial sulphur enhanced fertilizer sold globally.

"TSI is delighted with Ron Olson's eagerness to assist with the sulphur agronomy needs of our members", said John Bryant, TSI President. "Ron brings a highly applicable and successful background in sulphur fertilizers. Ron will also readily assist us with our important work on sulphur advocacy and other TSI services."

IFA has announced the appointment of its Senior Director of Agriculture, **Patrick Heffer**, as the organisation's Interim Director General as of May 1st. A formal search process for the next Director General has already been launched. Previous IFA Director General **Charlotte Hebebrand** stepped down at the end of April to assume a new role as Executive Vice-President and Chief Sustainability Officer at Nutrien, and says that she looks forward to continuing engagement with IFA.

During her nearly eight years' tenure at IFA, Hebebrand, working closely with the IFA board and secretariat, introduced a number of new areas of focus and initiatives, including a reshaping and expansion of IFA's market intelligence, a strong emphasis on product and nutrient stewardship, enhanced policy and research capabilities and an expansion of multi-lateral engagements and international cooperation.

"Charlotte has made significant and lasting contributions to IFA and to our industry" said IFA Chairman and CEO of OCP, Mostafa Terrab, who recognised in particular her commitment to dialogue and her far-sighted approach to long-term development and growth, such as the distillation of the plausible future scenarios as part of the IFA 2030 strategic exercise, as well as the creation of a Scientific Panel on Responsible Plant Nutrition. "The Board would like to thank her for her extraordinary service and leadership".

Patrick Heffer is a very experienced, longstanding executive team member who joined IFA in 2002 and for the past 18 years has coordinated the association's global agronomic, market and policy activities in relation to fertilizer use. Before joining IFA, he spent 15 years with the seed industry, including five years with the International Seed Federation, and two years with the FAO's Seed and Plant Genetic Resources Service.

Heffer, whose appointment coincides with the new global challenges caused by the Covid Pandemic, remarked: "I am grateful for this opportunity, and in cooperation with IFA's team of directors as well as IFA's experienced and devoted staff, I will make sure that the Association continues to deliver on its goals and objectives. In these trying times, we, at IFA, are even more committed to delivering the support, in terms of information, benchmarks, data, market insights, partnerships, policy analysis and reputation management tools, that our members and external stakeholders expect from us."

Gambarotta Gschwendt gas announce the appointment of **Davide Gambarotta** as its new Chief Executive Officer and sole owner designate. He replaces the former CEO with immediate effect, and will keep on his position as CEO and sole director of MDG Handling Solutions. Gambarotta Gschwendt and MDG will operate jointly under the Gambarotta Group, with Gambarotta Gschwendt responsible for the design and production of equipment for bulk material handling and MDG Handling Solutions offering complete EP/EPC packages.

In May **Roeland Baan** joined Haldor Topsoe as the company's new CEO, following the announcement of his appointment back in February. Baan was previously CEO of Finnish steel giant Outokumpu. On his first day in the office, Baan said: "This is a special day for me. Topsoe is an exceptional company that has made a huge difference for the refining and chemical industries for decades. I have no doubt that Topsoe has the potential to expand this strong market position and lead the way into a more sustainable and energy-efficient future. I have been looking forward to begin this journey together with the board and the leadership team as well as Topsoe's customers and dedicated employees."

Calendar 2020

! The following events may be subject to postponement or cancellation due to the global coronavirus pandemic. Please check the status of individual events with organisers.

SEPTEMBER

21-25
Brimstone Sulfur 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

OCTOBER

7-8
TiO2 World Summit, CLEVELAND, Ohio, USA
Contact: Shannon Siegferth, Smithers
Tel: +1 330 762 7441
Email: ssiegferth@smithers.com

NOVEMBER

2-4
Sulphur and Sulphuric Acid Conference 2020, THE HAGUE, Netherlands
Contact: CRU Events
Chancery House, 53-64 Chancery Lane, London, WC2A 1QS, United Kingdom
Tel: +44 20 7903 2167
Email: conferences@crugroup.com

2-6
RefComm Galveston 2020, GALVESTON, Texas, USA
Contact: Refining Community
Tel: +1 360 966 7251
Web: www.refiningcommunity.com/refcomm-galveston-2020/

16-19
European Refining Technology Conference, MADRID, Spain
Contact: Sandil Sanmugam, World Refining Association
Tel: +44 20 7384 7744
Email: sandal.sanmugam@wraconferences.com

24-25
European Sulphuric Acid Association Autumn General Assembly, VIENNA, Austria
Contact: Francesca Ortolan, Cefic
Tel: +32 2 436 95 09
Email: for@cefic.be

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52

Nickel West's site at Kalgoorlie, Western Australia

PHOTO: BHP

Sulphur and sulphuric acid in Australia

Sulphur demand in Australia has been boosted by the restart of the nickel leaching plant at Ravensthorpe, and new HPAL projects are under development, but a slew of new phosphate projects are not scheduled to consume more acid domestically.

In spite of having a population of only 25 million people, like Canada, Australia's huge size and mineral resources make it a major international player across many industries. Australia's economy is actually the world's 13th largest, and more importantly it holds the world's largest reserves of nickel and uranium, and the world's second largest copper reserve after Chile (13% of all global copper). Although domestic sulphur production is relatively low, acid production and consumption from metals processing runs at much higher levels, and Australia imports significant volumes of sulphur to feed phosphate and metals production.

Oil and gas

Sulphur production in Australia is relatively limited, and comes from the country's few remaining refineries. Australia's oil production ran at about 490,000 bbl/d in 2019, up from the previous year's figure but still below its pre-financial crash peak of 507,000 bbl/d in 2009. Most of the oil comes from the North West Shelf off Western Australia, and is heavy but sweet. Heavy sweet crude is in considerable demand worldwide, and the oil producing region of Australia is on the opposite side of the country to most of its refining capacity, so Australia actually ends up exporting most of its oil production, and relying upon imported oil to feed its refining sector. Only 20-25% of oil processed in Australia is actually produced domestically, with the rest coming from Malaysia, Indonesia and the Middle East.

Australia's refinery capacity is about 455,000 bbl/d from its four remaining refineries. These are located in Geelong and Altona (near Melbourne in the state of Victoria), Lytton (near Brisbane in Queensland) and Kwinana (Western Australia). Capacity has fallen from 750,000 bbl/d in 2011, with the closure of the Clyde and Kurnell refineries in Sydney and the Bulwer Island refinery near Brisbane. Australia's refineries cover only around 40-50% of the country's demand, and the rest is imported, mainly from Korea, Japan and Singapore. Furthermore, Australian fuel quality standards actually lag behind many other developed countries. Regulations for unleaded gasoline currently permit a sulphur level of 150 ppm for 91 octane and 50 ppm for 95/98 octane gasoline. A move to so-called Euro-6 sulphur levels (<10 ppm) has been pushed back by the current government to July 2027. This and the relatively sweet feeds used by Australian refineries means that domestic refinery sulphur recovery capacity remains quite low. For example, BP's Kwinana refinery, the largest in Australia, has only 23,000 t/a of sulphur recovery capacity. Overall, Australia's refinery sulphur production is only around 60,000 t/a.

On the gas side, Australia became the world's largest exporter of liquefied natural gas (LNG) in 2019, exporting 77.5 million tonnes from LNG hubs at Karratha in Western Australia, Gladstone in central Queensland and Darwin in the Northern Territory – home of both the Ichthys and Darwin LNG projects. Western Australia has become the giant, with almost 60% of production. Australia's LNG industry has grown rapidly in the past few years, and suffered a few growing pains in the process, such as dragging up domestic gas prices on the east coast. But the glut of new LNG projects has also flooded the world market, and that, coupled with the demand contraction caused by the Covid pandemic, has led to many of the remaining projects such as Burrup and Barossa being deferred this year. Gas condensate production has also significantly added to Australia's liquid fuel output, but gas processing again does not generate major volumes of sulphur. Some of Australia's gas is classified as sour, but this is mostly due to the presence of carbon dioxide rather than hydrogen sulphide. Typical values for H_2S content of Australian gas are around 150 ppm or less, a permissible level, and so sulphur recovery from LNG is not a major factor in domestic sulphur production.

Metals processing

In terms of sulphur in all forms, it is Australia's metals processing industry that both consumes and produces most of Australia's sulphur, as sulphuric acid. A number of base metals smelters generate considerable volumes of sulphuric acid. European metals company Nyrstar operates two smelters in Australia; a zinc smelter at Hobart in Tasmania and a lead smelter at Port Pirie north of Adelaide. According to Nyrstar, Port Pirie produced 97,000 t/a of sulphuric acid in 2018, and Hobart produced 347,000 t/a of acid. BHP Billiton has a nickel smelter at Kalgoorlie in Western Australia with a capacity of 740,000 t/a of acid, and a copper smelter at Olympic Dam in South Australia with a capacity of 530,000 t/a of acid. Sun Metals, a subsidiary of Korea Zinc, operates a zinc smelter at Townsville in northern Queensland which produces 360,000 t/a of sulphuric acid. Finally, at Mount Isa in Queensland, Glencore operates a copper smelter which sends its off-gases to a sulphuric acid plant operated by Incitec Pivot Ltd with the capacity to produce 800,000 t/a of sulphuric acid. A further 400,000 t/a of acid can be generated additionally from a sulphur burning plant at the same site, usually when the smelter is not in operation. In total, there is around 3.5 million t/a of sulphuric acid capacity from smelting in Australia.

Acid demand – nickel

Australia has the largest reserves of nickel in the world, with estimated resources of 20 million tonnes, just under one quarter of the world's total. Production in 2019 was around 180,000 tonnes of nickel, down from a peak of around 244,000 t/a in 2012. Virtually all of this is from Western Australia – the state holds around 90% of Australia's nickel reserves, and 95% of economically recoverable reserves. Much of the mined production is from nickel sulphide (komatiite) deposits, but in fact these represent a minority of the nickel reserves, while around 70% of nickel in Australia is found as oxide (laterite) deposits. Laterites tend to have lower nickel grades and be more difficult and expensive to process, but in the late 1990s a shortage of new sulphide deposits Australia to become a pioneer of the high pressure acid leach (HPAL) process to refine nickel laterite ore.

Several projects were initiated at the time – the first HPAL plants since Freeport's Moa Bay operation in Cuba, which began in 1957 – Anaconda Nickel at Murrin Murrin, Preston Resources at Bulong and Centaur Mining at Cawse, all beginning operations in 1998-99, and responsible for a huge boost to Australia's sulphuric acid consumption. Bulong and Cawse, the two smaller plants (9,000 t/a and 10,000 t/a of nickel respectively), were able to be fed in large part by acid from the Kalgoorlie smelter, but a 1.45 million t/a sulphur burning acid plant was built to feed production at Murrin Murrin. However, in spite of the boom in Chinese nickel demand for stainless steel production over the first decade of the 21st century which kept prices buoyant, the three producers all struggled with technical issues. Bulong was the first to close, going into receivership in 2002, and Cawse, after selling up first to OM Group and then Russia's Norilsk Nickel, closed in 2008. Anaconda Nickel went through a financial restructuring, re-emerging as Minara Resources, which was eventually bought by Glencore. By this time however Murrin Murrin had finally mastered the HPAL process and operations stabilised, reaching 80% of capacity in 2009. Nor did this experience put investors off – Australia's HPAL producers were joined in 2008 by a long-delayed BHP project at Ravensthorpe. In its first incarnation, Ravensthorpe also only operated to 2009 before being sold to First Quantum Minerals, who refurbished and reopened it in 2011. Ravensthorpe also includes a 1.45 million t/a sulphur burning acid plant.

The nickel industry did not go the way that the HPAL developers expected, however. Cheaper ways were found of processing laterite deposits to produce so-called nickel pig iron (NPI), and NPI producers in China, using cheap ores shipped from Indonesia, rapidly ramped up production for stainless steel use, sending nickel prices lower and undercutting more expensive HPAL production. The slow winding down of the Chinese economy during the 2010s also contributed to lower than expected demand for nickel, and by the end of the decade both Australian HPAL producers were struggling – Ravensthorpe was idled in 2017.

However, a combination of circumstances has begun to radically reorder the nickel industry. In the first case, Indonesia has banned export of low grade nickel ores as it tries to capture more value from domestic downstream processing, removing a significant chunk of supply, at the same time that demand for higher grade nickel – so-called Class 1 nickel – is expanding rapidly to feed battery production for electric vehicles. There is a projected global shortage of Class 1 nickel from 2024 onwards as new battery plants start up. At the moment, the only way of generating Class 1 nickel from laterite ores is via HPAL, and this has been a shot in the arm for HPAL producers. First Quantum have restarted production at Ravensthorpe, with the acid plant beginning operations in March this year. Production for 2020 is expected to be between 15-20,000 tonnes of nickel, rising to 25-28,000 t/a for 2021 and 2022, requiring up to 800,000 t/a of acid and consequently 250,000 t/a of sulphur.

New projects

Renewed interest in HPAL is driving new projects in Indonesia and the Philippines, and there are also new projects under development in Australia. One of these is the Clean TeQ Sunrise Project in New South Wales. Clean TeQ is aiming to produce an average of 20,000 t/a of nickel and 4,500 t/a of cobalt (as sulphates), as well as 80 t/a of scandium oxide and an estimated 80,000 t/a of ammonium sulphate production. The $1.4 billion project will include a sulphur burning acid plant to feed the HPAL autoclaves. Originally the Metallurgical Corporation of China was an investor, but parted company with Clean TeQ in 2019 and the project is looking for new partners. The definitive feasibility study was completed in 2018 and an early works programme was finalised this year. Clean TeQ says that the ore body has a low acid consumption compared to other HPAL projects, and at capacity should require 660,000 t/a of sulphuric acid. Although the split with MCC has put timings back (construction was originally scheduled to begin next year for completion in 2023), Clean TeQ hopes to be able to able to move forward with a final investment decision as soon as a partner is found.

Australian Mines is also developing a cobalt-nickel-scandium project at Sconi in northern Queensland. The company built a demonstrator plant in Perth to showcase the technology last year, and aims to scale this up to produce 12,000 t/a of nickel. There is also a company called Ardea Resources, looking to develop an HPAL plant in Goongarrie, Western Australia, to produce 9,300 t/a of nickel – Ardea is also looking to a sulphur burning acid plant. Both projects are also looking for offtake agreements and financial partners before moving forward, however.

In addition to these, BHP is planning to produce nickel sulphate at its Nickel West site at Kwinana. Powdered refined nickel from the nickel smelter will be reacted with sulphuric acid from the Kalgoorlie smelter to produce nickel sulphate for battery use. Phase 1 will produce 100,000 t/a of nickel sulphate and is under construction.

Uranium

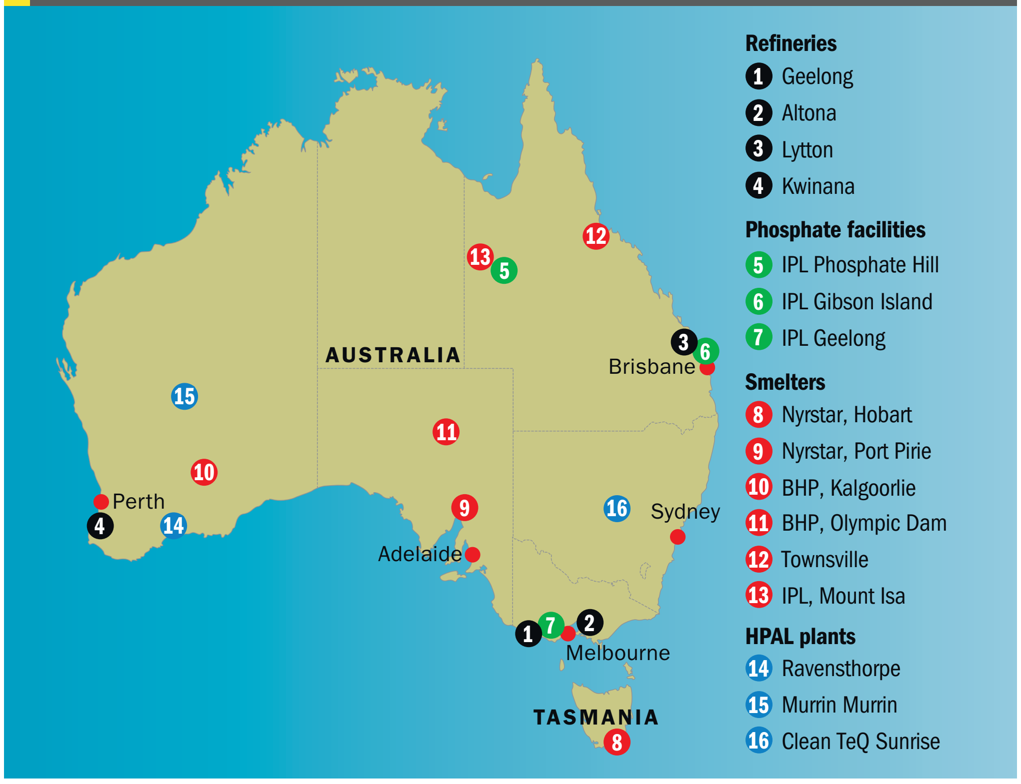
Australia is also the world's largest holder of uranium reserves. It is the world's third largest producer after Kazakhstan and Canada, at 7,800 t/a of U3O8 in 2019. Almost all production comes from three mines; Olympic Dam, Ranger and Four Mile. BHP uses an acid leach to recover the uranium from the ore at Olympic Dam; about 80% of the uranium is recovered in a conventional acid leach of the flotation tailings from copper recovery and most of the remaining 20% is from acid leach of the copper concentrate also produced at the site, with the acid coming from the nearby smelter. Ranger, in Northern Territory, also uses an acid leach to recover uranium.

Phosphate production

Australia's large acreages of farmland make the country a significant consumer of fertilizer. Australia produces about half of its fertilizer needs. According to Fertilizer Australia, the country's phosphate fertilizer capacity includes 2.5 million t/a of phosphate rock mining, 1.2 million t/a of diammonium phosphate and 350,000 t/a of single superphosphate. CI Resources also operates a phosphate mine on Christmas Island, an Australian territory south of Indonesia, but the mine there is nearly exhausted and expected to close in the next few years.

Incitec Pivot Ltd (IPL) is Australia's largest fertilizer manufacturer and its only significant phosphate producer. The company's largest site is at Phosphate Hill, Queensland (see Figure 1), where it has the capacity to produce 950,000 t/a of finished phosphates. Phosphate rock comes from Australia's only operating phosphate mine, the Duchess Mine 150km north of Phosphate Hill. Ammonia for MAP/DAP manufacture is produced on-site, and sulphuric acid is brought in from the smelter at Mount Isa, 160 km north.

Fig. 1: **Australian sulphuric acid production and consumption**



IPL also operates a single superphosphate (SSP) plant at Geelong, Victoria, with a capacity of 350,000 t/a. The company's other SSP plant, at Portland, closed last year with the loss of 180,000 t/a of SSP capacity. Sulphuric acid to operate the SSP plant comes from Nyrstar's zinc smelter in Tasmania (see above).

New phosphate projects

There are a number of phosphate projects under development in Australia. The furthest advanced is the Ardmore phosphate project in Queensland, being developed by Centrex Metals. Centrex completed work on building a 70 t/h processing plant at the site late last year, and was due to begin mining when prices fell and the company decided to defer start-up. The site was to have produced 800,000 t/a of phosphate rock concentrate at capacity, although customers were likely to be overseas. New Zealand's Ballance Agri-Nutrients had trialled the concentrate in SSP production.

Other phosphate developments include Verdant Minerals' Ammaroo phosphate project, sited 300km north-east of Alice Springs, Northern Territory. This is also aimed at producing phosphate rock concentrate for export (via Darwin), and was targeting up to 2 million t/a of output. Permits have been secured, but the company was taken over last year by UK-based CD Capital. Financing for the project remains ongoing.

Finally, Avenira owns the Wonarah phosphate project in the Northern Territory, one of the largest known phosphate deposits in Australia. A phosphate mining project has been under development there for over a decade, but Avenira is cash strapped due to its Baobab phosphate project in Senagal and Wonarah is on hold for now.

New demand for sulphur

With little domestic sulphur production, Australia was a major importer of sulphur for phosphate processing in the 20th century. However, closure of many of the phosphoric acid plants and the rise of domestic metal smelting capacity pushed sulphur imports to a minimum before the start-up of the HPAL plants in the early 2000s. In 2014, when both Murrin Murrin and Ravensthorpe were operating at high rates, sulphur imports had risen back to 1.2 million t/a, until 2017 when Ravensthorpe was idled. The re-start of Ravensthorpe this year will see sulphur imports increase again, and the diversion of Kalgoorlie smelter acid to nickel sulphate production may also mean increased acid imports – Australia imported a net 160,000 tonnes of acid in 2018. At the moment the new HPAL projects are still dependent upon finding funding, but with a projected Class 1 nickel shortage from 2024, when these plants would be starting up, the prospects of additional sulphur demand from 2024 onwards currently looks quite possible.

Sulphuric acid leaching

PHOTO: TENOVA

There was a rapid increase in sulphuric acid demand for copper, uranium and nickel leaching from 1995-2015, but over the past few years growth in this sector has slowed dramatically. Now however there are signs that demand is starting to pick up again with several new projects under development.

Metal oxide ores are often treated with sulphuric acid to recover the metal as a soluble sulphate. This leaching process is a major consumer of sulphuric acid, accounting for just over 10% of all acid demand in 2018, and consuming over 27 million t/a of acid. While precious metals and rare earths processing accounts for a small proportion of this, the three key demand sectors are copper, nickel and uranium.

Copper

Copper's use of sulphuric acid for leaching consumes around 15 million t/a of sulphuric acid. This figure grew rapidly in the early years of the 21st century, particularly in Chile, Peru and the USA. Hydrometallurgical recovery using solvent extraction/electrowinning (SX/EW) became a favoured technique because it can access lower grade ores in an economic manner, it is a relatively easy and simple technique, and avoids the high capital costs of smelting. However, it also generates acidic waste which must be treated, and it is often easier to idle in periods of low metal prices, something which became apparent when copper went through a period of low prices in 2015-2017, and a number of SX/EW plants were shut down.

There are few large copper mines now that run purely on SX/EW, and most are part of a combination with conventional concentrates production, with SX/EW often being used on lower grade mine tailings. Production from the largest SX/EW producer, Chile, is set to fall over this decade, as old mines become exhausted. This year Cochilco, the Chilean Copper Commission, forecasts that the country will recover 1.54 million t/a of copper via SX/EW. But by 2025 this is expected to fall to 1.34 million t/a, and by 2030 Chile will produce only 0.75 million t/a of copper by SX/EW; less than half its current value. In terms of overall copper output, this will be more than compensated for in Chile by a rise in copper concentrates production, but for sulphuric acid it will mark a decisive change in Chile's acid consumption, and possibly an end to Chile as a major importer of merchant acid. Whether it will also drive Chile to build more domestic smelter capacity remains to be seen.

Set against this fall, there is a new wave of SX/EW projects, together with re-starts of previously shuttered projects which are driving new consumption in places such as Mexico, Indonesia and the Democratic Republic of Congo and Zambia in southern Africa's 'copper belt'. In the United States, Freeport-McMoRan is starting up its new Lone Star mine in Arizona which will aim to produce 100,000 t/a of copper in its initial phase via SX/EW, with the potential for further expansion. However, overall, the International Copper Study Group forecasts that these will only just about balance reductions in SX/EW production from Chile out to 2023, with a slight overall uptick towards the end of that period to a total of 5.2 million t/a of copper from the current approximately 4.8 million t/a.

Nickel

Nickel oxide ores are not the most favoured for nickel production because they tend to be lower grade and more difficult to extract. However, in the 1990s a lack of available sulphide ore bodies led to a move towards nickel leaching via the aggressive high pressure acid leach (HPAL) process. In the 2000s, nickel demand for sulphuric acid leaching was mainly provided by the long standing Moa Bay HPAL plant on Cuba, together with four new projects in Australia (see our article elsewhere in this issue) at Cawse, Murrin Murrin, Bulong and Ravensthorpe. Technical difficulties and high operating costs led to two of these shutting down that decade, but at the same time other HPAL projects, in the Philippines, Papua New Guinea, New Caledonia and Madagascar were also under development, and all began ramping up production during the period 2010-2015. As a consequence, sulphuric acid demand for nickel processing rose rapidly during this period, almost tripling in five years to reach around 8 million t/a, most of it provided by dedicated sulphur-burning acid plants near the HPAL unit (although the first Philippine project, operating by Sumitomo, uses surplus acid from Sumitomo's smelters in Japan).

By the late 2010s, however, Chinese demand for nickel, mostly for stainless steel, began to move towards use of so-called nickel pig iron (NPI), an iron-nickel amalgam which can be produced relatively simply from lower grade iron-bearing nickel ores. This surge in NPI depressed nickel prices, and meant that most of the HPAL plants ended up operating at a loss. This led to the closure of Ravensthorpe in 2017, although it has since reopened this year. Two factors have turned this situation around. The first is Indonesia's ban on exports of low grade nickel ores, meaning that Chinese NPI producers have had to set up ferronickel operations in Indonesia instead, temporarily decreasing nickel supply and increasing costs. The second has been the need for pure grades ('Class 1') nickel for battery production, with an anticipated surge in electric vehicle (EV) production responsible. As HPAL is the leading process for producing Class 1 nickel from low grade laterite ores, there has been a huge increase in interest in the process and many new projects looking for funding.

Nickel demand for battery uses is growing rapidly. This year it is expected to be around 120,000 t/a, or about 5% of the nickel market, but by 2025 demand is forecast to be over 530,000 t/a, which will represent more than 20% of the nickel market at that time. Many countries are phasing out production of internal combustion engine vehicles from 2030 or 2040, and some earlier than that. CRU estimates that 2/3 of all new nickel demand out to 2040 will come from the EV battery sector.

Nickel prices have risen from a low of $9,500/tonne in 2017 to an average of $12-13,000/t (and peaks of $16,000/t), and a growing shortage of Class 1 nickel is forecast out to 2025, sufficient to justify investment in new HPAL capacity.

At the moment much of the interest in new HPAL production is in Indonesia, the world's largest nickel miner – there is a ready source of ore from existing mines, and the government is keen to encourage downstream processing to capture more value from them. There is heavy Chinese investment in these plants, as China is looking to massively increase EV use this decade. New projects under development currently include:

- PT Halmahera Persada Lygen, a joint venture between Harita Group and Ningbo Lygend at Obi Island) – 37,000 t/a of nickel capacity due on-stream in late 2020.
- Tsingshan, GEM and CATL at Morowali on Sulawesi – 50,000 t/a of nickel capacity, due for start-up in late 2021.
- The PT Huayue Nickel Cobalt joint venture between Zhejiang Huayou, Qingchuang, Woyuan, and IMIP, again at Morowali on Sulawesi – 60,000 t/a of nickel capacity, also claiming a 2021 timeframe for start-up.
- Sumitomo and PT Vale Indonesia at Pomalaa on Sulawesi – 40,000 t/a of nickel capacity scheduled for about 2025.

Outside of these projects, there are also considerable interest in Australia, which actually has the world's largest nickel laterite reserves. As discussed in our article this issue, these include the 20,000 t/a Clean TeQ HPAL project in New South Wales, a 12,000 t/a HPAL project for Australian Mines in Scandi, Queensland, and the 9,300 t/a Ardea Resources project at Goongarrie in Western Australia.

These projects are all currently seeking funding, but more certain are two other HPAL projects – an expansion at the Metallurgical Corporation of China (MCC) Ramu nickel mine on Papua New Guinea, which will add 35,000 t/a of capacity. Ramu is one of the few HPAL plants that has performed according to schedule. In Brazil, there is also an 18,000 t/a HPAL project (in Phase 1) being developed by Horizonte at Vermelho. Horizonte is targeting start-up in 2025 for Vermelho, along with a large scale ferronickel project nearby at Araguaia.

The raw material for batteries is actually nickel sulphate, and so as well as HPAL, companies are looking at other ways of producing nickel sulphate, either from recycling existing batteries or processing industrial waste streams, and this again occasionally requires sulphuric acid. In Australia, BHP is planning to produce nickel sulphate at its Nickel West site at Kwinana by acidifying nickel dust using sulphuric acid.

Uranium

Uranium recovery usually requires a leach step, often by pumping a leaching agent into the ore body itself (in situ leaching or ISL). Various leach agents are used, according to the rock type, including hydrogen peroxide or alkali hydroxides, but the most common is sulphuric acid. This has been used particularly in Kazakhstan, where the limestone-heavy rocks consume large quantities of sulphuric acid in the leach, using sulphur bought from the various sour oil and gas projects around the Caspian Sea. Current global demand for uranium is about 67,000 tU/a according to the World Nuclear Association. About 46% comes from conventional mine, 50% from in situ leach, and 4% is recovered as a by-product from other mineral extraction (copper or phosphates). Uranium leaching consumes around 4 million t/a of sulphuric acid, with Kazakhstan accounting for about 60% of that. Global uranium consumption was hit heavily by the Fukishima nuclear accident in Japan, which led Japan, a major nuclear power producer, to essentially close down its entire nuclear industry and switch to gas. However, countries such as France and the US have now delayed plans to phase out nuclear generation capacity, and the World Nuclear Association now forecasts a 15% increase in nuclear energy generation this decade, with most of the new capacity additions in China and India, leading to a modest increase in sulphuric acid consumption.

Nickel the star again?

With only modest increases forecast from new uranium and copper leaching, it is clear that any significant growth in acid consumption from this sector is likely to come from nickel HPAL plants. A note of caution must therefore be sounded, as these projects are expensive and technically challenging and temperamental, and historically have often taken several years to reach even 80% of nameplate capacity. The nickel market has been very volatile, with new techniques and political decisions like Indonesia's ore export ban driving prices up and down. However, the need for batteries for electric vehicles is a compelling commercial justification at the moment. In the period 2010-2015, acid consumption for HPAL nickel plants rose by more than 5 million t/a, and the rush of new HPAL capacity could see this repeated or even exceeded this decade. Most of these plants will include dedicated sulphur burning acid plants, and sulphur consumption in southeast Asia and Australasia will therefore rise accordingly. ■

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46
47 48 49 50 51 52

Sulphur forming project listing 2020

Sulphur's annual listing of new or recently completed sulphur forming projects worldwide covers both new sour gas and refinery sulphur forming projects as well as upgrades at existing units.

System manufacturer/ supplier	Operating company	Operating site	Units	Product type	Scheduled throughput	New project/ expansion	Scheduled completion
BAHRAIN							
Enersul	Bapco	Sitra	3	granule	1,500 t/d	new	2020
BELGIUM							
IPCO	Duval	Antwerp	n.a.	pastille	n.a.	new	2020
CANADA							
Enersul	Keyera	n.a.	2	prill	4,400 t/d	new	2022
Matrix PDM	Heartland Sulphur	Scotford	1	prill	2,000 t/d	new	2020
CHINA							
Enersul	PetroChina	Anyue	2	granule	700 t/d	new	2019
EGYPT							
IPCO	Midor	El Amreya	3	pastille	230 t/d	new	2021
INDIA							
Enersul	HPCL	Vizag	2	granule	1,000 t/d	new	2021
ITALY							
IPCO	Econova	n.a.	3	pastille	580 t/d	expansion	2020
IPCO	Econova	n.a.	1	granule	700 t/d	new	2021
KAZAKHSTAN							
Enersul	Caspian General Contr.	n.a.	3	granule	1,500 t/d	new	2020
KUWAIT							
Enersul	KNPC	Mina al Amina	1	granule	1,200 t/d	expansion	2020
Enersul	KNPC	New Refinery Project	4	granule	4,800 t/d	new	2020
MALAYSIA							
Enersul	Petronas RAPID	Pengerang, Johor	5	granule	2,000 t/d	new	2021
OMAN							
IPCO	Duqm Refinery	Duqm, Oman	3	granule	900 t/d	new	2022
QATAR							
Enersul	Qatargas	Ras Laffan	2	granule	2,400 t/d	expansion	2020
RUSSIA							
Enersul	Syzran Refinery	Samara	1	granule	350 t/d	expansion	2021
SINGAPORE							
Enersul	SPCA Advance Pte. Ltd	Singapore	4	granule	2,400 t/d	new	2022
SPAIN							
Enersul	Petroleos del Norte	Bilbao	1	granule	350 t/d	expansion	2020
THAILAND							
Enersul	Thai Oil	Sriracha	3	granule	1,500 t/d	new	2022
TURKEY							
Enersul	Aegean Refinery	Aliaga	3	granule	1,050 t/d	new	2019
US VIRGIN ISLANDS							
Matrix PDM	Limetree Bay Refinery	St Croix	1	prill	1,000 t/d	new	2020

Sulphur dust control through suppression

Fugitive dust emissions during the handling and storage of formed sulphur can result in negative environmental impacts and under specific conditions result in an explosion hazard. Enersul has developed a dust suppression system specifically targeted at controlling sulphur dust particles. The Enersul SafeFoam Transfer System (STS) reduces sulphur fines at critical transfer points throughout any sulphur handling system, resulting in a significantly safer and more environmentally friendly sulphur handling system.

Sulphur deficiency in arable soil has been becoming a major concern in the agricultural industry in recent years. Factors contributing to sulphur deficiency in soils include the fact that more sulphur is being removed from the soil due to the increase in agricultural production and less sulphur is being added back into the soil due to the use of sulphur-free fertilizers and lower sulphur dioxide emissions throughout the world. Sulphur is an essential nutrient required for plant growth and sustainability. Sulphur deficient soils produce crops that are both low in yield and in quality. Use of sulphur fertilizer helps to overcome these potential problems, increases overall fertilizer efficiency and consequently results in better economics for the producers.

Sulphur by nature is a combustible element and care must be taken during the handling and storage of solid sulphur. In any material handling process there is potential for dust formation due to shifting of product from one location to another. Fugitive dust emissions during the handling and storage of formed sulphur can result in negative environmental impacts and under specific conditions can engender an explosion hazard. A dust explosion will occur when fine dust in a certain concentration suspended in air is ignited. Combined with a confined environment, the burning mixture will release large quantities of harmful gaseous product, resulting in a pressure rise and therefore a possible explosion. The LEL (lower explosion limit) for sulphur dust particles in air is 35 g/m^3, making sulphur dust one of the easiest ignited materials found in the bulk handling industry. Sulphur dust clouds found above the lower explosion limit of 35 g/m^3 also have a very low ignition energy of 15 mJ; this means that that these dust clouds can be set off with the presence of a frictional or static spark, which is a common occurrence during the handling of solid sulphur. As mentioned earlier, the initial explosion will occur within a confined environment, but if the reaction from this initial explosion disturbs settled layers of dust in the surrounding area it can cause a secondary, much bigger explosion. Lack of consideration in sulphur handling can be costly economically, but it can also become a major safety issue. It is critical to put careful consideration into both the design of material handling systems and proper mitigation operational procedures.

The design of the material handling system must be carefully examined and standard precautions should be taken to eliminate any potential risks. The focus needs to be on reducing the potential for the creation of fines (particles less than 500 µm in diameter) and keeping any fines that are generated from becoming airborne. The design and operation of storage and handling facilities needs to recognise the importance of regular housekeeping to keep the plant running safely, limiting the amount of horizontal surfaces where dust can build up, using rubber and non-sparking material for conveyor belt material, designing electrical equipment for the proper hazardous area zones and never using compressed air to remove dust from a surface as this can create dust clouds. Other considerations should look at minimising the drop heights at product transfer points, and application of dust suppression systems should be considered.

Even after efficient design, dust generation cannot be completely eliminated and hence must be controlled. The two main dust control system available are dust collection and dust suppression. Dust collection is usually done by one of two methods, by using a dry dust collector or by using a wet dust collector which is also known as a wet scrubber system. Both of the dust collection techniques have distinct benefits and drawbacks. The wet dust collector is an objectively effective and safe mechanism for collecting sulphur dust. The wet scrubber system collects dust at the point of application, uses water to capture this dust in an air stream and then releases the collected dust in the form of a slurry byproduct. The issue with this solution is that the slurry byproduct is very corrosive to any metallic plant equipment it comes into contact with and that it requires proper disposal. The dry dust collector also collects dust at the point of application, but it does not use any water so there is no slurry byproduct. One major issue with the dry dust collector is that it captures fine sulphur dust particles in a confined environment and consequently provides the conditions for a possible explosion to occur. This issue generates the need for either use of

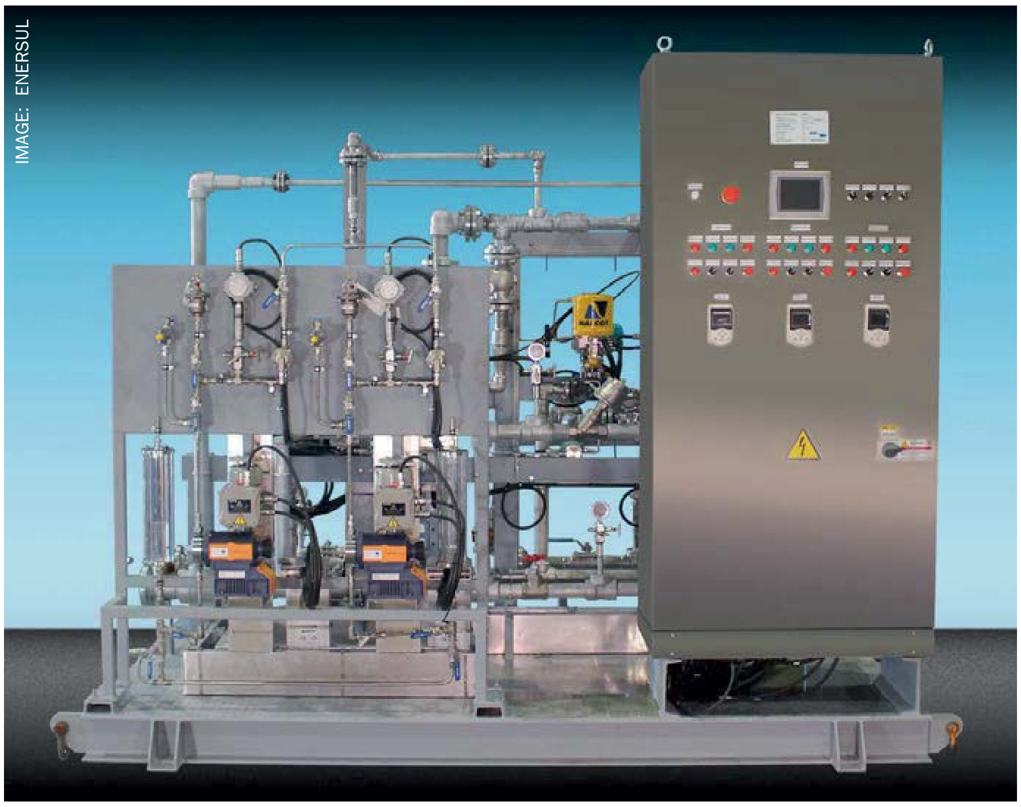


Fig. 1: Modular dust suppression skid.

IMAGE: ENERSUL

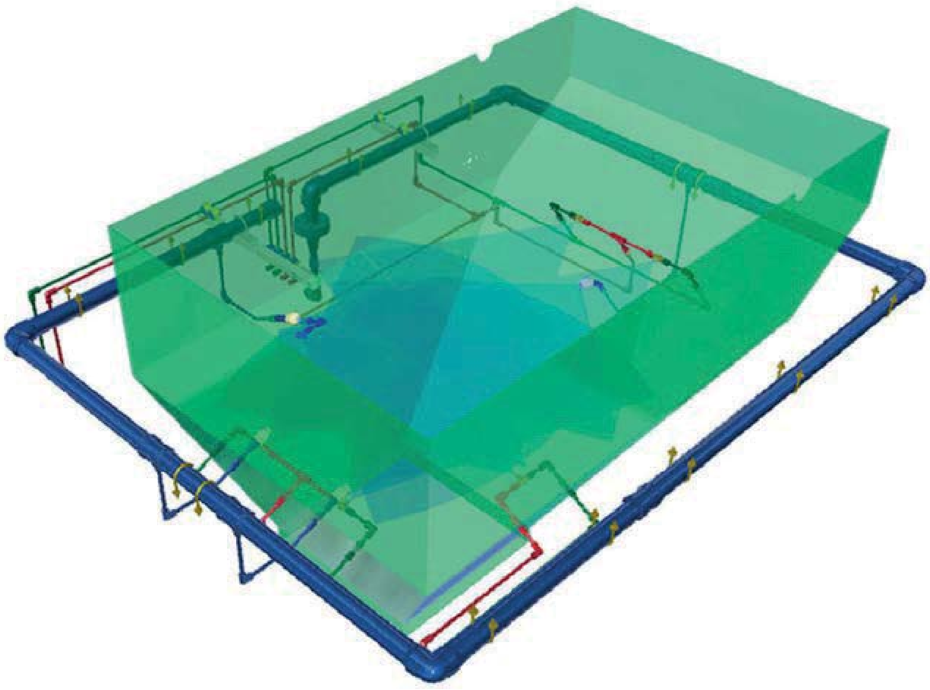


Fig. 2: Typical spray pattern.

explosion venting to provide a controlled release mechanism or the use of a gas inerting system to suppress the explosions. Explosion venting does not get rid of the explosion problem, it is only used as a protection measure and gas inerting is a highly complex system itself. There are very high operating and maintenance costs associated with both of these systems and therefore this is not the most economical or preferred solution for controlling sulphur dust.

In place of dust collection there is another means of dust control; dust suppression systems. This method looks at controlling the propagation of the dust and ensuring that it does not become airborne. There are many dust suppression systems available in the market but the major drawback of most of these systems is that they use large quantities of water to suppress the dust. There are a few issues with using large amounts of moisture to suppress the dust. First of all the combination of moisture and elemental sulphur can be very corrosive to steel and therefore this may largely affect the lifetime of the equipment and plant. Corrosion further produces a byproduct of iron sulphide, which when mixed further with wet bio-oxidised elemental sulphur forms a dangerous hydrogen sulphide gas. Presence of hydrogen sulphide is a huge safety concern which must be closely monitored and controlled.

In response to increasingly stringent environmental and safety standards Enersul has developed a SafeFoam Transfer Dust Suppression System called STS, specifically targeted at controlling fugitive sulphur dust. This system uses a 1:100 water chemical mix to control the dust, which minimises the amount of additional moisture added to the product and also provides a coating that adheres to the product for a longer duration of time, allowing the product to be transported through the system without the need for additional dust suppressant application.

The innovative aspect of Enersul's system, along with the modular skid and dust suppression chemical, is the arrangement of the nozzles. The nozzles are sized to generate adequate fineness of mist and are arranged in such a manner to be able to coat majority of the fines resulting in a high degree of dust suppression. The chemical leaves a thin layer on the product and degrades only marginally with time. Enersul generally does not design the system as a one-size-fits-all application that is simply placed at all transfer points and results in over-coating the product with dust suppression chemical; rather Enersul uses its many years of experience to assess the material handling system and recommend the best location for dust suppression to be applied. The key to effective dust suppression is not to drench the product in dust suppression chemical at each transfer point, this can lead to high chemical costs and objectionable increase in moisture content of the product; instead application at selective locations is most effective.

STS description

Water and chemical are mixed in a ratio of 100:1. This mixture is piped to a header mixing chamber at the selected transfer points where air is injected to convert the mixture to foam. This foam is then discharged through the spray header nozzles and is applied to the product. Fig. 1.

shows the modular dust suppression skid which is used for the metering and control process.

Chemical supply system

Dust suppressant chemical is pumped from chemical storage tanks to the common water/chemical header by a metering pump. The chemical mixes with the stream of water and the mixture flows under pressure to the spray header installed at individual dust control points.

Water supply system

Plant water is generally utilised for the dust suppression system. An on-skid water pump is used to boost the water pressure to an optimum level (3 barg) as required for foam formation.

Atomising air system

Plant service air is utilised for atomising the water/chemical mix and spraying it at the right amount of pressure to capture the fugitive dust at the various installation points. The required pressure for effective atomisation is around 7 barg which is finalised during commissioning based on water flow rates. Fig. 2. Shows a typical spray pattern at an application point.

System control

A local PLC is used to monitor pressures, flow rates, and liquid levels. These parameters are used to control the water flow rate and detect anomalies such as nozzle plugging. Should any adverse conditions develop, the PLC will automatically provide system alarms to warn the system operator of the process variations outside normal parameters.

Benefits of STS

The benefits of the STS dust suppression system:

- "foam" stays with sulphur granules during transport and storage;
- minimises additional moisture content;
- minimises operating costs;
- product is applied based on actual product loading rate;
- drastically reduces adverse environmental impact;
- eliminates empty belt spraying.

The SafeFoam Transfer System skid is pre-assembled and shipped ready to be installed on site. Transportation and construction are consequently much easier as each unit arrives on site 90% assembled. This reduces not only assembly time and costs but also commissioning time; as most system checks are completed prior to shipment.

Sulphur inherently needs proper care. Due to the properties of sulphur, using a dust suppression system is the most effective way of controlling fugitive sulphur dust.

Enersul, who has been a leader in the sulphur forming and handling industry for over 60 years has had much experience in both forming and handling sulphur products and has used this knowledge to develop the SafeFoam Transfer System, one of the most effective dust suppression systems specifically targeted at controlling sulphur dust particles.

With the proper material handling procedures in place and effective implementation, the risks associated with sulphur handling can be easily managed and safe plant operations can be obtained.

1 47 2 48 3 49 4 50 5 51 6 52 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46

High capacity, low maintenance continuous drum granulation.

PHOTO: IPCO

IPCO's first drum granulation plant in Europe

IPCO provides an update on its latest activities, with flexible processes enabling IPCO's project for the first drum granulation plant in Europe to remain on track despite unprecedented Covid-19 restrictions.

IPCO, one of the world's leading suppliers of sulphur processing and handling systems, is working to deliver what will be its first mid-capacity drum granulation plant in Europe. The project, scheduled for commissioning in Q3/Q4 2020, remains on track despite restrictions imposed due to the coronavirus pandemic.

IPCO's SG20 sulphur granulator has a solidification capacity of 500-800 t/d. Based on rotating drum technology, this sulphur granulator is a fully automated process delivering high productivity 'once through' performance and a uniform end product of a definable size.

The company also produces an SG30 model, a unit capable of granulating up to 2,000 t/d, the highest capacity solution available to the sulphur processing industry.

Seed or nuclei particles of solid sulphur are generated outside the drum by freezing sprays of liquid sulphur in a water bath at controlled pressures to form the desired size range. These particles are then augered into a slowly rotating drum with appropriately placed flights attached to its inner surface. The flights create curtains of particles inside the drum as well as gently moving them towards the discharge end.

As the nuclei particles travel along the drum, they are progressively enlarged to the required size by means of sulphur sprayed from a bank of nozzles running the length of the drum. The temperature in the drum is moderated by the evaporation of water from spray nozzles located inside the drum.

A fan is used to draw a stream of air through the drum to sweep out the water vapour as well as any fugitive dust inside the drum. The dust is scrubbed out of this exhaust stream using a wet scrubber before the process air stream is released to the atmosphere.

The underflow from the wet scrubber cyclone is pumped to the same settling/dewatering tank that is used to generate the seed particles. Here the fines settle out and are augered up along with the sulphur particles generated by the seed generator sprays.

IPCO sulphur granulators are supplied prefabricated for quick and easy installation, and are designed to offer high productivity with low maintenance requirements. A simple design with minimal rotating equipment enables continuous operation with no need for routine shutdown, while the horizontal 0° drum minimises stress to keep maintenance requirements low. No sulphur pre-conditioning is required and no solid waste streams or liquid effluents are produced.

The spherical shape of the granules, along with the repeated spraying and cooling of thin layers of molten sulphur as they pass through the granulator, accommodates the natural shrinkage of the product as it completes the transition from melt to solid, without weakening the product.

SUDIC quality product

The SG20 will produce a high quality product that satisfies the shape criteria and Stress Level I and II friability parameters of the SUDIC product specification. This ensures efficient, clean and environmentally safe storage and handling during transportation (formed sulphur can be handled as many as 15 times between solidification and subsequent reprocessing).

Another major factor in terms of achieving SUDIC specification is moisture content; excess moisture not only adds weight, leading to unnecessary transportation and melting costs, but also results in increased acidity, causing corrosion in conveyors, silos, trucks, rails cars and ship holds. A 'wetter' product is also more susceptible to freezing into lumps during cold weather, a significant factor in colder climates.

According to the SUDIC definition, quality sulphur will meet the specifications shown in Table 1 21 days after forming.

Table 1: **SUDIC quality sulphur specification 21 days after forming**

Mean size	between 2 and 5 mm
Size distribution	less than 5% larger than 6.3 mm
	minimum 75% smaller than 5.6 mm
	minimum 75% larger than 2.8 mm
	less than 2% smaller than 1.18 m
	less than 0.5% smaller than 0.3 mm
Moisture	less than 0.5% by weight
Friability	less than 1% fines (< 0.3 mm) under stress level I
	less than 2% fines (< 0.3 mm) under stress level II
Bulk density	1,040 kg/m^3 loose, 1,200 kg/m^3 agitated
Angle of repose	not less than 25°
Compaction	below 0.2% fines by weight (< 0.3 mm) under static load
	below 0.5% fines by weight (< 0.3 mm) under dynamic load

Source: IPCO

PHOTO: IPCO

Premium Rotoform solidification for small to medium capacity requirements.

Complete family of sulphur processing and handling systems

The development of the SG sulphur granulator family is just the latest addition to a range of sulphur solidification and handling systems that began in 1951 with the installation of a continuous sulphur slating line at an oil refinery in Mexico.

IPCO has since expanded its capabilities to encompass equipment for liquid sulphur degassing (capable of reducing hydrogen sulphide to less than 10 ppm), molten loading for truck and rail, downstream storage and reclamation, as well as bulk loading for truck, rail and ships.

In terms of solidification, systems are available to meet all throughput requirements. Block pouring offers a practical and economical solution for the medium to long term storage of high volumes of sulphur, and IPCO can provide a full consultancy service as well as the physical equipment such as pouring towers and forms. Complementing this is a range of low maintenance, skid-mounted remelters with predictable, high capacity throughput.

Rotoform sulphur pastillation systems

For small to mid-size capacity solidification requirements, IPCO's proven Rotoform system is a single step, liquid-to-solid process that, like the SG granulators, produces a SUDIC-quality premium product. The uniform shape and size of Rotoform pastilles makes them free-flowing for easy handling, while high bulk density is a major advantage in terms of storage and transportation.

With more than 750 installations completed to date, Rotoform is the world's most widely used process for the production of premium quality sulphur. While the basic operating principle has remained unchanged since the first model was introduced in the 1980s, the Rotoform family has undergone constant improvement and the latest models specially designed for sulphur processing are the Rotoform S8, with a capacity of 140 t/d, and the Rotoform HS, a high speed model with a capacity of up to 350 t/d.

The Rotoform consists of a heated cylindrical stator, which is supplied with molten sulphur via heated pipes and filter, and a perforated rotating shell that turns concentrically around the stator. Drops of the product are deposited by the nozzle bar across the whole operating width of a continuously running stainless steel belt.

A system of baffles and internal nozzles built into the stator provides uniform pressure across the whole belt width, providing an even flow through all holes of the perforated rotary shell. This ensures that all pastilles are of uniform size, from one edge of the belt to the other.

The rotation speed of the Rotoform is synchronised with the speed of the steel cooling belt to allow gentle deposition of the liquid droplets onto the moving belt. Heat released during cooling and solidification is transferred via the steel belt to cooling water sprayed underneath.

This water is collected in tanks and returned to the water recooling system; at no stage does it come into contact with the product.

After the drop has been deposited onto the steel belt, any product residue on the outer shell is returned to the Rotoform via a heated refeed bar which keeps the outer shell clean.

The sulphur droplets are then discharged as solid, hemispherical pastilles at the end of the cooling system. To eliminate the possibility of damage to the pastilles during discharge, a thin film of silicon-based release agent is sprayed onto the steel belt.

This process offers a number of environmental advantages. As the cooling water never comes into direct contact with the sulphur, there is no risk of cross contamination. Secondly, solidification takes less than ten seconds so there is little time for H_2S to escape, resulting in very low emission values. And low levels of sulphur dust levels mean no need for exhaust air treatment.

End-to-end systems and engineering partnerships

IPCO's expertise, gained through nearly 70 years' close involvement with the oil and gas industry, extends to the design, supply and commissioning of complete end-to-end systems covering everything from receipt of molten sulphur to storage and loading of solid material.

The company has partnerned with several international engineering companies that service the petrochemical industry. Activities range from cooperation during FEED (front-end engineering design) to EPC (engineering procurement construction) contracts, and turnkey solutions include liquid sulphur supply, solidification and downstream handling of solid sulphur as well as utility equipment and control systems.

IPCO can also provide what it refers to as its Life Cycle Concept. An extensive after sales service is available to provide customers with continual support throughout the lifespan of the equipment supplied, including inspection and preventative maintenance contracts.

Facing up to the challenges of the Covid-19 crisis

This end-to-end capability, built on an in-depth understanding of customer needs and priorities, has held IPCO in good stead in these unprecedented times, enabling the company to continue to support refineries around the world with both new installation and the servicing and maintenance of existing systems and equipment.

With a local presence in more than 30 countries, IPCO's global service capability has been a key factor in this. By following World Health Organization guidelines and adhering to local restrictions, the company's service teams have been able to provide a basic level of support.

The restrictions on travel and face-to-face meetings due to the coronavirus crisis have driven IPCO to look at new ways of working. For example, client meetings, and many internal ones too, now take place on Teams or Zoom instead of in an office.

IPCO has also been making use of video streaming to offer system trials from its productivity centre in Fellbach, just outside of Stuttgart.

"We had a number of customer visits scheduled for Q2," says Johan Sjögren, Managing Director of IPCO's Equipment division. "Instead of cancelling, we have made use of digital media to allow these customers to assess our systems remotely. Our aim is to try to maintain a level of service as close to normal as the current circumstances permit."

This ability to provide support, reassurance and delivery guarantees has been key to keeping the SG20 sulphur granulator on track. However, with markets suffering understandable uncertainty, other orders in the pipeline have been put on hold. "Previously you would have got on the next plane and flown directly to the customer to clarify the situation but this simply isn't possible now," says Sjögren.

"We all have to get used to new ways of communicating. Flexibility and the ability to think outside the box will be key and we need to demonstrate that we can continue to work effectively and offer customer-oriented solutions."

Industrial Internet Of Things (IIOT)

It is obvious that digitisation will have a central role to play in future ways of working and IPCO had already made significant moves in this direction before the arrival of Covid-19.

"The market is changing," says Johan Sjögren. "Customers are looking for suppliers whose capabilities go beyond the simple provision of hardware, however efficient it might be."

To this end, IPCO has been focusing on the connectivity of its systems, a capability often referred to as the Industrial Internet of Things (IIOT). In this instance, digitisation means offering remote access to the control panel based on a cloud solution, recording and evaluating of process-related parameters, 'messenger' functions and visualisation of maintenance intervals with indication of the required spare parts.

This ability to monitor, collect and analyse information remotely has the potential to transform system performance and productivity, driving efficiencies throughout the sulphur solidification and handling process.

As Johan Sjögren explains: "Access to real-time production data offers a window into the efficiency of a system and can reveal potential for additional capacity. Sensors can enhance safety, providing alerts to issues before they have a serious impact, and machine-to-machine communication can streamline production across every stage of the process, from receipt of molten sulphur, through solidification, to downstream storage and loading."

"We have customers who are looking for production support or even the complete operation of their plant. A combination of digitisation and our existing application expertise will enable us to offer completely new levels of customer care and support." ■


DUPONT
Clean Technologies

Modernisation of an old sulphur forming technology

Kreber's R&D department has been researching the prilling of sulphur in pursuit of the ideal process. In this article, **T. Nieboer** of Kreber recounts the history of prilling up to today, tracing the developments and highlighting the challenges that still remain.

Fig. 1: Example of a modern prilling tower.

Legend has it that one night in 1782, William Watts, a plumber from the city of Bristol in the UK was walking home after a long night of drinking ale. On his way home he decided to take a rest near St Mary Redcliffe church, which he had worked on, helping to renovate the lead roof. As he lay on a bench thinking about his loving wife, who was home alone, he drifted into a sleep full of dreams in which his wife's anger kept haunting him. He saw her towering on top of the church, and in her anger she poured molten lead down the tower onto his face. The lead didn't fall in a stream but instead formed perfect spherical droplets, which rained down upon him in the shape of solidified lead pellets. He woke up to find that it was only the Bristol rain falling down on him.

The next day he decided to experiment and together with his wife climbed the spiral stairs onto the roof of the church. They drilled holes in the bottom of a cooking pan, melted some lead and poured it through the holes. As in the dream, the molten lead formed droplets, which solidified into perfectly spherical lead pellets. These pellets became known as patent lead shot, which was used in shotguns for hunting[1]. Previously, lead shot was produced in a slow and cumbersome moulding process, producing irregular (and expensive to produce) lead balls. Watts, a hobby hunter himself, was so convinced of this production method that he decided to build the world's first prilling tower, right on top of his house[2].

Until this day, spherical products from the chemical industry are produced in very much the same way as it was invented by William Watts; although the process is now known as prilling.

The pan has been replaced with a prilling machine, where the melt is forced through nozzles. From these nozzles, a jet is ejected, which breaks up into spherical droplets and subsequently solidifies in the air. The priller provides greater control of the breakup of the liquid jet and therefore greater control of the process quality and product shape or size. The tower is optionally operated with forced convection and can be equipped with a filter installation or scrubber to counter dust emissions.

Prilling was, and still is, mainly utilised in the world of fertilizers and plastics finishing. These high capacity production processes demand an easy to use and stable finishing technology that can both handle production fluctuations and production of a free flowing product with a narrow particle size distribution (PSD). One of the main reasons prilling is utilised in the market, is that the process requires very few moving parts and is capable of processing very high quantities.

Prilling of sulphur

In the world of sulphur, converting molten sulphur into large quantities of solid particles has always been a challenge. Crushing a solid block into smaller chunks was formerly utilised as the main method of obtaining transportable sulphur pieces. Due to considerable dust formation while handling solid sulphur pieces in this form, the industry started looking for new technologies to form sulphur.

One of the adapted technologies was air prilling, which was already utilised by the fertilizer industry. The finished product from these prilling facilities was large quantities of small, yet perfectly spherical pellets with a polished surface and a relatively narrow PSD, leading to a free flowing product. At this point, when prilling was the most dominant method of producing solid sulphur, the well-known SUDIC specification (Sulphur Development Institute of Canada) was also introduced, leading to a market standard for all sulphur finishing technologies.

The industry developed new ways of production, such as granulation, (steel belt) pastillation and wet prilling, which took over the role of being the most dominant method of particle engineering in the sulphur industry.

This shift in production method was the result of two main concerns[3]. Firstly, the prilling towers designed in the 1960s operated on an open air design. This meant that all cooling air used for solidifying the prills was immediately ejected into the environment. All the dust particles formed during the prilling process, as well as any vapours from the sulphur melt, were transported with the air stream into the environment. This led to environmental problems in the downwind areas of the prilling plant.

Secondly, a disastrous fire incident in the Middle East led to the conclusion that dry prilling should be considered as a high risk technology[4]. The low ignition energy, combined with the potential build-up of static charge in the solidifying prills, can lead to dangerous sparks. The combination of these two aspects, coupled with a hot climate, led to the disastrous incident in the Middle East.

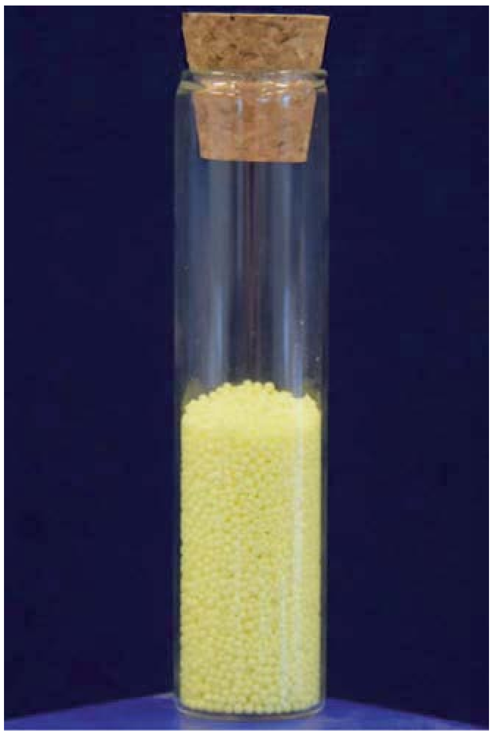


Fig. 2: Sample of sulphur prills.

Safer and more sustainable future

In the last few years, prilling has been under development to handle a wide variety of products. The addition of an air treatment section was applied in the late 1980s, where either a dry filter or wet scrubber is utilised to drastically cut down on (dust) emissions from prilling towers. However, as the environmental impact of all industrial plants on their surroundings became more apparent, laws became more and more stringent on prilling towers. This resulted in a surge of new research on prilling with a closed loop process as one of the main achievements.

In the closed loop process, the cooling medium (in this case air) is first led to an air treatment section and then to a heat exchanger. The resulting cleaned and cooled air can be reused in the tower. The main benefit of closing the loop, is the fact that emissions are reduced to zero. In addition, the heat removed from the cooling medium can be reused elsewhere in the plant, leading to a higher degree of heat integration of the total plant.

Prilling is already widely applied in other industries, where the same hazards with regard to fire and dust explosions exists, mainly near the air treatment section. When applying the closed loop principle, all of the cooling medium is recycled, eliminating the need to use ambient air as the cooling medium. Practically any gas can be chosen as any wastage of the cooling medium will be very limited. Currently, the first prilling towers with inert nitrogen gas as cooling medium have started to emerge, leading to an intrinsically safe method of prilling with no emissions and low fire hazards.

These prilling towers provide a safe and high capacity production method of converting melt into a preferable finished product. These innovations are showing promise in the field of sulphur as well. It is already empirically proven that sulphur prills can be formed and that they have a range of benefits over other finishing technologies. The main challenge now is to alter the closed loop prilling system that is used in the world of plastic and fertilizer prilling, towards a system that can safely handle sulphur.

Future developments

From its origins in the 18th century until now, prilling has gone through many developments. The latest innovations are mainly in the off-gas section and a higher degree of control of the total process, which have led to a safe and trustworthy process to create prills from melt. With their narrow PSD, and free flowing properties, prills have unique product qualities compared to the other main finishing technologies.

Currently, the main challenge is to find a way to prill sulphur in a safe and economical way. Closed loop prilling with an inert cooling medium shows great promise in making this achievable. There are still a handful of challenges to overcome before this stage is reached. Kreber stands ready to pool its resources with any interested party in order to achieve the ideal prilling process that will result in benefits for all involved, whether economically or environmentally.

References

1. Harrison D.: “Dream lead to invention”, Bristol Times, 26 November 2002.
2. Watts W.: “Small Shot”. 1347 United Kingdom, 10 December 1782.
3. D’Aquin J.: “SUDIC 40 years on”, *Sulphur* no. 378, pp. 26-35, Sep-Oct 2018.
4. Kent, J.A. Kent and Riegel’s Handbook of Industrial Chemistry and Biotechnology, Springer Science & Business media, 2010

Caustic scrubbing of molten sulphur vent streams

With increasing frequency, companies that have molten sulphur on site must put environmental controls on the vent streams from molten sulphur pits, storage tanks and loading operations. This article* describes the typical characteristics of molten sulphur vent gas streams as well as some of the important chemistry related to these systems in caustic scrubbers. Solids deposition issues observed in the field with caustic scrubbers operating on actual molten sulphur vent gas streams are presented. Design and operational strategies to mitigate plugging in molten sulphur vent gas scrubbers are also summarised in this article by **D. J. Sachde**, **K. E. McIntush**, **D. L. Mamrosh**, and **C. M. Beitler** of Trimeric Corporation.

The removal of hydrogen sulphide (H_2S) from sour gas streams can be achieved with many different technologies, one of which is caustic scrubbing. Caustic solution is often used in various processing steps in refineries and its availability and familiarity make it a reasonable choice for removing H_2S from vent streams from molten sulphur operations. While caustic scrubbing is an established technology that can readily remove H_2S, its use on molten sulphur vent streams is complicated by the presence of elemental sulphur that can plug different areas of the processing equipment.

The elemental sulphur in the vent gas and in the associated caustic scrubber system may be in various forms (vapour, aerosols/fog, sulphur sols [in liquid], and solid particulate) so that solids plugging can occur in the piping from the source and in the scrubber itself. Minimising sulphur plugging can be accomplished by including certain design features in the equipment and by managing the dissolution of elemental sulphur in the caustic solution.

Molten sulphur vent gas

Vent streams from molten sulphur pits, storage tanks, and loading operations are generally composed primarily of air or nitrogen, but also contain H_2S, sulphur dioxide (SO_2) and elemental sulphur (S_8) that must be treated to meet regulatory requirements and prevent unwanted solids deposition. The amount of sulphur compounds in the vent gas varies significantly depending on the source of the molten sulphur and the handling conditions. For example, the sulphur produced in the Claus process in an oil refinery contains soluble H_2S and hydrogen polysulphides (H_2S_x). During the storage of the sulphur, the H_2S_x compounds will decompose slowly to elemental sulphur and H_2S as the sulphur cools and is agitated.

The dissolved H_2S in the liquid sulphur can desorb into the gas phase. With a stagnant head space, the H_2S then accumulates in the vapour space above the liquid sulphur. Sweep gas is often used to keep the H_2S concentration above the surface of the molten sulphur below a maximum of 25% of the lower explosive limit for H_2S in air[1]. However, the health and safety hazards of H_2S and SO_2 along with environmental regulations may necessitate treatment of any vent vapour streams from the sulphur handling operations.

The presence of elemental sulphur represents a unique challenge when treating vent gas in molten sulphur operations. The vent gas is commonly assumed (conservatively) to be saturated at its temperature and pressure with elemental sulphur vapour. Literature sources indicate that elemental sulphur vapour may be present as S_2, S_4, S_6, and S_8 with larger molecules (through S_{12}) found in certain cases and predicted by theory[2,3]. At the conditions expected in sulphur vent gas (250-300°F/121-149°C), the larger molecules, in particular S_8, are favoured[2].

The problem is further complicated by the various physical phases and forms of elemental sulphur that may be present in the vent gas and associated caustic scrubber system, including:

- sulphur vapour;
- sulphur aerosols/fog/mist or entrained sulphur droplets;
- sulphur sols;
- sulphur particulates/solid.

The sulphur vapour can change phases as it leaves the high temperature molten sulphur operation and enters the lower temperature scrubbing system, and may be in any of the forms listed above. Thus, the actual amount of elemental sulphur travelling through the vent system/caustic scrubber system is difficult to quantify. Further, H_2S in the gas can also react with SO_2 and/or oxygen from the sweep air to form additional elemental sulphur.

This article on reliable design and operation of caustic scrubbers for molten sulphur storage and transport vent streams by Darshan Sachde, Kenneth E. McIntush, Darryl L. Mamrosh and Carrie Ann M. Beitler of Trimeric Corporation is a modified version of a paper previously presented at the Brimstone Sulfur Symposium[12].

Industry experience

Although the exact number of caustic scrubbers that treat vent gas from molten sulphur systems is not known, a knowledgeable industry contact from a company that stores, markets, ships, and uses molten sulphur ("merchant sulphur industry" for short) guessed that there might be on the order of 50 caustic scrubbers in this service around the world. Further, Trimeric's exposure to some data from operators of oil refineries and gas plants suggests that there are at least a dozen or more in oil refineries, probably mostly in the United States.

As a result of work with clients with these systems, Trimeric gathered confidential input from operating companies (primarily refining) regarding caustic scrubbers in this application. As detailed later, features mentioned that were associated with improved operation included: the use of venturi contactors prior to conventional packed scrubbers, caustic sprays at the point where the vapour line enters the scrubber, and on-line washing of the scrubber overhead equipment and lines to clean out those areas.

Important chemistry

Because H_2S and SO_2 are hazardous gases with strong odours, emissions tend to be limited by regulations, and the vent streams from the molten sulphur handling operations commonly must be treated to remove these compounds. Caustic scrubbing of vent streams usually involves counter-current contacting of the gas phase with a recirculating caustic solution in a packed or tray tower. The chemistry and operation of the caustic scrubber for H_2S and SO_2 removal is not the focus of this article and is not covered in detail. However, it should be noted that reliable design of the caustic scrubber in this application requires a full understanding of the chemistry to prevent salts precipitation, meet treatment specs, and maximise utilisation of the caustic solution[4].

Elemental sulphur dissolution and caustic chemistry

This section will provide a brief overview of the dissolution of elemental sulphur in aqueous caustic solutions, with a focus on data available in the literature. It is important to note that the following discussion is limited in scope in several ways compared to the complexity present in a caustic scrubbing system applied to a molten vent gas stream in the field:

- Other species present in vent gas streams (e.g., H_2S, SO_2, and oxygen) will potentially complicate the chemistry significantly.
- Reaction pathways will change with specific operating conditions, particularly pH and temperature. Literature data may not be representative of specific conditions in a caustic scrubber.
- The experimental methods used to measure dissolution may not be representative of a caustic scrubber (particle size distribution of elemental sulphur, agitation, temperature control, etc.).

Even sulphur dissolution in neat caustic solution includes multiple mechanisms that impact the rate and extent of dissolution:

- wetting of solid sulphur particles by aqueous solution;
- physical solubility of elemental sulphur in the aqueous solution;
- chemical reaction of caustic solution with elemental sulphur;
- diffusion of reactants and products through the solid/liquid interface boundary layer.

These mechanisms, in turn, are a function of the physical properties and conditions (temperature, pH, concentrations, etc.) of the solution. In general, sulphur has a low physical solubility in caustic solution, but chemical reactions enhance solubility. The most stable form of elemental sulphur in the temperature range of interest is S_8 (orthorhombic sulphur), which is hydrophobic and not readily wetted by caustic solution. Some research indicates that reaction rates are strongly influenced by the surface area of elemental sulphur particles (i.e., reactions take place on the surface of the particles)[5,6]. Therefore, wetting of elemental sulphur must be considered alongside any reactions. This article is focused on total solubility of elemental sulphur in caustic solutions (combination of physical solubility and chemical reaction), but in practice the other mechanisms discussed will be important.

The reactions of elemental sulphur with caustic can include multiple pathways depending on the conditions of the solution. However, two general routes for the reaction of elemental sulphur with caustic solution will be considered:

- disproportionation (also called alkaline dissolution of elemental sulphur);
- addition reaction with sulphide/bisulphide.

Disproportionation reaction

$$\tfrac{1}{2}S_8 + 4OH^-_{(aq)} \rightarrow S_2O_3^{2-}{}_{(aq)} + 2HS^- + H_2O_{(aq)} \quad (1)$$

(Simplified chemistry and stoichiometry represented in reference 16)

$$S_8 + 6OH^-_{(aq)} \rightarrow 2S_3^{2-}{}_{(aq)} + S_2O_3^{2-}{}_{(aq)} + 3H_2O_{(aq)} \quad (2)$$

(Alternative disproportionation chemistry proposed in reference 15 that reflects formation of polysulphides)

Addition reaction/poly sulphide formation

$$\left(\frac{n-1}{8}\right) S_8 + HS^-_{(aq)} \rightarrow S_n^{2-}{}_{(aq)} + H^+_{(aq)} \quad (3)$$

(Presented in reference 14)

$$\left(\frac{n-1}{8}\right) S_8 + S^{2-}_{(aq)} \rightarrow S_n^{2-}{}_{(aq)} \quad (4)$$

(Generic form of reaction presented in reference 15, where n=2)

The disproportionation reaction is written in two forms that are presented in literature (reactions (1) and (2)). Reaction (2) yields a polysulphide (S_3^{2-}) species. The chemistry of polysulphides is beyond the scope of this paper; however, polysulphides are generally thermodynamically unstable and will decompose in the presence of caustic[7]. Therefore, only reaction (1) will be considered further in this article.

This article assumes that the sulphur dissolves via reactions (1) and (3) to calculate a stoichiometric limit in the following table as follows:

- Every 4 moles of caustic present (either NaOH or KOH) consumes ½ mole of elemental sulphur (S_8) and produces 2 moles of bisulphide (HS^-) according to equation (1).
- The two moles of bisulphide can then consume ½ mole of elemental sulphur to produce polysufide in the form of S_3^{2-} according to equation (3).
- In total, 1 mole of elemental sulphur is consumed for every 4 moles of caustic consumed for this proposed pathway.
- The stoichiometric limit of solubility can then be calculated based on the total caustic present in solution (weight % of caustic).

The choice between addition reactions (3) and (4) is unimportant to the calculation of the stoichiometric limit – bisulphide or sulphide will consume the same stoichiometric amount of elemental sulphur.

Note that this approach is only approximate – a specific reaction pathway was

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52

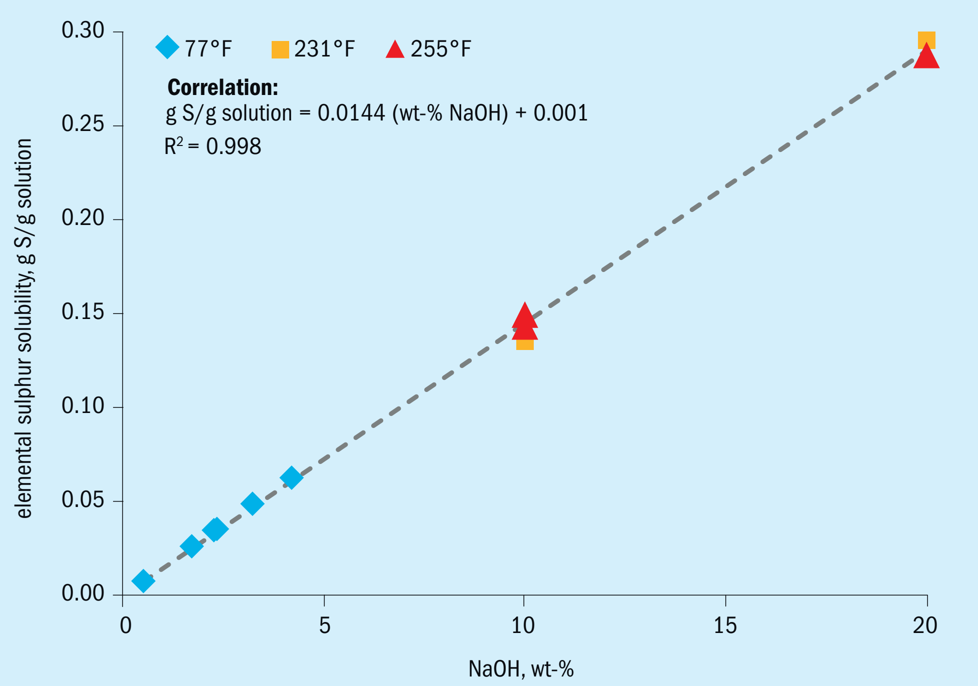
Table 1: **Solubility of elemental sulphur in caustic solution as a function of temperature and NaOH concentration (wt-%)**

From data source			Calculated	
Temperature °F (°C)	**NaOH wt-%**	**Sulphur solubility g S/g soln****	**Stoichiometric solubility limit* g S/g soln****	**Stoichiometric solubility limit* g S/g NaOH**
77 (25)	0.5	0.0076	0.008	1.6
77 (25)	1.7	0.0260	0.027	1.6
77 (25)	2.2	0.0344	0.036	1.6
77 (25)	2.3	0.0354	0.037	1.6
77 (25)	3.2	0.0487	0.052	1.6
77 (25)	4.2	0.0629	0.067	1.6
231 (111)	10	0.135	0.160	1.6
255 (124)	10	0.143	0.160	1.6
255 (124)	10	0.149	0.160	1.6
231 (111)	20	0.295	0.321	1.6
255 (124)	20	0.287	0.321	1.6
Room temp	66	0.215	n/a	n/a

**Calculated by assuming reactions (1) and (3) occur*

***Unit refer to grams of sulphur added per grams of initial or starting solution (sodium hydroxide and water)*

Fig. 1: **Solubility of elemental sulphur in caustic solution as a function of temperature and NaOH concentration (wt-%), limited to 0-20 wt-% NaOH**



Source: Trimeric (data from Table 1)

selected and limitations on physical solubility/reaction rates are ignored in the calculation. However, Table 1 indicates the estimated stoichiometric limit agrees reasonably well with the experimental data. Table 1 includes solubility data of elemental sulphur in caustic solutions from various literature sources [8, 9, 10]. The first set of data (shaded in grey) comes from reference 8, the second set of data (shaded yellow) comes from reference 9 and the last set of data comes from reference 10. The data point from the Sulphur Data Book[10] lacks sufficient detail to be considered with the overall NaOH set and is reported only for general reference and completeness.

Fig. 1 plots the sulphur solubility as a function of caustic concentration in the relevant range of caustic scrubbers (< 20 wt-% NaOH).

The available data show little temperature dependence, as the sulphur solubility is effectively linear in caustic concentration despite the range of temperatures considered (77-255°F / 25-124°C). These data indicate that with sufficient NaOH the elemental sulphur dissolution reactions go essentially to completion; the rate of sulphur dissolution is likely to be strongly influenced by temperature, however. Additional data over a broader range of temperatures and concentrations would be needed to confirm these findings. Similar data from literature is also available for KOH (not presented here)[11, 12]. Recently, NH_3 in water has also been shown to dissolve S[33].

Experimental and field data also support solubility of sulphur in more complex caustic solutions. For example, caustic solutions with sulphide species present (e.g., from the absorption of H_2S) have exhibited higher rates of dissolution and capacity for sulphur uptake than comparable neat sodium hydroxide solutions [13, 14, 15, 16, 17]. In addition, DuPont Clean Technologies reported higher than expected caustic and hydrogen peroxide consumption (based on stoichiometry of H_2S and SO_2 removal) in their scrubbing system when applied to a sulphur melter offgas[18]. The higher consumption was attributed, in part, to disproportionation reactions of elemental sulphur in the scrubbing solution.

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52

Difficulties with caustic scrubbers

The operability of caustic scrubbers in molten sulphur vent service can sometimes be difficult due to the formation of solids and plugging in the system. In some systems, the caustic scrubber can run for extended periods of time, while solids build-up in other systems requires frequent shutdown and cleanout of the equipment. The solids deposition can result from a variety of sources, as discussed below.

Salts precipitation

Solids can form if the operating temperature drops below the precipitation point for the salt species in solution. Localised cold spots in equipment, or instrumentation that is not insulated or heat traced properly can also be a source for salts precipitation. Liquid carryover with the gas from the scrubber system may lead to solid salts build-up in downstream equipment as well.

The formation of solids from salts precipitation can generally be avoided or minimised by understanding the solution properties at the operating conditions of the system. There are much literature data and some simulation tools that can be used to predict the precipitation temperature for the various components in solution. Once the precipitation temperature is known, the scrubbing system only needs to be operated at temperatures safely above this (10-15°F higher). If the necessary operating temperatures cannot be maintained in the system for some reason, a more dilute caustic solution could be used instead.

Elemental sulphur deposits

The more common and difficult to manage source of solids deposition is from elemental sulphur. Vent gas from molten sulphur operations contains sulphur vapour that can deposit on solid surfaces when the gas is cooled. The temperature of the vent stream entering the scrubber is often below the melting point of sulphur. Also, the temperature of the caustic scrubbing system itself is often low enough that any elemental sulphur vapour entering the scrubber changes phases.

Specifically, submicron aerosol or fog formation is a risk, as documented in condensers of Claus processes[19]. Aerosols form when the sulphur vapour is rapidly cooled below the condensation point of elemental sulphur. Rapid cooling leads to a supersaturated vapour. If nuclei are present in the vapour and the kinetics of nucleation are sufficiently fast relative to the residence time of the supersaturated vapour, sulphur vapour will condense in the gas phase rather than forming a continuous liquid phase as in typical surface condensation processes.

Researchers have developed theoretical approaches to identify the limiting conditions (partial pressure of sulphur, temperature gradient, etc.) necessary for aerosol formation[19]. Submicron aerosol particles are difficult to capture by traditional impaction methods (e.g., mist eliminators) as they will follow streamlines in the vapour.

Elemental sulphur in the liquid phase can exist as sulphur sols[20]. Sulphur sols are emulsions of small droplets of liquid sulphur within a continuous bulk liquid phase in which the sulphur is sparingly soluble (e.g., aqueous solution). Sulphur sols can exist at temperatures far below the normal freezing point for elemental sulphur.

Stretford plants have experienced absorber plugging, "sticky" sulphur, and sulphur deposits in piping and downstream equipment that can be attributed to sulphur sols[21]. In the Stretford process, a mechanism for sol formation exists because elemental sulphur is formed in the aqueous solution via oxidation of absorbed H_2S[16]. However, experimental methods have also generated sulphur sols by directly contacting sulphur vapour with cold aqueous solution, which could be a mechanism for sol formation in a caustic scrubber[20].

Additionally, solid sulphur particulate is common in these vent streams. Solid sulphur can form by continued cooling of sulphur liquid in various forms (condensed vapour, sols, aerosols) in the system or be carried in the vent as solid particulate from the upstream process. Elemental sulphur is hydrophobic and will often build a layer of floating sulphur powder in the sump of the scrubber.

The location of sulphur deposits in the system coupled with knowledge of the different forms of sulphur may provide insight into the source of elemental sulphur in the system. For example, collection/plugging in mist eliminators indicates particles captured by impaction (larger aerosols or solid particulate). Sulphur that passes downstream of the scrubber (and mist eliminator, if present) in the vent gas may be indicative of small aerosols forming in the bulk vapour.

Elemental sulphur collecting or plugging in the lower portion of the column/sump or in liquid piping may be indicative of sulphur sols or captured sulphur which is not sufficiently reactive with the solution.

Design strategies to mitigate plugging of molten sulphur vent gas scrubbers

Caustic scrubbing is typically done using a variety of equipment including packed or trayed towers, sparged tanks, in-line contactors, venturi contactors or a combination. An example of a common (not necessarily optimal) design for a packed tower caustic scrubber on a molten sulphur vent gas stream is shown in Fig. 2 as a reference for the reader through the remainder of this discussion.

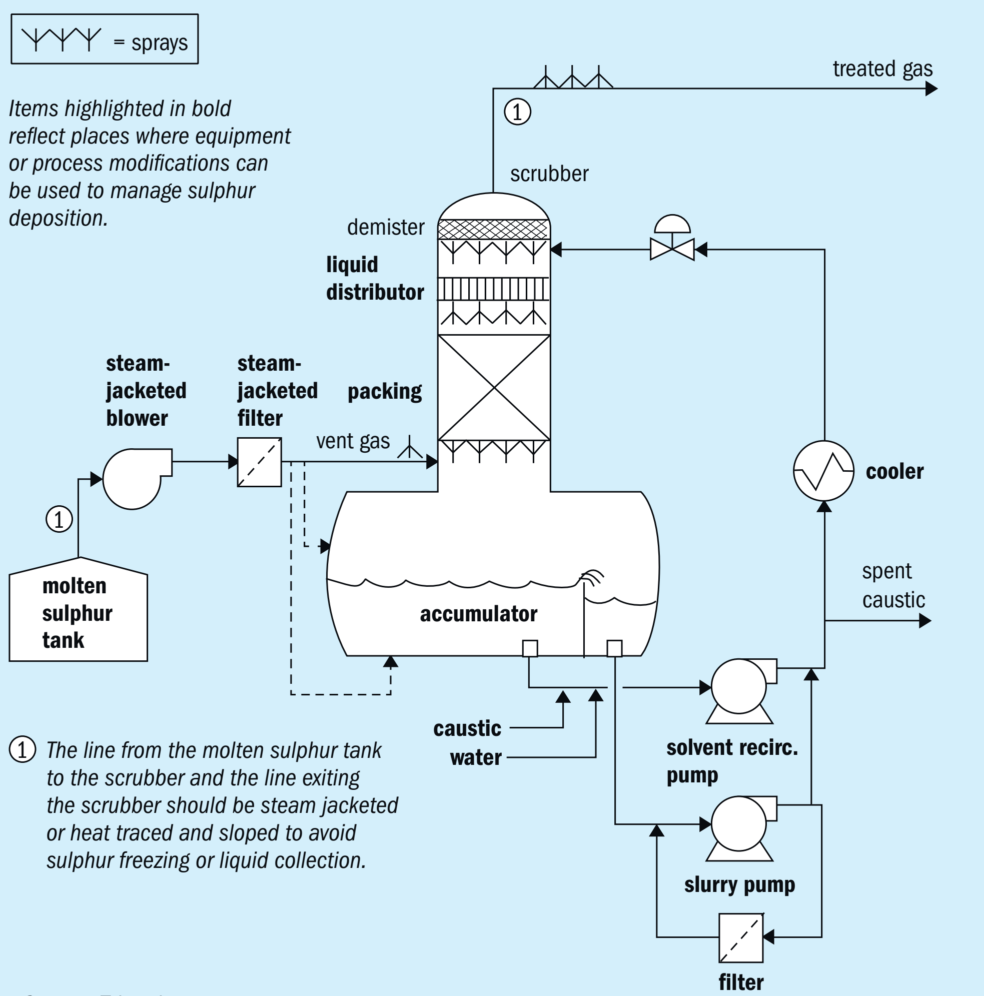
In Fig. 2, the vent gas leaves the upstream process and is sent to the caustic scrubbing system via a motive device (blower, ejectors, eductors, etc.). The line from the molten sulphur tank to the scrubber and line exiting the scrubber should be steam jacketed or heat traced and sloped to avoid sulphur freezing or liquid collection.

The vent gas may pass through a steam jacketed filter as the first place where solid sulphur could be removed. The vent gas enters the caustic scrubber below the packed bed, where it countercurrently contacts caustic solution. The gas leaves the packed section of the column and passes through a demister which removes entrained liquid or large particulate. The treated gas leaves the column (typically vented).

The caustic solution absorbs the various sulphur species, and passes to the sump of the vessel. The solution is then pumped back to the top of the column, with a portion bled to remove spent caustic. A liquid filter may be used to remove any solids carried in the solution. The solution passes through a cooler (or heater in some cases), which controls the temperature of the caustic feed, and finally, the solution enters the top of the packed bed via a liquid distributor. Make-up caustic and water are added to the recirculating caustic stream.

There are many design features that can be incorporated into the caustic scrubber system to mitigate the plugging of the equipment from elemental sulphur solids as described in the subsections below.

Fig. 2: **Generic caustic scrubbing process flow diagram**



Source: Trimeric

Improved gas-liquid contact

The goal of improved gas-liquid contact is to remove elemental sulphur from the gas via the liquid where the sulphur can be more easily managed. Once in the liquid, it is important to keep any solids that form suspended in solution until they either dissolve or reach an appropriate point for removal from the system. The liquid load to the scrubber can be increased by using a high recirculation rate and packing with a large open area suitable for large liquid loads. High liquid loads in the caustic scrubber may provide the following benefits:

- Enhanced physical removal of sulphur from the gas (via increased gas-side pressure drop and eliminating gas bypass paths).
- Prevent accumulation of sulphur solids on packing surfaces by sweeping away existing solids and wetting the packing surface to eliminate places for condensation and crystallisation.

These methods are primarily effective via increased gas pressure drop, droplet/particle impaction, and physical washing of surfaces. Therefore, submicron particles (solid particulate "dust" or liquid aerosols) are unlikely to be effectively managed by these approaches.

Removal of elemental sulphur solids

The dissolution of elemental sulphur into the caustic solution is the ideal approach to manage elemental sulphur and scrubbers in this service should ideally be designed and operated to facilitate dissolution.

However, if dissolution is not possible in the specific system (sulphur content is too high; temperatures limit reaction rates; system is built and cannot be modified to enhance dissolution; etc.), then it is important to manage the solids with minimal process interruption. Existing systems may be modified in order to implement some of these approaches.

Suspended elemental sulphur solids can be removed from the liquid phase in a variety of ways. The solids could be allowed to settle in a separate vessel and then be removed. A weir installed in the scrubber sump (see Fig. 2) to allow for overflow of a floating powder layer (if present) has been used in this service. Liquids could also be filtered to remove solids.

Liquid sprays could be considered to remove solids at different locations in the process (e.g. just above the gas entry in the scrubber, in the gas entry pipe itself, mist eliminator, or gas exit piping)[12].

Alternative equipment and process flow schemes

There are several other approaches that have been applied or considered for this application that have been presented in the literature[12] – the following list provides an overview of a few:

- A venturi contactor (an eductor) with caustic as the motive fluid at a high circulation rate to provide the needed contact between the gas and liquid phases (also potentially serving as a motive device for the downstream scrubber). Venturi scrubbers are a known means of particulate removal and should reduce the particulate load to a downstream caustic scrubber.
- Proprietary commercial scrubbers have been designed to counter-currently contact the vent gas with caustic solution in a reverse jet nozzle that then separates in a wide open vessel (with chevron mist eliminator) to minimise places for sulphur solids to accumulate[22].
- Water scrubbing (in a tower or venturi) for particulate control prior to a caustic scrubber is also used; in Trimeric's experience, this approach has mixed results in practice.
- Cross-flow (horizontal) scrubbing arrangements have been reported to withstand more than an order of magnitude more particulate than vertical counter-current scrubbers[24] and have been used on vents from molten sulphur operations[25].
- Redundancy in the caustic scrubber design could be used to minimise downtime and allow cleaning. The extent of redundancy (fully redundant scrubber vs redundant components) will be an economic optimisation.

Operating strategies to mitigate plugging

There are also several operational changes that could be implemented to control the formation of solids or manage solids in the system. These strategies are reviewed in the following subsections.

Additives

Additional chemicals could be added to the scrubbing liquid to help wet elemental sulphur particles to enhance dissolution. Research has indicated that surfactants (e.g., sodium dodecyl sulphate, SDS) can increase the amount of elemental sulphur suspended in aqueous solution and enhance reactions by other mechanisms[14, 26]. Examples of surfactant use in field applications include surfactants with caustic to remove sulphur solids in gas production wells[9] and surfactant in scrubbing solution to resolve level measurement issues (sulphur accumulation at gas-liquid interface) in a sulphur melter offgas application[18]. Other additives such as oxidisers and diesel oil have also been used[16].

Caustic temperature and strength

Temperature control of the caustic scrubbing system can be used to prevent or manage elemental sulphur in the system. High-temperature scrubbing could be used to prevent condensation of sulphur vapour and enhance the reaction rate of sulphur with the caustic solution. Controlling the temperature in different parts of the scrubber could be used to prevent the formation of aerosols and liquid sols (prevent rapid cooling of sulphur vapour in the scrubber) and control the growth of aerosols. Steam sparging could be used in specific areas (e.g., mist eliminators, column vapour inlet) to maintain localised higher temperatures with the added benefit of wetting surfaces. Trade-offs of high-temperature scrubbing must be considered carefully, however, as performance (ability to meet treatment specs) and cost of the scrubber (materials of construction) may be significantly impacted. Higher caustic concentrations will lead to enhanced reaction rates with elemental sulphur, improving dissolution. The caustic strength has the same challenge regarding column material selection as with higher temperature operations. If the system is operated with regular feed of fresh caustic to maintain original caustic strength, this may also help with dissolution of sulphur.

Exercising the unit

In other process systems where salt and solid sulphur plugging often occurs, 'exercising' the unit has been found useful to extend run times. An example of such a system where plugging has been experienced is a liquid redox sulphur recovery system (e.g., Sulferox, LO-CAT, Stretford). In this context, exercising the unit means varying flows, levels, and other operating conditions temporarily with the specific purpose of keeping the system clean. Control valves may be cycled, manual valves cycled, motor speeds changed, levels built and dropped with the goal of dislodging any material that is beginning to accumulate so that the material can be moved through the system to a point where it can be removed (or solubilised). In Trimeric's experience, units that have implemented a regular system of 'exercising' the process have operated much longer than systems that had no such programme.

Cleaning the unit

If solids plug the system, then there are several approaches for cleaning it. The system could be opened and cleaned; however, this is a labour intensive process that could require significant down time. Other approaches have been applied in similar applications[12] and could be adapted to molten sulphur vent scrubbing:

- Use of warm caustic (~140°F / 60°C) to remove sulphur solids. Applied in oil and gas and mining applications[27].
- Use of higher strength caustic for cleaning a unit. This approach has been used in other processes (e.g., in Stretford absorbers), including methods to clean while operating[28].

Materials compatibility should be reviewed for these approaches.

Managing upstream operations

Finally, the operation and monitoring of the upstream molten sulphur process may help with sulphur deposits as well. For example, a molten sulphur tank can be operated with reduced levels or lower temperatures to minimise the sulphur vapour pressure and reduce fog formation potential. The tank should also be regularly monitored for the presence of steam leaks in any internal coils, which is believed to cause additional elemental sulphur particulate to be present in the tank vapours.

Conclusions

Caustic scrubbing of molten sulphur vent gas streams has occurred with varying degrees of reliability due to the presence of elemental sulphur that can exist in several different forms (vapour, aerosol/fog, sols, and solids particulate). However, there are many design and operational modifications to enhance the performance of even the most difficult applications. Design changes can range from enhancing the gas/liquid contact with increased circulation rates, installing spray nozzles in different areas of the process, removing solids from the solution with filters or decanting floating solids, and using redundant or alternative contacting devices (dual contacting devices, piping, etc.). Operational changes can include the use of surfactants, elevated operating temperatures, and increased caustic strength. Understanding the chemistry and dissolving of the elemental sulphur into the caustic solution represents the ultimate mitigation technique, because the formation of solids is eliminated (or greatly reduced). The mechanisms for dissolving sulphur in caustic that are presented in this article can be used to aid in the development of a more robust caustic treating system for molten sulphur vent gas streams.

References

1. McIntush K. et al.: "Molten sulphur storage tank, loading, and vapour ejection systems review," in Brimstone Sulfur Symposium, Vail (2015).
2. Wong M.W., Steudel R. and Steudel Y.: "Speciation and thermodyna mics of sulphur vapor," in Elemental Sulphur and Sulphur Rich Compounds I, Berlin, Springer Berlin Heidelberg, pp. 117-134 (2003).
3. Meyer B.: "Elemental Sulphur," Chemical Reviews, vol. 76, no. 3, pp. 367-388 (1976).
4. Mamrosh D., McIntush K. and Fisher K.: "Caustic scrubber designs for H_2S removal from refinery gas streams," in American Fuel & Petrochemicals Manufacturers Annual Meeting, Orlando, Fla. (2014).
5. Kleinjan W. E., de Keizer A. and Janssen A .J.:"Kinetics of the reaction between dissolved sodium sulphide and biologically produced sulphur," Industrial and Engineering Chemistry Research, vol. 44, no. 2, pp. 309-317 (2005).
6. Hartler N., Libert J. and Teder A.: "Rate of sulphur dissolution in aqeuous sodium sulphide," Industrial and Engineering Chemistry Prcess Design and Development, pp. 398-406 (1967).
7. S. Licht S. and Davis J., "Disproportionation of aqeuous sulphur and sulphide: Kinetics of polysulphide decomposition," The Journal of Physical Chemistry B, vol. 101, no. 14, pp. 2540-2545 (1997).
8. Arntson R., Dickson F. and Tunnell G.: "Systems $S\text{-}Na_2O\text{-}H_2O$ and $S\text{-}H_2O$: Application to the mode of origin of natural alkaline polysulphide and thiosulphate solutions," American Journal of Science, vol. 258, pp. 574-582 (1960).
9. Sample Jr T.E.:, "Method for removing elemental sulphur in sour gas wells". United States of America Patent 3,909,422, (30 Sep 1975).

10. Freeport Sulphur Company, The Sulphur Data Book, New York: McGraw-Hill (1954).
11. Tartar H. V.: "On the Reaction between sulphur and potassium hydroxide in aqueous solution," Journal of the American Chemical Society, vol. 35, no. 11, p. 1741–1747 (1913).
12. McIntush K. E., Mamrosh D. M., Sachde D. J. and Beitler C. A. M.: "Use of caustic scrubbers on vent streams from molten sulphur storage and shipping equipment," in Brimstone Sulfur Symposium, Vail, CO (2017).
13. Dickson F., Arntson R. and Tunell G.: "Saturation curves of orthorhombic sulphur in the system S-Na_2S-H_2O at 25C and 50C," Science, pp. 716-718, (1958).
14. Garcia Jr A. A. and Druschel G. K.: "Elemental sulphur coarsening kinetics," Geochemical Transactions, vol. 15, no. 11, pp. 1-11 (2014).
15. Moscardo-Levelut N. and Plichon V.: "Sulphur chemistry in equimolar NaOH-H_2O Melt: II. Chemical reactions between sulphur, sulphide, polysulphide, and oxyanions," Journal of The Electrochemical Society, vol. 131, no. 7, pp. 1545 – 1551 (1984).
16. Trofe T., McIntush K. and Murff M.: "Stretford process operations and chemistry report," Gas Research Institute (Prepared by Radian Corporation), Chicago (1993).
17. Richardson F. P. and Young D. A.: "Method of prevention and removal of sulphur deposits from H_2S absorption equipment". United States of America Patent 3975508 (17 Aug 1976).
18. Puricelli S.: "Sulphur melter hygiene is Ob(li)vious (DuPont Clean Technologies)," Presentation at Sulphur 2017, Atlanta (2017).
19. Johnstone H., Kelley M. D. and McKinley D.: "Fog Formation in Cooler-Condensers," n.d.
20. Steudel: "Aqueous sulphur sols," in Elemental Sulphur and Sulphur-Rich Compounds I, Berlin, Springer Berlin Heidelberg, pp. 153-166 (2003).
21. Steudel R.: "Mechanism for the formation of elemental sulphur from aqueous sulphide in chemical and microbiological desulphurization processes," Industrial Engineering and Chemistry Research, vol. 35, no. 4, pp. 1417-1423 (1996).
22. Myer S., Juno E. and Watts N.: "Dynawave wet gas scrubbing: A new alternative for claus unit tail gas clean-up," Laurance Reid Gas Conditioning Conference, Norman, OK (2006).
23. Heidenreich S., Vogt U., Buttner H. and Ebert F.: "A novel process to separate submicron particles from gases – a cascade of packed columns," Chemical Engineering Science, vol. 55, no. 15, pp. 2895-2905 (2000).
24. Cheremisinoff P.: "Packed wet scrubbers," in Air Pollution Control and Design for Industry, New York, Marcel Dekker, Inc., p.p. 283 (1993).
25. Shields M. and McKee S.: "Vapour emissions scrubbing of off-gases from liquid elemental sulphur," in Sour Oil and Gas Advanced Technology Proceedings of the 10th International Conference, Abu Dhabi, UAE (2014).
26. Pirzadeh P., Lesage K. L. and Marriott R. A.: "Hydraulic fracturing additives and the delayed onset of hydrogen sulphide in shale gas," Energy & Fuels, pp. 4993-5001 (2014).
27. Monroe Jr J.E.: "Process for removal of deposits from sulphur mining pipes using hot caustic solution". United States of America Patent 2,771,284 (20 Nov 1956).
28. Herich C. A.: "Method for on-line cleaning of sulphur deposits". United States of America Patent 5,979,470 (9 Nov 1999).
29. Dean J., Lange's Handbook of Chemistry Fourteenth Edition, McGraw Hill (1992).
30. Johnson J. and Hatcher N.: "Hazards of molten sulphur storage and handling," Laurance Reid Gas Conditioning Conference, Norman, OK (2003).
31. Lagas J. et al.: "Understanding the formation of and handling of H_2S and SO_2 emissions from liquid sulphur during storage and transportation," Sulphur Seminar, Amsterdam (1999).
32. Marriot R., Clark P., Davis P., Fitzpatrick E. and Lesage K.: "A re-examination of H_2S solubility in liquid sulphur," in Brimstone Sulfur Recovery Symposium, Vail, CO (2007).
33. Lavery C.B., Dowling N.I., Sui R., Loftali M.K., and Marriott, R.A.: "Ammonia and corrosion rates within the Claus plant," in Brimstone Sulfur Recovery Symposium, Vail, CO (2018).

Super selective hydrogen sulphide removal

The removal of hydrogen sulphide (H_2S) has become increasingly important as the oil and gas industry moves towards more efficient and sustainable production of lower emission clean fuels. BASF and ExxonMobil* have jointly developed a proprietary amine, OASE® sulfexx™, to help refiners and gas processors achieve sulphur removal targets while reducing their carbon footprint via lower energy consumption. This new solvent technology is suitable for low and high pressure applications and shows superior performance characteristics over generic and promoted MDEA formulations, as well as sterically hindered amines such as FLEXSORB™ SE and SE Plus.

Technologies that provide selective removal of H_2S from gas streams are a key component of achieving more efficient and sustainable production of lower emission clean fuels. The current choices for selective solvents are based on generic or promoted methyldiethanolamine (MDEA) or severely sterically hindered amines. In this article, real operating data is presented to demonstrate the superior selectivity of OASE® sulfexx™, a highly energy efficient gas treating technology jointly developed by BASF and ExxonMobil to help refiners and gas processors achieve sulphur removal targets while reducing their carbon footprint via lower energy consumption. The key to the technology is a new proprietary amine that can achieve high selective removal of H_2S while minimising the co-absorption of carbon dioxide (CO_2). Selective treating permits full utilisation of the solvent for greater H_2S absorption, thereby reducing circulation rate and increasing energy efficiency. When compared to conventional amine solvents, the advancement is a considerable leap forward, leading to a new standard for gas treatment.

* *The authors of this article are* ***S. Nyuon*** *of ExxonMobil Research & Engineering,* ***J. Seagraves*** *of ExxonMobil Corporation,* ***G. Sieder*** *and* ***G. Vorberg*** *of BASF SE and* ***J. Habayeb*** *of BASF Middle East.*

The challenge

The world needs energy to support the growing population and rising living standards. The removal of H_2S is an essential processing step in the production of clean fuels to satisfy future energy demands. As new fuel sources are being explored, more stringent regulations on SO_2 emissions are being implemented around the world. Many countries are intensifying efforts to lower carbon dioxide emissions to meet Paris Climate Accord commitments. One way to reduce carbon footprint is to reduce energy consumption and to use more sustainable technologies.

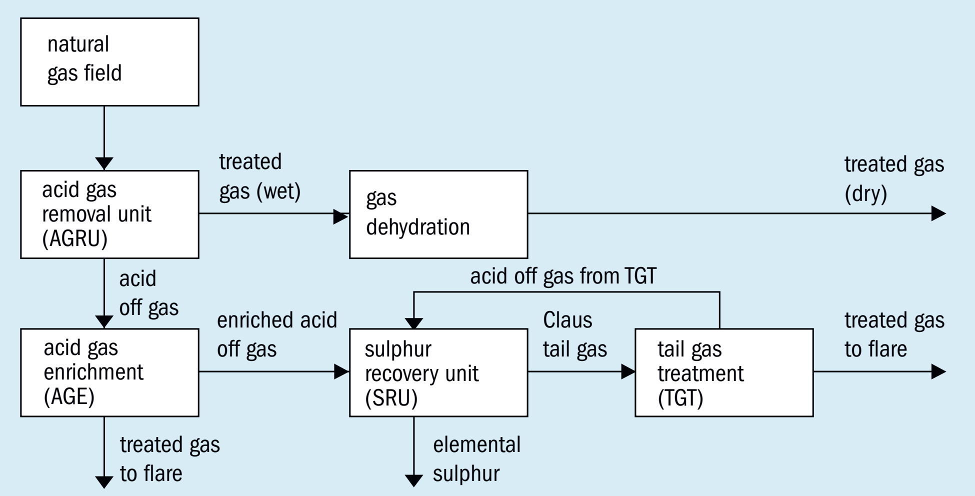
Regulations such as IMO-2020, as mandated by the International Maritime Organization, have resulted in the largest sulphur content reduction of a transportation fuel taken at any one time. Some refiners will revamp their facilities to meet these new regulations, while others will look toward processing less costly sour crudes in order to increase profitability. Improved technologies are needed to handle the increased sulphur loads on existing sulphur complexes.

Natural gas fields with compositions that were once deemed uneconomical or technically challenging to develop are now being re-evaluated as potential new sources of supply. Obviously, processing gas with extremely high levels of H_2S would necessitate the need for higher capacity solvents. At the other end of the spectrum, processing gas streams containing low concentrations of H_2S relative to CO_2 will require advanced solvent technology to enrich the acid gas feed to the sulphur recovery unit. High quality acid gas feed enables stable operation of the sulphur recovery unit and reduces the fuel consumption of the process.

From a global perspective, the majority of the world's sulphur production is now being produced in the Middle East. In this geographical location, high ambient temperatures combined with a lack of available cooling and process water require a robust solvent technology able to perform under these conditions.

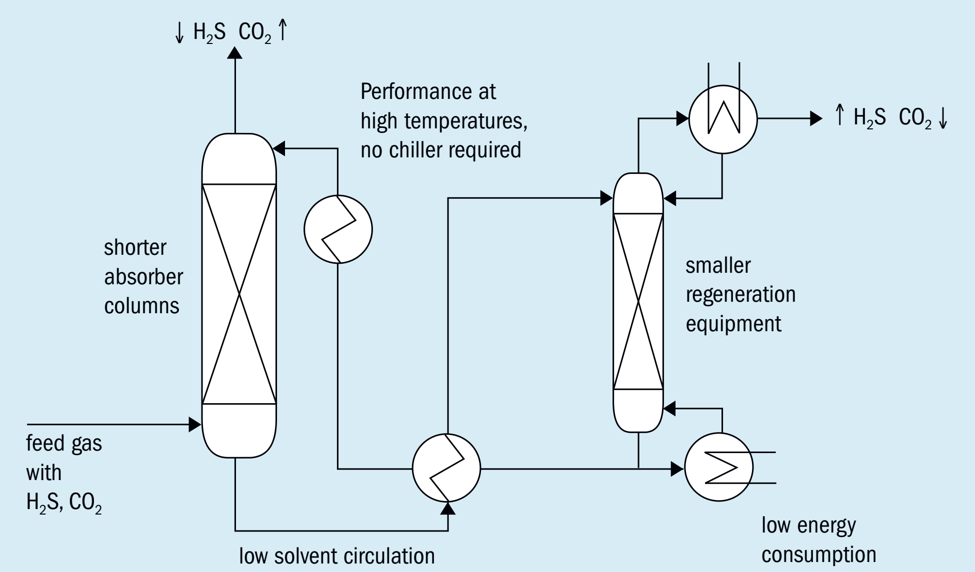
Industry can expand to meet future demands and changing regulations by adding more equipment. However, this is expensive and may not lead to a reduction in emissions. Older technologies such as generic MDEA are less efficient for highly selective H_2S removal because of the capacity limitations of the solvent molecule. A better alternative is to use a more advanced energy efficient solvent to minimise modification of the existing equipment. For grassroots projects, the new technology will lower initial capital investments due to smaller equipment size and lower operating costs.

Fig. 1: **Selective treatment in gas processing**



Source: ExxonMobil and BASF

Fig. 2: **Benefits of selective H_2S treatment**



Source: ExxonMobil and BASF

Benefits of selective treatment

OASE sulfexx exhibits superior performance characteristics over generic and promoted MDEA formulations, as well as sterically hindered amines such as FLEXSORB SE and SE Plus. The solvent is suitable for low pressure applications and even for selective high-pressure applications. The technology is suitable for use in Claus tail gas treating (TGT), acid gas enrichment (AGE), and high pressure acid gas removal (AGR) units where selective removal is required (see Fig. 1).

The new proprietary amine is specifically tailored to maximise H_2S absorption in the presence of CO_2. This property allows the solvent to achieve high H_2S cleanup and selectivity at low solvent circulation rates. In grassroots units, this leads to substantial savings in investment and operating costs. In retrofit situations, the technology may be used to debottleneck the unit and achieve lower sulphur emission targets or allow the unit to achieve higher throughput with minimum hardware modifications. In both cases, the solvent improves the quality of the acid gas. Fig. 2 highlights the areas of the amine unit where the technology can provide benefits.

To illustrate the benefits of the new solvent, Figs 3 and 4 compare the performance of generic MDEA, promoted MDEA, and FLEXSORB SE Plus against OASE sulfexx in a typical TGT unit. These results were calculated using the OASE Connect design and simulation tool developed by BASF[1].

The feed gas to the TGT unit contains 2 vol-% H_2S and 10 vol-% of CO_2 at slightly above atmospheric pressure. The lean amine temperature is set at 45°C. The feed gas flow is the same for all four cases. The results are normalised against generic MDEA. At these conditions, OASE sulfexx exhibited high H_2S absorption capacity and selectivity relative to the alternative amine solvents. These features translate into lower operating and capital expenditures (opex and capex). For example, compared to MDEA, the new solvent reduced the circulation rate by 40% and the energy consumption by over 50% (Fig. 3).

Fig. 4 shows the relative equipment costs for the TGT unit. The total estimated capex for OASE sulfexx is about 30% less than MDEA. The cost of cooling is particularly important to gas processing facilities located in hot, arid regions of the world. For instance, an increase in lean amine temperature will impact capex and opex significantly depending on the cooling medium. In locations where access to cooling water is limited, the use of air coolers will require higher capex in exchange for lower opex. However, once additional propane chilling of the solvent becomes necessary, opex and capex can easily rise threefold to fivefold. OASE sulfexx technology can be operated with lean amine temperatures that exceeds 55°C. The inherent heat tolerant properties of the solvent avoid costly investment and operational expenses associated with additional chillers.

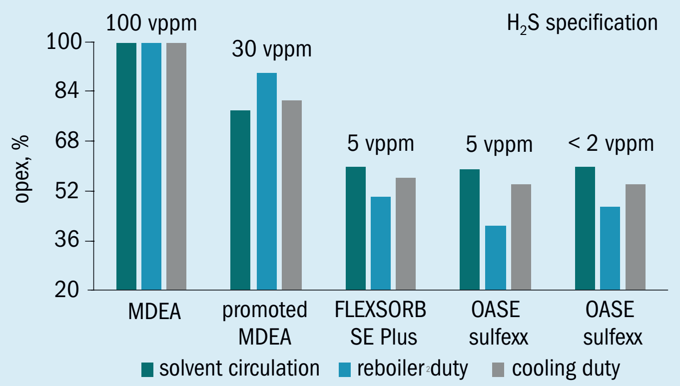
Commercial demonstration

The sulphur train at a North American refinery consists of two Claus sulphur recovery units with one common TGT unit. The TGT unit is an original FLEXSORB SE design by ExxonMobil that was commissioned in 2010. Assuming 93% overall end-of-run recovery in the upstream SRUs, the FLEXSORB SE TGT unit was designed to achieve less than 250 ppm H_2S in the absorber overhead under all operating scenarios. The combined tail gas from the SRUs is sent to a hydrogenation step followed by a quench tower and then the FLEXSORB SE TGT unit.

The feed to the TGT unit contains approximately 2 vol-% H_2S and up to 7 vol-% CO_2. Just prior to the solvent swap to OASE sulfexx, the absorber outlet had an average of around 10 vppm H_2S.

OASE sulfexx fits into the refinery's

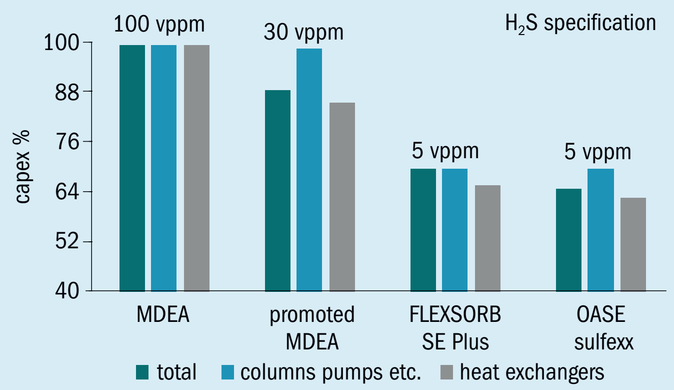
Fig. 3: **Comparison of relative operating costs**



Gas treating solvent comparison (% of MDEA) at different H_2S specifications for the same TGTU case

Source: ExxonMobil and BASF

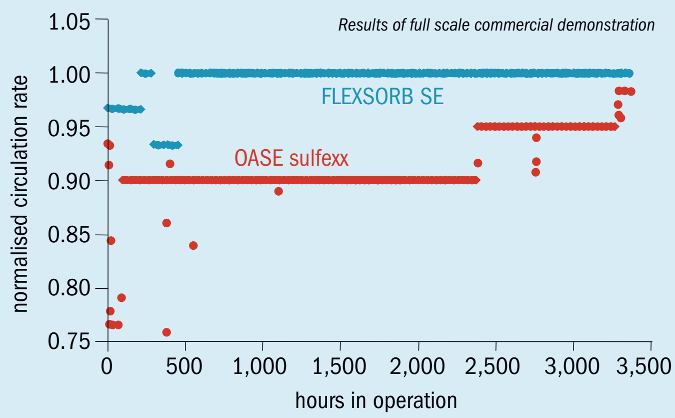
Fig. 4: **Comparison of relative capital costs for equipment**



Gas treating solvent comparison (% of MDEA) at different H_2S specifications for the same TGTU case

Source: ExxonMobil and BASF

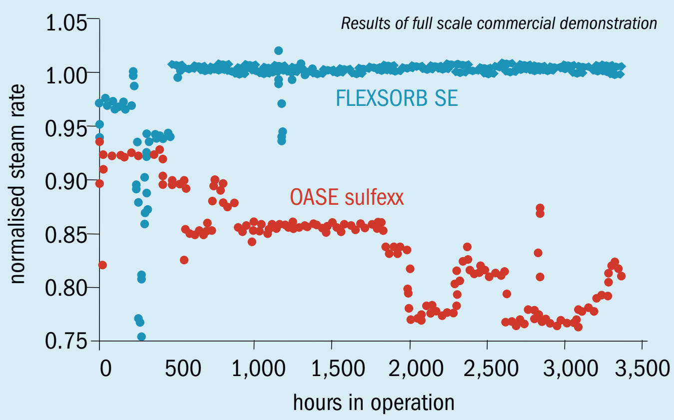
Fig. 5: **Normalised* solvent circulation rate**



*(Normalised by dividing both FLEXSORB SE and OASE sulfexx rates by typical FLEXSORB SE rate)

Source: ExxonMobil and BASF

Fig. 6: **Normalised* reboiler steam rate**



*(Normalised by dividing both FLEXSORB SE and OASE sulfexx rates by typical FLEXSORB SE rate)

Source: ExxonMobil and BASF

strategic plan to reduce their carbon footprint. The goal of the field trial was to improve the energy efficiency of the site by reducing the regenerator reboiler steam consumption.

The FLEXSORB SE solvent was swapped to OASE sulfexx solvent during a very short three day turnaround. The system was drained and refilled with the new solvent. Prior to the swap, detailed gas analysis was performed by a third party testing service. Baseline data were obtained on the feed, treated and stripper acid gas streams to confirm the material balance. The gas analysis also served to confirm online analyser measurements. The analyses were then repeated during the OASE sulfexx performance test. The baseline data obtained from the unit showed very good fit and reproducibility.

During the initial days of the trial, the unit was run at different circulation rates and reboiler duties. As the trial progressed, solvent circulation and steam rates were adjusted to ensure that the performance was acceptable throughout the entire operating envelop. During these adjustments, the H_2S level was well below the 50 vppm maximum limit set by the test plan. These changes to the flowrates are reflected in the far left quadrant of Figs 5 and 6.

As a reference, performance data of FLEXSORB SE operating under similar feed gas conditions were overlaid in Figs 5 and 6. These figures show that OASE sulfexx can operate at 90 to 95% of the circulation rate of FLEXSORB SE, and approximately 75 to 85% of the steam rate of FLEXSORB SE.

Similarly, the solvent performance in the absorber was also evaluated. The average results of the tests are summarised in Table 1. With the absorber operating at less than 10 vppm H_2S in the overhead, OASE sulfexx showed improved selectivity over FLEXSORB SE. Tests showed CO_2 slip improvement of 6% above the baseline on average. The high selectivity also reduced the amount of CO_2 in the gas recycled back to the SRU.

As a next step, the two companies are conducting additional tests to further improve and refine the technology. ■

Reference

1. Internal BASF study using OASE connect design and simulation tool.

Table 1: **Analytical results of the gas streams**

	FLEXSORB SE	OASE sulfexx
H_2S absorber treated gas, vppm	< 10	< 10
CO_2 slip absorber treated gas, %	~ 85	~ 92
H_2S in stripper off gas, %	~ 67	~ 81

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52

Solving amine foaming problems

Although amine solution foaming problems have been studied and reported extensively, direct correlations about the root causes of foaming have not been completely established. This article approaches the problems of foaming from a different perspective, rather than theoretical discussions, the topic is centred exclusively on Amine Experts' field-related experiences with amine foaming episodes.

Amine solution foaming is a phenomenon that has been intensively studied and reported elsewhere. Several foaming root causes have been determined throughout the years, however, the latest experiments suggest that the predominant mechanism for foaming is related to contaminants in the form of surface-active materials, or surfactants. These contaminants can enter the unit in solid, liquid or gas phases and often modify the solution properties in such a way that foam (in gas contactors) and emulsions (in liquid-liquid treaters) is produced leading to a series of negative effects, predominantly hindering the process from meeting specifications and causing amine solution losses.

Foam is initiated when energy is imparted on the solvent, most commonly by means of agitation. The tendency for a foam to form is directly related to how much energy occurs at the surface of the solvent. In some cases, the foaming tendency correlates with the surface tension of the solvent. It is an inverse correlation, as the surface tension decreases, the foaming tendency increases. Amine solvents have been observed to have low foam tendencies as they have high surface tensions. Contaminants such as liquid hydrocarbons, or heat stable salts have low surface tensions, increasing the foaming tendency as they accumulate in concentration. These foam events can be short lived, and in many cases, go unnoticed as they may not affect the amine system in a significant way. While the foam is being created through energy, it is also being broken; its ability to maintain its form is known as foam stability. When surfactants and other compounds that change the interfacial rheology of the foam are present, there is not only an increase in foaming tendency but also an increase in foam stability. If this type of foaming occurs, it does not go unnoticed and several process changes may be observed, such as:

- differential pressure increases across the trays/packing in the contactor and/or regenerator;
- decrease in contactor and/or regenerator bottoms liquid level, or more likely a closing of the absorber/regenerator level control valve to maintain the setpoint;
- temperature bulge position changes inside the contactor tower;
- increasing liquid level in the amine contactor outlet knockout drum, as amine solution is carried over with the treated gas (leading also to amine losses);
- increase in H_2S or CO_2 levels in the treated gas (in the case of selective MDEA service, the CO_2 levels in the treated gas may reduce, as a foaming MDEA picks up more CO_2);
- increased liquid level in the reflux drum;
- amine, hydrocarbon and surfactant contamination of the regenerator reflux water.

Foaming of the amine can often lead to carryover from the contactor or regenerator with the treated gas or acid gas, respectively. Most amine units have separation vessels after the contactor outlet to recover the carryover. In extreme cases, amine carryover may exceed the removal capabilities of the knockout drum and reach downstream systems such as dehydration units, mercaptan removal beds, mercury removal beds and others. Foaming in a regenerator is also detrimental as foaming amine will not regenerate. Furthermore, flooding of the reflux accumulator can result in carryover with the acid gas, which can reach the sulphur recovery units, flare systems, acid gas injection units or other downstream processes. In cases of CO_2-only processing, the carryover may manifest itself as amine spraying out a vent stack into the surrounding environment or process units.

Determining the source of foaming requires thorough investigation of several possible sources. Following is a list of some of the many contaminants and sources that have been determined to be the root cause of amine foaming:

- Ineffective inlet separation leading to contaminant ingress
  - pipeline chemicals such as corrosion inhibitors, hydrate inhibitors, fracture fluid organic acids, dispersants, soap sticks
  - liquids from pigging
  - compressor lubrication oils
- Ingress of gas-phase contaminants carried with the feed gas (such as BTEX)
- Hydrocarbon condensation inside the contactor by not maintaining appropriate temperature differential between lean amine and inlet gas (or more accurately, the hydrocarbon dew point) when processing heavy hydrocarbon-rich feed gas
- Problems in the activated carbon bed
  - incorrect type of activated carbon (exposed to phosphorous-based activation)
  - spent activated carbon beds releasing contaminants into the outlet stream

- High concentration of suspended solids in the amine
- High soluble iron in the lean amine (resulting in fast/high solids formation in the contactor)
- Problems with the antifoam
  - incorrect antifoam (some antifoams will cause foam)
  - excess antifoam injection (excess antifoam use can, in some cases, stabilise or induce foam)
- Contaminants present in the fresh amine and/or make-up water
- Incompatible filter media or materials of construction
- Cleaning chemicals not properly flushed before filling system with amine

Because amine foam is stabilised by contamination of one type or another, foaming can be eliminated or greatly reduced in severity and/or frequency if efficient inlet separation (filtration and coalescence) is in place upstream of the amine contactor. However, if the amine solution does become contaminated, a proper amine filtration system and activated carbon adsorption beds are helpful in removing the contaminants. Antifoam use is a common method to temporarily control the detrimental effects of foaming, however, the effectiveness of a given antifoam may be limited depending on the type of antifoam used and the location where it is injected. Some plants use antifoam on a regular basis, but this could harm the solution and plant in the long term.

Root cause analysis of foaming and the elimination of its source are the best ways to deal with a foaming amine solution. Nevertheless, antifoam may need to be required when sporadic foaming incidents occur, and the source of foaming agent has not yet been identified.

Plants should proceed with caution when adding antifoam to keep the unit under control, especially when operating at high production rates. The antifoam will usually separate as a top layer in the unit flash tank, sump or surge tank surface. It can also be removed by certain filters and carbon adsorption beds (for most types of antifoam), hence, their build-up in the circulating solution can be controlled. Typical antifoams used in amine service fall into the following categories: silicone-based, silicone esters, polyglycols, high molecular weight alcohols and polyalkyl ethoxylates. The correct antifoam for the system is best determined with onsite foam testing. However, silicone-based antifoams are perhaps the most effective products, but at the same time the least chemically compatible with amine solvents.

War stories from the foaming front

Field experiences in amine unit foaming, testing and troubleshooting are critical factors to better understand the foaming phenomenon, its origins and how to combat its effects. Foaming can be a tricky problem to solve, as it involves investigation into the chemical, operational and design aspects of the unit. The following case studies provide examples of how thorough, disciplined reviews of various foaming incidents resulted in mitigation of the foaming problems.

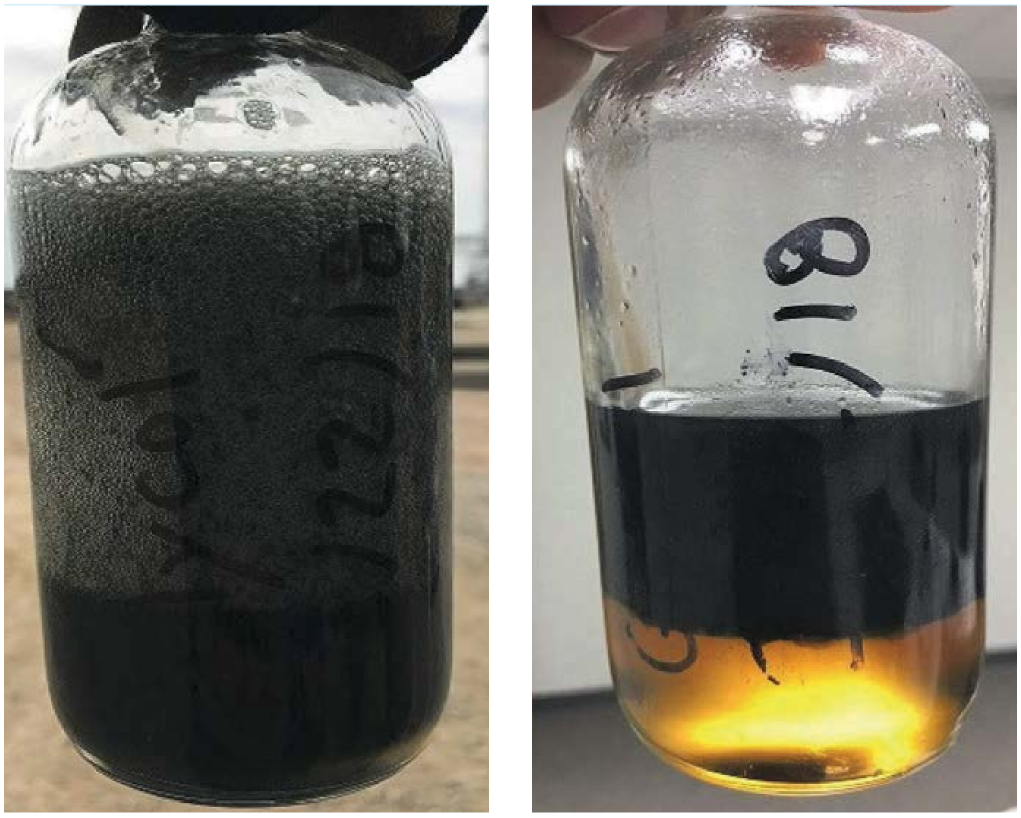
Case study 1

A Southern US gas processing plant rated for 200 million std ft^3/d, using activated MDEA, was shut down because the plant could not meet its H_2S specification well below rated capacity, because of severe foaming. Onsite work was performed to determine the root cause of the original foaming event, but it became an ongoing foaming study when the newly replaced solvent continued to show significant foaming and fouling, even with reduced gas flows entering the amine unit. The operators were perplexed, because the system had what would normally be considered a very good system preparation and filtration set up. The plant had a large slug catcher, a post-compression separator and a newly installed helical inlet filter/coalescer. There were particle filters and a carbon bed on the lean amine, as well as particle filters on the rich. Feed contaminants should have been reasonably removed, but if they did enter the system via inlet carryover, the in-system filtration should have been successful at cleaning up the amine.

Root causes

Solving the foaming problem was made more urgent when the downstream glycol dehydration system also showed signs of severe foaming (and fouling) when some of the feed gas entered the glycol unit without having first passed through the amine unit (low feed gas H_2S and CO_2 composition meant some gas could bypass the amine unit, and when blended with the amine treated gas, would still meet pipeline specification). Not only did the glycol foam uncontrollably, similar to the amine, but the previously water-white glycol suddenly became black and viscous. Fig. 1 shows the foaming glycol after taking the sample and a day later after allowing phase separation. The solution looked remarkably like the amine prior to the shutdown.

It appeared that if gas rates were maximised to the facility, significant contamination of the process units was inevitable. The contaminant not only increased foam



PHOTOS: AMINE EXPERTS

Fig. 1: Lean TEG sample showing foam (left) and with phase separation 24 hrs later (right).

PHOTOS: AMINE EXPERTS

Fig. 2: Inlet KO Drum Fluids.

Fig. 3: Foam Test of Black Powder Solvent added to Amine Solvent.

tendency and stability but also the fouling of the systems. The source had to be found immediately, or the entire plant would need to be shut in.

Tracing back from the inlet to the amine unit, and downstream of the helical separator, dark, black liquids were found in a low spot in the gas line. When introduced to both fresh amine and TEG, it increased the foam tendency and stability of the foam. Had the coalescer been working properly, this fluid should not have been in the gas line. Testing with a "gas super coalescer" test unit (GASCO test rig) showed that the new coalescer was only separating at 77% efficiency, well below its rated efficiency of 99.9% of solids down to 0.3 micron and 99.5% of liquids 0.3 micron and larger. Optimisation of this coalescer was left to the manufacturer.

Sampling further back to the large inlet horizontal separator, what looked like an eruption of foaming grey fluids was found filling the lower half of the knock-out drum. Fig. 2 shows the foaming inlet separator fluids, which were being swept downstream of the knockout KO) drum at maximum gas rate conditions.

Discussion with operations staff indicated the inlet separator had level control issues after a new black powder (pipeline cleaning product) solvent was injected upstream of the plant feed gas header. A sample of the solvent was added to fresh amine and caused the solution to foam right out of the test frit. Fig. 3 shows the results of the foam test.

The new pipeline flow control solvent was indeed the cause of the bad plant foaming and fouling. It was surmised that at lower gas rates, the inlet separation devices didn't entrain as much of the foam/froth from the inlet knock-out, and any material that did pass through was primarily removed by the new coalescer.

However, at high gas rates, excess froth was swept out of the knock-out and through the poorly performing coalescer and into the amine and glycol systems. The product's high surfactant properties increased the foaming in the systems, and its solid removal properties cleaned any residual solids off the vessel walls and piping in both the amine and glycol systems, leading to the elevated solids loads in the systems.

The major foam event was solved, and plans put in place to discontinue the high solvent injection rates and install a more effective element-based filter/coalescer downstream of the helical unit. The amine and glycol solvents were replaced after cleaning the units and circulated with clean, dry sales gas flow to prevent precontamination of the system before the new separation device was installed.

Unexpectedly, the amine solution continued to foam quite severely even with clean gas and new solvent.

This problem required further technical support to solve. A gamma scan was performed on the contactor, showing that the foaming was taking place at the top of the tower. This was the first indication that foaming was likely being caused because of the foam tendency exhibited by the lean amine solution. If the foaming occurred at the bottom sections of the contactor, it would suggest that the feed gas had the foam promoting contaminants. Testing of the make-up water and fresh amine in storage (diluted with distilled water), showed no foam formation. Both factors were discarded as the foam root cause.

The carbon bed should have been able to clean up any foam promoting residuals in the system. However, it appeared to be ineffective. Samples of the amine entering and exiting the carbon bed both showed foaming. Evaluation of the carbon indicated that it was an inferior product for the application and it was replaced with a material having the correct pore distribution for the type of contaminants that are typically found in amine systems. There were definitely shortfalls in the carbon adsorption bed, but why the elevated foaming tendency with clean amine in a clean system? That required further evaluation.

The pleated-style rich amine filters used yellow cellulose as the filter media. The materials in the filter (filter media, screens, adhesive), showed good chemical compatibility with the amine solution after testing and did not contribute to appreciable foam stabilisation. Attention was then turned to the lean amine filters, which were located between the regenerator and the lean/rich exchanger. The harsh chemical environment combined with the high temperatures in this location significantly limits the materials compatibility and the possible options for filtration. Fig. 4 shows a simple chemical compatibility test, foam formation and stabilisation with 50% activated MDEA solvent taken from the fresh amine storage tank. A test soak conducted on all material components in the filter element indicated that the white cellulose filter media was causing severe foam stabilisation. Foam was stable up to two hours after a few minutes contact with the amine solvent. The test was conducted at ambient temperature. Therefore, at the much higher regenerator outlet temperature, it is expected that the effect is exacerbated.

The fact that the yellow cellulose (rich filters) did not cause amine solution foaming but the white cellulose (lean filters) did,

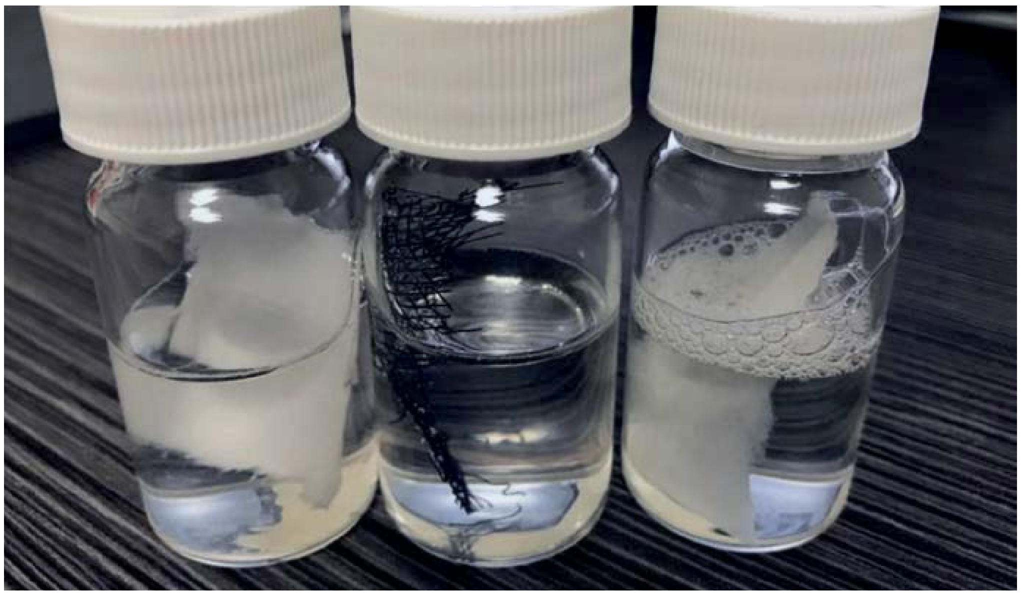


PHOTO: AMINE EXPERTS

Fig. 4: Soak and foam test of the materials in the lean amine filter using fresh 50% formulated MDEA. Test was performed at 77°F for 4 hrs. The vials were agitated for 1 minute. The image was taken after 5 min resting. Left: cotton media (no foam formation). Middle: filter support screen (no foam formation). Right: white cellulose media (high foam formation and high foam stability).

called for a more in-depth investigation. After a review of the available information, it was determined that the yellow cellulose is impregnated with a phenolic resin that is amine compatible, whereas the white cellulose is impregnated with polyesters and other amine incompatible components. The impregnation process is used to impart mechanical resistance to the cellulose material. The adhesive in the filter element was not tested and became irrelevant as the media was much more important in comparison.

It is important to know that some cellulose materials should not be used in amine units. Only properly specified cellulose filter media, with correct compatibility properties, will function in amine units properly and not cause any foaming.

There are several aspects to consider in materials compatibility in an amine unit. Some of these can promote foaming and some affect the process negatively but not necessarily cause foam. The key aspects in materials compatibility in an amine unit are outlined below:

- Chemical degradation of filter materials. Leaching residues released from the filter material can be foam promoters.
- Media erosion and distortion (physical changes, not necessarily associated directly with foaming, but reduce the particle-removal efficiency of the filter, which can then lead to increased foam stability)
- Filter media fibre release (can also lead to foam stabilisation)
- Thermal compatibility related to melting or softening of filter materials. High temperatures can compromise certain filter materials enhancing also any possible chemical degradation.
- Mechanical compatibility related to the tensile strength of the filter material at the actual process conditions.

Chemical incompatibility is perhaps the leading cause of materials compatibility leading to amine foaming. An example of such a situation is the use of polyester filter media in an amine unit process. Polyester will suffer a chemical reaction with amine solution, essentially causing the fibre to dissolve, leading to an eventual filter media damage, rupture and by-pass. It can also often promote foaming.

Conclusions

Solving foaming in the short and long term at this plant was challenging and required a multi-pronged approach. Improving inlet liquids removal, better materials compatibility and ceasing injection of foam promoting chemicals at the plant inlet. The plant was required to install a high efficiency gas coalesce downstream of the helical coalescer. This improved liquids removal efficiency at the inlet of the unit and ensured minimal contaminant ingression. The plant also optimised its antifoam program using a more efficient antifoam, which was determined through proper laboratory testing of several different products. The lean amine filter media was changed from a chemically incompatible cellulose to cotton; in addition, the filter O-ring elastomers were switched from Viton to EPDM (best compatible material with amine solutions).

Finally, the plant ceased the injection of the black powder solvent into the feed gas at the inlet of the plant. The combination of these items alleviated considerably the foaming incidents in the amine unit and any further foam incidents were controlled much more effectively.

Case study 2

A large gas plant (using Diglycolamine, DGA®) experienced almost continuously high absorber differential pressure readings and bottoms level control problems during the winter months (the effect was not as pronounced in the summer). Unless antifoam was continuously injected in the winter time, the contactor level controller would close flow, causing the flash tank level controller to close flow and ultimately starving the regenerator of amine solvent.

This plant had excellent inlet gas separation and coalescing filtration. The amine was also very clean and had an appropriate filtration process. The amine was maintained at a temperature of 5°C warmer than the inlet gas, other than the summer months when the ambient temperature prevented adequate cooling of the amine and the differential temperature increased to approximately 15°C. Foam testing of both the lean and rich amine revealed very low foaming tendency and stability levels.

This plant was brand new, clean, well-operated and showed no signs of contamination. So, what was the problem?

Root causes

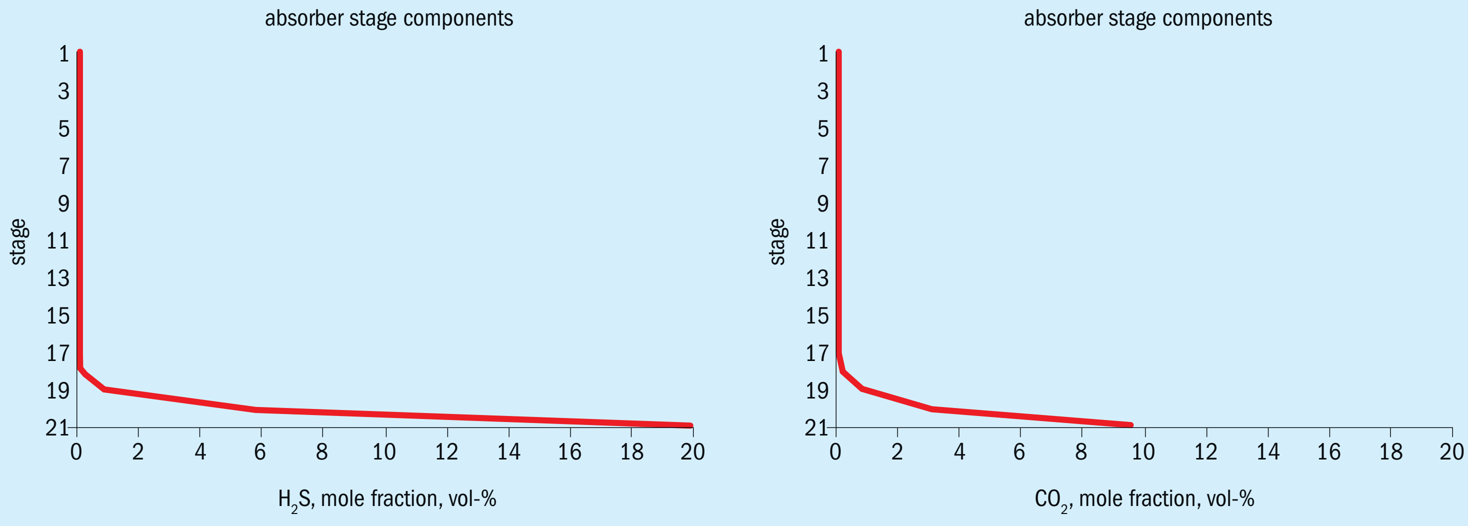
The root cause of this foaming problem was related to the condensation of hydrocarbons within the absorber.

Table 1: **Comparison of inlet and treated gas streams from the absorber**

Component	Inlet gas	Treated gas
H_2S	24.3	0
CO_2	9.7	0
C1	58.1	88.2
C2	3.9	5.8
C3	1.47	2.2
C4	0.93	1.4
C5	0.52	0.8
C6	0.2	0.3
C7	0.06	0.09
C8	0.099	0.15
C9	0.05	0.08

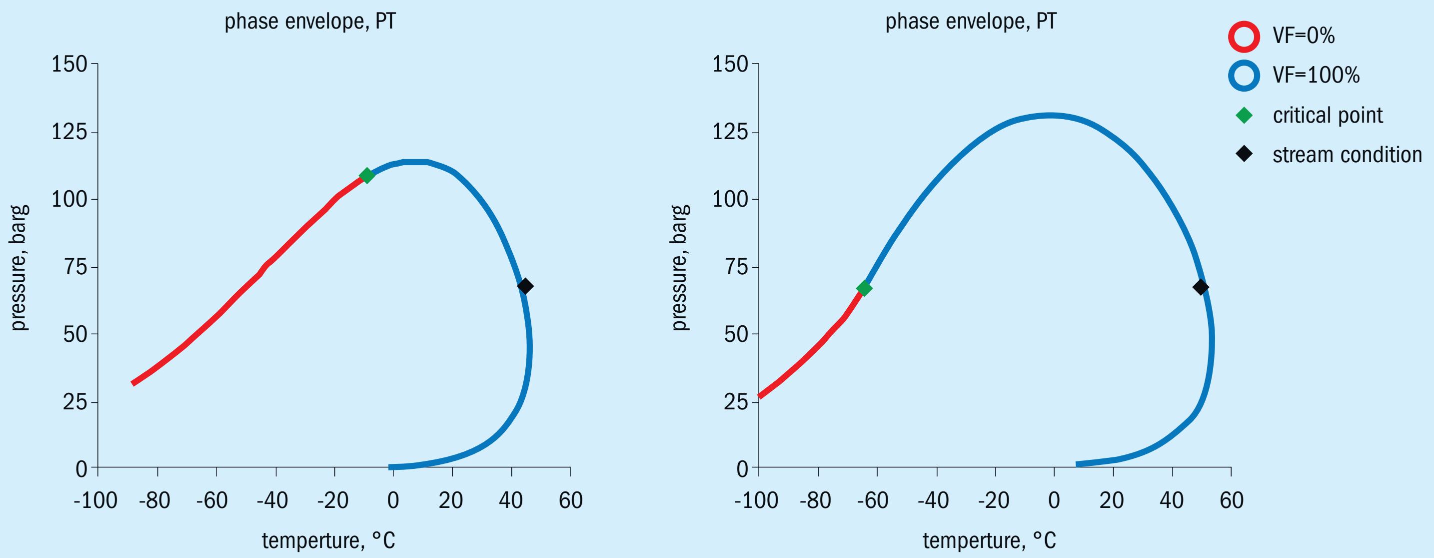
Source: Amine Experts

Fig. 5: **H_2S and CO_2 removal profiles**



Source: Amine Experts

Fig. 6: **Inlet gas (top) and treated gas (bottom) phase envelopes**



Source: Amine Experts

Table 1 lists the acid gas and hydrocarbon composition of the inlet and outlet gas streams of the absorber.

Because the large volume of H_2S and CO_2 being removed by the DGA resulted in a concentration of the remaining hydrocarbons, the hydrocarbon dew point was dramatically shifted as the gas bubbled up through the trays. Fig. 5 shows the H_2S and CO_2 removal profile, and Fig. 6 shows the inlet/treated gas hydrocarbon dew point phase envelopes.

As shown in Fig. 6, the hydrocarbon dew point in the inlet gas (at the absorber pressure) was 42°C, whereas in the treated gas it was 50°C, which was exactly the same as the set point of the lean amine. In the summer months the amine could not be cooled to the set point, instead it operated at temperatures of 55°C-60°C, which was above the hydrocarbon dew point. It was in the winter time, when ambient conditions allowed for better amine cooling, that the hydrocarbon dew point line was crossed.

When the dew point of the treated gas matches the lean amine temperature, it is almost certain that hydrocarbons have been condensed inside the absorber, and therefore, these components do not appear in the treated gas analysis; they were liquefied and do not exit with the treated gas.

Because the DGA was so powerful at removing the acid gas components from the inlet gas, the gas was "sweet" after passing through only the bottom three trays of the absorber. Once there was no more exothermic reaction occurring, the gas simply cooled to the same temperature as the lean DGA, which was 50°C. This cooling happened by tray 5 from the bottom, which is where the foaming would have originated. The first symptom operators noticed was an increase in differential pressure, followed roughly two minutes later by a closing of the absorber level control valve. The reason for the delay in the valve closing was it takes roughly two minutes for the bottom couple of trays to drain once the foaming amine above stops flowing downward. Because the inlet gas is now contacting dry trays, the temperature bulge shifts upwards, as does the foam and, if antifoam was not added, eventually there would have been H_2S breakthrough, and amine carryover. Because of the lack of rich amine flow the operators added antifoam long before this ever occurred.

Solutions and mitigations

Because of the large volume of acid gas removed, which greatly shifted the hydrocarbon dew point, the typical "rule of thumb" to keep the lean amine 5°C warmer than the inlet gas temperature was not adequate. In this case, the required differential temperature between the lean amine and inlet gas was closer to 15°C (which the plant was doing in the summer months). This adjustment was made, and antifoam is no longer required at this facility, although the operators keep it on hand.

In most amine systems, this level of differential temperature would put the plant at high risk of going off specification on H_2S (because hot absorbers do a poor job of H_2S removal). Luckily, a combination of very high H_2S and CO_2 partial pressures in this absorber and the usage of a primary amine such as DGA allowed this facility to remain operating within required parameters and specifications, even at higher temperatures.

Conclusions

The so called "rules of thumb" should not be used to determine operating setpoints in amine units. What works for five units in a row may not work for the sixth unit. For lean amine temperature, it should be set as low as possible but still above the treated gas hydrocarbon dew point.

Final remarks

One of the most important lessons learned over many years of work in various amine units and solving foaming problems globally is that there can be a multitude of factors causing an amine unit to experience foam. Only in some cases is there a single factor as the main cause leading to foaming: often there are several items contributing to foaming. Perhaps one of the most important factors in foam promotion are inlet contaminants, so contamination control at the unit entry is a critical step for ensuring minimal foaming episodes.

The majority of the plants that do not consider this step often fight against foaming in addition to high operating costs, low reliability of equipment, and many other adverse incidents with economic and environmental impacts. Other sources of foaming should also be considered, such as operational practices and of the materials being used within each piece of the amine plant equipment. Sometimes the culprits can be found where one least expects. Therefore, a comprehensive testing plan, with systematic analysis protocol, should always be performed, not only to determine the cause(s) of foaming but also to form a plan for effective, long term foaming mitigation. ■

Acknowledgement

This article is an abridged version of the paper "War stories from the foaming front" by Dr David B. Engel of Nexo Solutions, Ben Spooner, Steven Ayres and Michael Sheilan of Sulphur Experts/Amine Experts. Four further case studies are presented in the full paper.

Advertisers' index

Next issue: September/October 2020

Distribution at:
Sulphur + Sulphuric Acid 2020, The Hague, Netherlands

- Abu Dhabi – sulphur powerhouse
- Metal leaching
- SO_2 emissions control
- State of the art sulphur melting
- Mercaptans removal

Closing date for advertisement space booking is 7 September 2020
For further information and to book advertisement space contact:
Tina Firman, Publishing Director: tina.firman@bcinsight.com
Tel: +44 (0)20 7793 2567 Fax: +44 (0)20 7793 2577

Editor: RICHARD HANDS
richard.hands@bcinsight.com

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

Contributor: MEENA CHAUHAN
meena.chauhan@argusmedia.com

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

Subscription rates:
GBP 440; USD 880; EUR 680

Subscription claims:
Claims for non receipt of issues must be made within 3 months of the issue publication date.

Sales/Marketing/Subscriptions:
MARLENE VAZ
Tel: +44 (0)20 7793 2569
Fax: +44 (0)20 7793 2577
marlene.vaz@bcinsight.com
Cheques payable to BCInsight Ltd

Advertising enquiries:
TINA FIRMAN
tina.firman@bcinsight.com
Tel: +44 (0)20 7793 2567

Agents:
Japan: (also subscription enquiries)
KOICHI OGAWA
O.T.O. Research Corporation
Takeuchi Building
1-34-12 Takadanobaba
Shinjuku-Ku, Tokyo 169, Japan
Tel: +81 3 3208 7821
Fax: +81 3 3200 2889

Previous articles from *Sulphur* from 1995 to the present are available digitally in PDF format. To make a purchase, or for a list of available articles, please see: www.bcinsight.com

ISSN: 0039-4890

Design and production:
JOHN CREEK, DANI HART

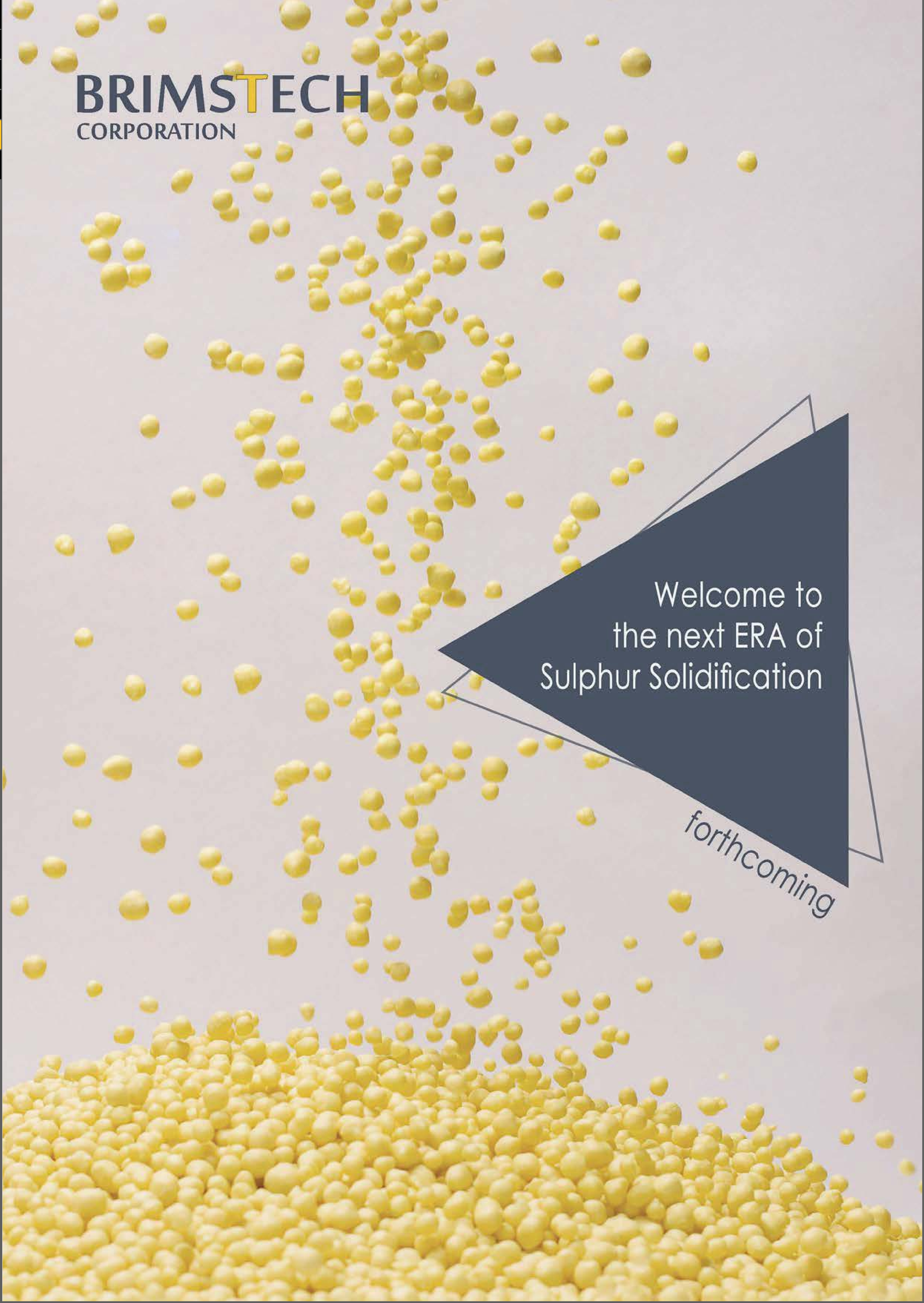
Mixed Sources
Product group from well-managed forests and other controlled sources
FSC

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

BCInsight

Published by: BCInsight Ltd
China Works, Unit 102,
100 Black Prince Road,
London SE1 7SJ, UK
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52



1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52