1 47
2 48
3 49
4 50
5 51
6 52
7 53
8 54
9 55
10 56
11 57
12 58
13 59
14 60
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 408

September | October 2023

SULPHUR

www.sulphurmagazine.com

70 YEARS ANNIVERSARY 1953-2023

Welcome to our iPad version of Sulphur Issue 408

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.

ⓧ CLOSE COPYRIGHT NOTICE

Sulphur + Sulphuric Acid 2023 Conference

Unlocking sour gas reserves

Demand for sulphur fertilizers

Sulphuric acid recycling

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 53 54 55 56 57 58 59 60

Cover: *Fireworks in the French Quarter, New Orleans.*
franckreporter/iStockphoto.com

SULPHUR

www.sulphurmagazine.com

NUMBER 408 SEPTEMBER | OCTOBER 2023

CONTENTS

18 **Demand for sulphur fertilizers**
While phosphate fertilizer production represents the main slice of demand for elemental sulphur and sulphuric acid, sulphur fertilizers continue to be a growing sector of demand due to changes in the way that we use sulphur.

24 **Is LFP the 'next big thing'?**
Lithium ion battery production is driving major expansions in nickel and cobalt extraction, but lithium iron phosphate (LFP) battery use is growing rapidly.

26 **Sulphuric acid recycling**
As producers and regulators become increasingly concerned about the 'circular economy', there is increasing focus on regenerating waste sulphuric acid for re-use.

30 **Join the debate in New Orleans**
CRU's Sulphur + Sulphuric Acid 2023 Conference & Exhibition takes place at the Sheraton New Orleans, Louisiana, USA, 6-8 November 2023.

32 **Unlocking the power of sour gas reserves**
TarT technology, one of 8 Rivers' decarbonisation technologies, shows promise as an economical, efficient, sour gas sweetening process with near-zero carbon dioxide emissions, and may be key to unlocking access to the world's sour gas reserves.

38 **Keep your sulphur recovery unit online and efficient**
Comprimo and Ametek now offer the Analyser Air Control Technology (2ACT) Solution to the industry which enables operating companies to control their assets closer to design capacity at higher recovery efficiency and with fewer unscheduled outages.

44 **Protecting your assets with PFA**
In this case study, AGRU Kunststofftechnik reports on how a new condenser design, engineered by OMV and INWA AG using PFA sheets from AGRU, was implemented at OMV refinery in Austria to address maintenance problems due to corrosion of the WSA condensers and the follow-up units.

48 **TGU catalyst poisoning and deactivation**
With the aid of a rigorous kinetic model for TGU hydrogenation reactors, incorporating catalyst deactivation mechanisms, designers and operators can forecast the life expectancy of reactor catalyst beds.

54 **Monitoring for refractory failure in Claus reactors**
WIKA discusses a novel and easy way to monitor the shell temperature of the Claus thermal reactor using proven technology and highlights the benefits a purge-less thermocouple system for high temperature measurement.

56 **A novel combustion solution**
A new burner design for the combustion of natural gas with either combustion air or pure oxygen as the oxidiser has been developed by CS Combustion Solutions. The new Oxijet®-Burner has been designed to perform both start-up and main operation functions with one burner.

REGULARS

4 **Editorial**
China's troubled transition

18

Sulphur as a fertilizer

Increasing demand for a vital agronomic product

44

New condenser design

Making maintenance easier

Read this issue online at:
www.sulphurmagazine.com

Published by:
BCInsight

China's troubled transition

All is not well with the Chinese economy. Growth has slowed to a fraction of what it was, only 0.8% in 2Q 2023, and has not bounced back as expected as covid lockdowns were eased. Exports and imports are both falling, debt has reached 300% of GDP, youth unemployment is running at 20%, and the property market is collapsing, with huge property developers like Evergrande and Country Garden only avoiding bankruptcy via government arranged loan restructurings. Consumer prices have fallen year on year, raising the spectre of deflation, and productivity growth has fallen from 4.5% year on year in 2006-7 to around 0.8% today. The yuan is trading at a 16-year low against the dollar.

Coming after four decades of breakneck growth, instituted by Deng Xiaoping's economic reforms in 1978, the slowdown has a been a return to earth after the boom years, driven in no small part by a huge demographic shift as the long term effects of increased longevity and the One Child policy lead to a rapidly ageing population with fewer new workers to replace those retiring. The government been trying to ease the country's transition from a low wage industrial economy that is 'the workhouse of the world' to a middle income, consumer driven economy, but the property crash is a sign of low consumer confidence and low household incomes.

All of this has had a knock-on effect on commodity markets, which had been rising in anticipation of a Chinese post-covid bounce back. The dislocations caused by economic sanctions on Russia are easing, and with Chinese demand still slack and structural overcapacity remaining in many Chinese industrial sectors, prices are falling again, though there are still some bright spots, such as copper and nickel demand for renewable power and electric vehicles. Low margins at smelters are also leading to some shutdowns, affecting both domestic copper and acid production.

Meanwhile, China's Belt and Road Initiative, a programme of strategic partnerships and investments, was supposed to secure raw materials for the country's economic growth, but it has also led to major trade deficits for partner countries who did not see the Chinese market access they had hoped for, while the pandemic led to a buildup of bad debts.

China's impact on sulphur markets is seeing its own transition, as domestic phosphate production falls, and the country's sulphur production increases. Chinese MAP and DAP production has fallen by 5 million t/a over the past five years as the government tries to tackle overcapacity, environmental emissions and overapplication of fertilizer, and exports have fallen by a similar amount due to export quotas to keep domestic prices low – DAP exports were just 3.6 million t/a in 2022. At the same time, sulphur production from sour gas and particularly new refineries is rising. Chinese sulphur production has risen from 6.4 million t/a to 9.7 million t/a from 2018-22. For a long time China has been far and away the world's largest importer of sulphur, and this continues to fall. Sulphur imports for 2022 were down 10% to 7.6 million t/a, and down from 11.7 million t/a in 2019, and stocks remain high. Increased production of sulphuric acid from smelters has also reduced demand for imported sulphur.

In the same way that we are approaching Peak Oil (at least in terms of demand), it is beginning to look like we may have reached 'Peak China'. New sulphur demand is coming from Indonesia's nickel production, and Saudi Arabia's and Morocco's phosphate industries, and new production from Asian refineries and Middle Eastern sour gas projects. ■

> **"We may have reached 'Peak China'."**

Richard Hands, Editor

1 47
2 48
3 49
4 50
5 51
6 52
7 53
8 54
9 55
10 56
11 57
12 58
13 59
14 60
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

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 53 54 55 56 57 58 59 60

Price Trends

MARKET INSIGHT

Maria Mosquera, Editor of the Argus Sulphur Report and **Liliana Minton**, Editor of the Argus Sulphuric Acid Report at Argus Media assess price trends and the market outlook for sulphur and sulphuric acid.

SULPHUR

Sulphur prices have firmed during the third quarter following the soft trend of the second quarter. The c.fr China granular sulphur price lifted by $32/t in the six weeks from 6 July to 24 August- with further firming for September deliveries evident. The rising phosphate fertilizer market encouraged offers to move up, with September tonnes offered to buyers consistently at and above $130/t c.fr to several markets.

With phosphate fertilizer prices and demand lifting operating rates, sulphur demand and prices have lifted during the quarter. This has been led by Chinese demand, and while the bullish sentiment from returning demand and price increases in the DAP and MAP markets are lifting sulphur prices in September, high inventory levels provide a downward signal. The upcoming autumn fertilizer application season and strong fertilizer export sales supported producers in keeping production rates high in September; up to 70-80% in the river regions and 70% in the south during August. DAP export prices lifted by $53/t in the space of a month from 5th July to 3rd August, and continued to rise through August. DAP prices f.o.b. China rose by $153/t in August from early July.

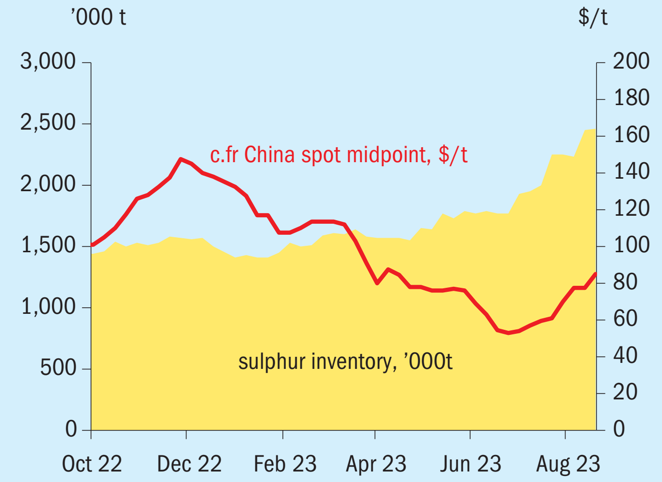
However, some Chinese import demand was from traders already holding substantial port inventories, and looking to add to these in order to average out stock cost and dilute the high cost of tonnes bought when the market was firmer last year. This had the impact of lifting port inventory levels to a substantial 2.45 million tonnes, a level not reached since 2021, when stock levels briefly reached 2.6 million tonnes. That followed the high stock build up during the 2020 pandemic, when stocks reached an unprecedented 3.1 million tonnes in March and April, before beginning to fall off. In the early part of this year stocks have been consistently rising, and c.fr China import prices reducing, with stocks building until June.

This is despite increasing domestic sulphur production from new domestic refineries adding to readily available inventory. Chinese domestic sulphur production has risen by around 5% compared to 2022. Last year, when port stocks briefly rose to similar levels, the period of heavy import activity was followed by trading, mainly taking place in local currency from existing port stocks, leading to falling import demand. This, in turn, also eroded prices with a sudden lack of Chinese import demand weighing on global demand. This is likely to be repeated this year, particularly when the DAP market softens.

Indonesian buyers have moderated buying for the nickel leaching sector since the bulk-buying of 400,000 t in the space of a few weeks led to a price increase in the first quarter. Now buyers are either consuming existing stock amid a slow ramp of full operations in the case of PT Huayue, receiving contract shipments and sulphuric acid cargoes in the case of PT Halmahera Lygend or buying sulphur stock at a more moderate pace. With a large ramp up to Indonesia's sulphur demand last year by as much as 1 million tonnes, this year the rise will be moderate with sulphur demand to ramp up further in the second half of the year, bringing import expectations for the year to around 2 million tonnes.

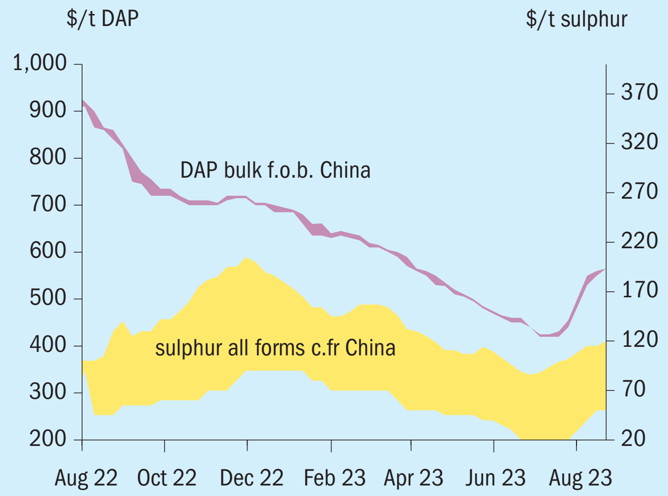
The gap between east of Suez and the softer markets west of Suez increased during the quarter. Since much of the demand in the west was covered under contract, length in the US Gulf secured lower prices for product and Morocco made use of ample Kazakh availability of both granular and crushed lump sulphur. Demand was also subdued due to fertilizer stock that needed to be placed. In July and August the difference between c.fr pricing in China and Southeast Asia for sales to Indonesia and key buyers in the west like North Africa and Brazil ranged between $10-20/t. With freight rates high, a gap of around $10-20/t

Fig. 1: **Chinese sulphur inventories (left) and spot sulphur price (right)**



Source: Argus Sulphur

Fig. 2: **DAP (left) vs sulphur prices (right) in China**



Source: Argus Sulphur

is still below the freight differential to encourage a steady flow of shipments from west to east, though some Russian supply is finding its way to markets as far afield as China and India. However, the gap is expected to close once the latest round of Chinese demand has been covered.

In Western European molten sulphur market the Benelux quarterly contract price for third-quarter supply settled at a substantial reduction of $40/t on the second quarter, equating to a price of $87-103/t c.fr Benelux. This reflected the slow-down in consumption from much of European industry amid competition from lower-priced chemical imports and higher energy costs. Due to the lower consumption, the reduced sulphur production arising from the stoppage of Russian crude imports to European refineries was not felt by most consumers, leading to a logistical exercise of moving product within the region.

SULPHURIC ACID

Sulphuric acid prices started the third quarter of the year with an east/west of Suez divide, which was determined by demand – or the lack of it. This factor dominated market sentiment specially in July and into August and resulted in fob prices to fall to three-year lows. It was the continued absence of spot demand from the world's largest acid buyers – Chile and Morocco's OCP – which pressured acid prices globally and led to trade flows being determined by freight costs.

East of Suez, China and South Korea/Japan prices fell to their lowest level in three years on 20 July, when China and South Korean/Japanese acid fell to -$12.50/t f.o.b., both on a midpoint basis, as ample availability was coupled with a lack of spot demand. Furthermore, persistently high freight rates across the Pacific have impeded some of the trade flows and limited the outlets for acid.

> “Sulphuric acid demand from Indonesia is expected to remain robust.”

A factor that surprised nearly every market participant was the strong demand from Indonesia seen so far this year, which provided a much-needed outlet to supply to producers in the east of Suez, and it impeded a further erosion on fob netbacks. Indonesia imported 564,000 t of acid between January-June this year, of which China has supplied 284,000 t of acid, a jump of nearly double the 144,000 t of acid imported from China in 2022, according to trade data, thus becoming the largest offtaker of Chinese acid, displacing Chile as the number one home for acid from China. Looking forward to the remainer of the year, sulphuric acid demand from Indonesia is expected to remain robust owing to the development of new metals projects that commenced operations in Halmahera and Sulawesi in 2021.

In contrast, sulphuric acid prices west of Suez remained in positive territory in the third quarter, despite the sluggish domestic demand from the downstream sector and weak spot demand from Chile – which has become the largest outlet for Northwest European acid producers – and Morocco's fertilizer producer OCP.

And while Northwest EU fobs fell to a three year low at the start of the quarter, prices were above zero and averaged $5.50/t f.o.b. in the first three weeks of July. But spot buying from OCP and Chile finally arrived by mid-August, and supported a recovery in f.o.b. pricing owing to tight availability, as producers remained committed for the short term.

The much-awaited demand from Chile stemmed from an outage at a domestic supplier in the country, which resulted in the domestic balance to switch to negative and led to end users to enter the spot market to secure cargos for prompt arrival.

In North Africa, demand from finished phosphate producer OCP finally came back after several months of inactivity as a pick-up in phosphate prices globally awakened appetite for feedstocks to produce fertilizers.

Overall, the short term picture is more positive for the coming months, and it is expected that sulphuric acid prices will remain firm in the fourth quarter, as tight supply is met with robust demand from large offtakers. ■

Price Indications

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

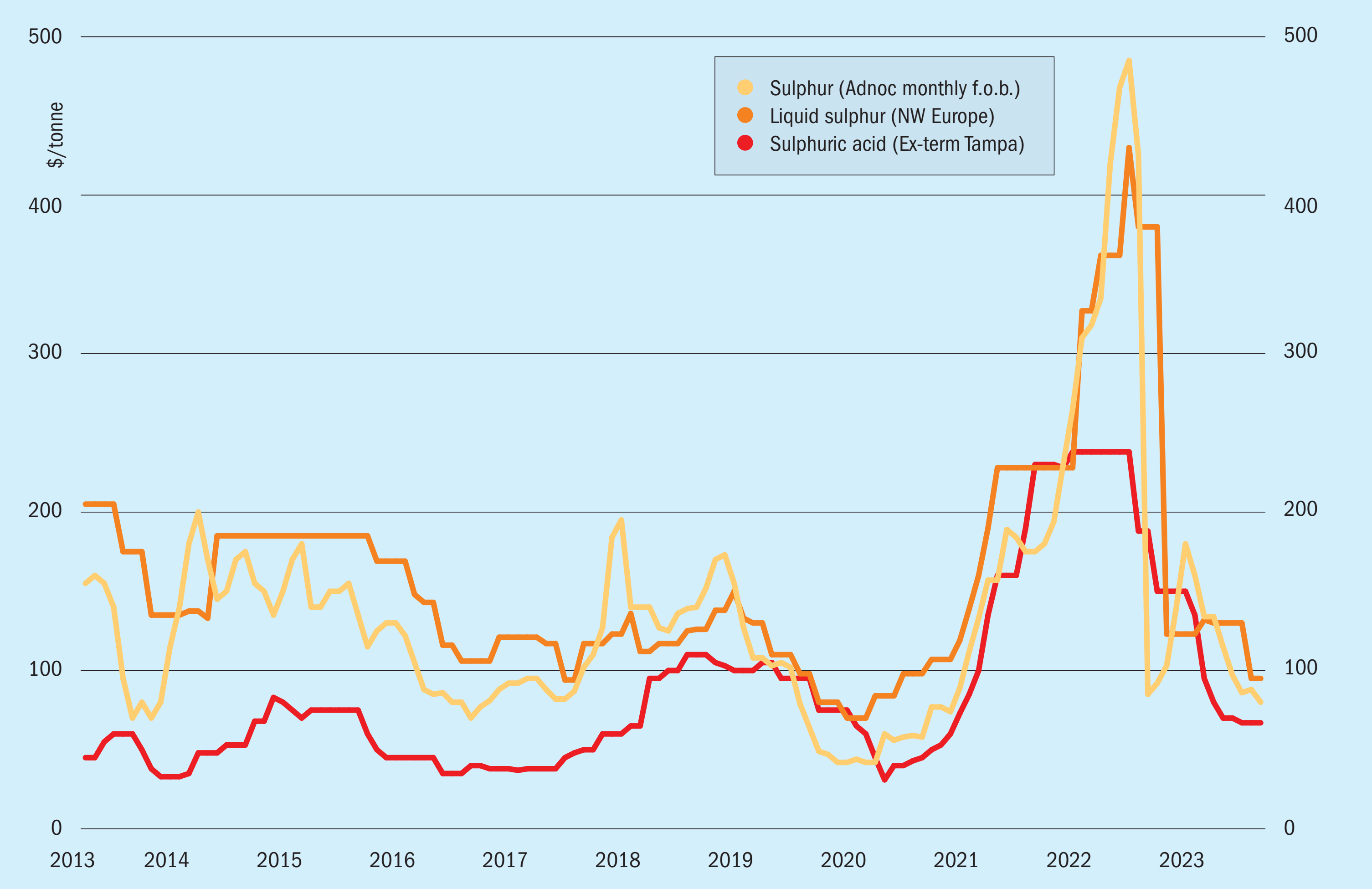
Cash equivalent	April	May	June	July	August
Sulphur, bulk ($/t)					
Adnoc monthly contract	115	97	86	88	80
China c.fr spot	132	118	112	113	113
Liquid sulphur ($/t)					
Tampa f.o.b. contract	103	103	103	55	55
NW Europe c.fr	130	130	130	95	95
Sulphuric acid ($/t)					
US Gulf spot	70	70	67	67	67

Source: various

1 47
2 48
3 49
4 50
5 51
6 52
7 53
8 54
9 55
10 56
11 57
12 58
13 59
14 60
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

Market Outlook

Historical price trends $/tonne



Source: BCInsight

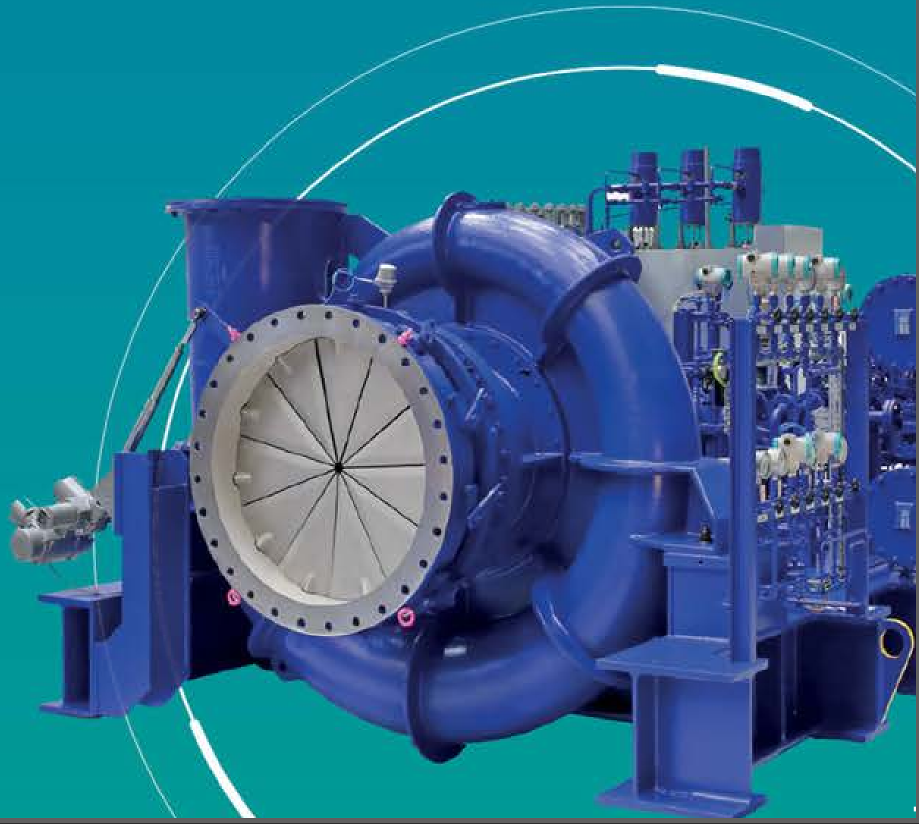
SULPHUR

- New supply is weighing on the market. In addition to increased exports in the second half of the year from upgrades and new refining projects from the Middle East, crushed lump sulphur is also again entering the market in higher quantities from both the FSU and the Middle East, and displacing granular product in some markets, notably Morocco and China.
- Firming DAP market and higher operating rates have been key factors in pushing up sulphur prices. This is expected to give way to a seasonal slump from October for the rest of the year and into 2024.
- Chinese port stock build up will erode import demand and prices in the fourth quarter.
- Indonesian metals buyers are moving into a more predictable pattern of buying. This is removing some of the volatility from the market. The gap between east and west of Suez pricing is expected to close in the fourth quarter once prices come off in the east of Suez markets.
- **Outlook:** Prices are poised to continue to lift on the back of rising phosphate fertilizer demand and pricing in September. However, with sulphur in healthy supply and Chinese port stock levels rising to match levels reached briefly in April 2021, a correction is expected to follow by October once fertilizer demand has been largely covered and operating rates start to fall.

SULPHURIC ACID

- Indonesia's sulphuric acid imports are set to rise in the second half of the year as a result of higher demand from new metals projects. Buying momentum is expected to remain strong in the second half of the year on the back of higher demand and firm supply, according to market participants.
- Chinese acid supply is expected to continue to increase owing to the expansion of smelter capacity in the Baiyin, Hubei and Shanxi regions, which is projected to add another 2 million t/a of production capacity this year, according to Argus estimates.
- Maintenance at three Japanese smelters will tighten merchant acid availability in the fourth quarter. This could remove over 280,000 tonnes/month of acid in the fourth quarter, depending on outage length.
- Chile's demand will determined by how the domestic supply situation is progressing for the rest of the year, this as lower ore grades mined has resulted in less smelter acid produced thus tightening the domestic market and forcing end users to enter the spot market to buy sulphuric acid.
- **Outlook:** Sulphuric acid prices are expected to continue to recover in the short term on the back of robust demand from key offtakers. The continuation of spot demand from Morocco's OCP and Chilean end users will influence price movements. In Asia, supply availability will tighten from September onwards as key smelters in Japan start a period of heavy maintenance, and this will impede a further erosion on prices, as availability will be restricted in the fourth quarter.

1 47
2 48
3 49
4 50
5 51
6 52
7 53
8 54
9 55
10 56
11 57
12 58
13 59
14 60
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



1 47
2 48
3 49
4 50
5 51
6 52
7 53
8 54
9 55
10 56
11 57
12 58
13 59
14 60
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

Sulphur Industry News

UNITED ARAB EMIRATES

Shah achieves record output

Following the completion of expansion work on the ultra-sour gas Shah field in May 2023, production has been ramped up. Occidental, which owns 40% of the Shah project and which operates the field in conjunction with ADONC Sour Gas, reported in July that it had achieved record output at Shah, with gross gas sales reaching 722 million scfd in Q2 2023 (equivalent to 1.1 billion scf/d of raw gas, which is 23% H2S and 10% CO_2). The expansion has taken processing capacity at Shah to 1.45 billion scf/d and forms part of the UAE's plans to achieve gas self-sufficiency by the end of the decade. The expansion was conducted by Saipem, who were awarded a $510 million contract in 2021 to expand output from 1.3 billion scf/d to the current 1.45 billion scf/d. Work was completed two months ahead of schedule, according to Occidental. ■

Tecnicas Reunidas wins Ghasha contract

Técnicas Reunidas and its Emirati partner Target have been awarded a $950 million contract by the Abu Dhabi National Oil Company (ADNOC) as part of the Ghasha concession, the world's largest offshore sour gas development. The scope of the project consists of the design and execution of the land-side facilities for processing of gas from the Dalma field., including the engineering, procurement and construction of gas conditioning facilities for dehydration, compression and associated utilities on the island of Arzanah, 80 kilometers from Abu Dhabi city. The offshore Dalma Gas Development Project is being carried out by a joint venture led by ADNOC 190 km off the northwest coast of the United Arab Emirates. Shareholders in the Ghasha concession include ADNOC (55%), Eni (25%), Wintershall (10%), OMV (5%) and Lukoil (5%).

The Ghasha region consists of several fields with significant gas reserves still under development (Hail, Ghasha, Hair Dalma, Satah, Bu Haseer, Nasr, SARB, Shuwaihat and Mubarraz), which have been identified by ADNOC. The project is expected to be completed in 2025 and will allow the Dalma field to produce some 340 million sscf/d of natural gas.

ADNOC awards $1.3 billion contract for artificial islands

ADNOC has awarded the $1.36 billion dredging, land reclamation and marine construction contract to create several artificial islands in the UAE as part of the first phase of development of the Ghasha concession. The contract has been awarded to UAE's National Marine Dredging Company (NMDC). NMDC is now to construct 10 new artificial islands and two causeways, as well as expand an existing island, Al Ghaf. In total, the project is slated to take around 3 years.

Dr Sultan Ahmad Al Jaber, Minister of State and ADNOC Group CEO, said: "This award accelerates the development of the Hail, Ghasha and Dalma sour gas offshore mega-project, which is an integral part of ADNOC's 2030 smart growth strategy. As one of the world's largest sour gas projects it will make a significant contribution to the UAE's objective to become gas self-sufficient and transition to a potential net gas exporter."

UNITED KINGDOM

Fluor wins contract for SAF production

Fluor has been awarded a contract by LanzaTech UK Ltd to provide front-end engineering and design (FEED) services a commercial sustainable aviation fuel (SAF) plant in Port Talbot, Wales. Fluor will help advance LanzaTech's Project DRAGON – a play on the Welsh national symbol, which stands for Decarbonising and Reimagining Aviation for the Goal of Net zero – to convert locally derived waste gases to ethanol. The ethanol will be converted into SAF, meeting the UK government's mandate that at least 10% of jet fuel should be made from sustainable feedstock by 2030.

"Decarbonising aviation fuel will aid the aviation industry in meeting its net zero carbon emission goals," said Jim Breuer, group president of Fluor's Energy Solutions business. "We are confident that Fluor's renewable fuels expertise, paired with LanzaTech's carbon capture and utilisation technology, can help accelerate the energy transition in this important sector."

SAUDI ARABIA

Aramco evaluating proposals for tail gas treatment

Saudi Aramco has reportedly received bids from two consortia for its programme of upgrading sulphur recovery units at its gas processing plants and is currently evaulating them. Aramco invited expressions of interest in October 2021 for the programme, which aims to bring sulphur recovery at seven gas processing plants up to 99.9% using tail gas treatment units. Proposals for the programme had initially been asked for in September 2022, but this was later extended several times to May 2023. The programme must also bring SO_2 emissions from the gas plants in line with regulations set by the country's Environment, Water & Agriculture Ministry which set maximum SO_2 emissions from stationary sources at 250 ppmv (dry and


PHOTO: SAUDI ARAMCO

The Berri gas plant, Saudi Arabia.

1 47
2 48
3 49
4 50
5 51
6 52
7 53
8 54
9 55
10 56
11 57
12 58
13 59
14 60
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

0 per cent oxygen basis). The gas plants involved are: Berri, Haradh, Hawiyah, Khursaniyah, Shedgum, Uthmaniyah and Wasit. The treatment facilities are being offered on a public-private partnership basis, either build-own-operate or build-own-operate-transfer. The two consortia who have submitted bids are reported to be: India's Larsen & Toubro Energy, with Saudi partner Vision Invest, and a consortium consisting of Hynudai, Enerflex, Broofield, Korea Overseas Infrastructure and Urban Development Corporation and the Export-Import Bank of China. The project is scheduled for completion by 2027.

WORLD

Most new refinery capacity in Asia and Africa

Asia continues to dominate global refinery fluid catalytic cracking unit (FCCU) capacity additions by 2027, according to GlobalData. The continent will be responsible for around 58% of total capacity additions by 2027. This represents a total FCCU capacity addition of 1.83 million bbl/d. Of this, 1.4 million bbl/d is likely to be from new-build refineries while the rest is from the expansion of existing refineries. Within that figure, China is expected to add the highest capacity, with an additional 513,000 bbl/d from seven refineries over the period 2023-2027. India is next with 388,000 bbl/d of capacity additions during the same period. Vadinar refinery, located in India, is the largest upcoming FCCU project in the region and is likely to add 187,000 bbl/d 2024. Nayara Energy Ltd, the operator of the Vadinar refinery, is expanding the cracker as part of the company's plans to diversify its petrochemicals portfolio and meet the growing demand for polypropylene in India.

The Middle East is another significant contributor to global FCCU capacity additions, accounting for 16.8% of additions by 2027, with Iraq is likely to account for most of the capacity additions of 308,000 bbl/d of capacity. Africa follows closely at 16.7%. Here the Lagos I refinery expansion in Nigeria is expected to add the highest capacity addition of 163,000 bbl/d by 2027. Akwa Ibom III, Port Sudan III, and Lobito are the other major upcoming projects with 50,000 bbl/d of FCC capacity expected to be added in each of the refineries during 2023–2027.

DENMARK

Joint venture to accelerate global SAF production

Topsoe and Sasol have signed an agreement to establish a 50/50 joint venture to accelerate their joint commitment to produce sustainable aviation fuels (SAF). The aviation sector contributes 2-3% of global carbon emissions and sustainable aviation fuels are in demand for decarbonising air transport by industry and regulators alike. The partners say that the joint venture will go beyond their combination of technologies, capabilities and industry experience in the scaling up of sustainable aviation fuel production. It will develop, build, own, and operate sustainable aviation fuel plants, and market sustainable aviation fuels derived primarily from non-fossil feedstock, using green hydrogen, sustainable sources of CO_2 and/or biomass with a specific focus on Sasol's Fischer-Tropsch and Topsoe's related technologies.

Fleetwood Grobler, Sasol president and CEO, highlighted the long-term ambitions of Sasol in sustainable aviation fuel, stating: "Sasol is delighted to join forces with Topsoe, furthering our global sustainable aviation fuel aspiration. This is an important milestone in advancing our long-term strategy to become net zero by 2050."

Roeland Baan, CEO at Topsoe, added: "As part of our proven partnership, this future business is an important moment of progress at a critical time. We need to keep the world open by creating more sustainable ways of flying, and our shared commitment to accelerating sustainable aviation fuels is a vital part of this. We believe no one is better placed than the company formed by Sasol and Topsoe to deliver the means to scale SAF production".

PHOTO: AMETEK

The 888L sulphur recovery tail gas analyser.

UNITED STATES

Sulphur recovery analyser

AMETEK Process Instruments has introduced a new sulphur recovery tail gas analyser, the 888L. The company says that it is suitable for end users and end use locations that require the analyser electronics and user interface to be located away from the sampling location. Using smart diagnostics, customers can communicate and react to process trends and problems from a location remote from the sample point. It takes advantage of proven measurement technology, operational hardware and diagnostic software from the existing AMETEK 888 air demand analyser to provide reliable performance, with minimal downtime. It can be installed in a wide range of ambient conditions and temperatures of up to 60°C (140°F). If mounting an analyser at the sample point is restricted due to physical limitations, or if the decision is to mount the user interface and analytical hardware in a protected enclosure, its demister probe can be installed at the sample point, allowing heated sample lines to transport the process sample gas to measurement cell. ■

Sulphuric Acid News

INDIA

Copper smelter looking to March 2024 start-up

Adani Enterprises says that its new greenfield copper smelter at Mundra in Gujarat, being developed by its subsidiary Kutch Copper Ltd, will begin operations in March 2024. The $1.1 billion project will have an annual production capacity of 1 million t/a of copper once the second phase is complete, but the March 24 start-up will be for the first, 500,000 t/a phase. The plant will also produce 25 t/a of gold, 250 t/a of silver, and 1.5 million t/a of sulphuric acid and 250,000 t/a of phosphoric acid as by-products. India currently imports roughly two million t/a of sulphuric acid since the closure of the Vedanta smelter in Tamil Nadu.

Copper demand is rising in India for renewable energy, telecommunications and electric vehicles, and is expected to reach 750,000 t/a this year. However, domestic supply has not been able to meet this demand, and for the year to March 2023 India imported 180,000 tonnes of copper. Copper demand is expected to rise to 1.7 million t/a by 2027 on the back of huge demand from the green energy industry. ■

FACT seeking part-privatisation

State owned Fertilisers And Chemicals Travancore Ltd (FACT) has urged the Indian government to consider a part-privatisation of the company. FACT has achieved a remarkable turnaround in its operations over the past four years, with the share price rising more than tenfold from $0.51/share in January 2019 to $5.75/share today. A central government disinvestment of 15-20% of its 90% shareholding would net it $500-600 million, according to Kishor Rungta, chairman and managing director of FACT. The proposal is reportedly under consideration by the Department of Public Enterprises, who had previously favoured the sale of FACT to another company.

FACT had been a loss-making enterprise until 2019, when it made a profit of $19.8 million. Total revenue for the financial year ended March 2023 reached $767 million, with profits of $75 million, and turnover has been rising 25-30% year on year. Production capacity is scheduled to expand from 100,000 t/a to 150,000 t/a in June-July 2024, as part of a $75 million expansion which also includes new infrastructure, including an ammonia tank, phosphoric acid tank, sulphuric acid tank and a new barge.

UZBEKISTAN

Phosphate production to rise this year

The new $100 million NEOFOS phosphate mine and processing facility is expected to be completed by the end of 2023, according to owner and operator Ferkensco Management Ltd. NEOFOS, in the Navoi region, includes a 45.7 km2 quarry with a depth of up to 50 m that relies on more than 30 units of large equipment such as diesel-hydraulic excavators, a milling combine, dump trucks, bulldozers and graders and will increase the production of phosphate rock in Uzbekistan by 2.0-2.5 million t/a. The associated phosphate processing plant will produce concentrate which will be used as a raw material for fertilizers at the Samarqandkimyo plant, which is also under construction.

Samarqandkimyo will become the largest producer of phosphorus fertilizers in Uzbekistan, producing up to 910,000 t/a, which will not only cover the needs of local farmers, but will also enter the export market.

CANADA

First Phosphate signs acid supply deal

First Phosphate Corp has signed a non-binding memorandum of understanding with NorFalco, a division of Glencore Canada, to secure a supply of sulphuric acid for its planned phosphate plant at Saguenay-Lac-St-Jean, Quebec. Under the terms of the MoU, pending the parties' agreement on a definitive sulphuric acid supply arrangement, First Phosphate will have access to NorFalco's sulphuric acid supply for its planned phosphoric acid and other industrial facilities located in Quebec province.

First Phosphate says that the partnership with NorFalco represents a significant first step in establishing an ongoing supply relationship with a major local supplier. Sulphuric acid plays a vital role in the production of phosphoric acid, which is central to First Phosphate's plans for sustainable development, including the establishment of a purified phosphoric acid facility at the Port of Saguenay, Quebec, in partnership with Prayon Technologies SA of Belgium. The phosphoric acid plant is part of the company's strategy to establish a localised lithium iron phosphate (LFP) battery supply chain in North America. Purified phosphoric acid demand in North America is predicted to double by 2045.

GERMANY

Aurubis profits up 20%

Europe's largest copper producer Aurubis AG is forecasting good profits for its current financial year after showing a 20% increase in 3Q profits for the quarter ending June 30th. The company said that it anticipated full year operating earnings before taxes (EBT) of €450-550 million ($495-605 million) for the 2022-23 annual year. EBT in the third quarter ended June 30 rose about 20% to €115 million year-on-year.

Aurubis said that the reasons for the good results included increased charges to process copper concentrate (ore), high price premiums for the copper it produces and strong demand for copper wire, although these were offset by a significant drop in revenue for by-product sulphuric acid, decreased demand for flat-rolled products and inflation-led costs. The quarterly result was achieved despite a 40-day maintenance shutdown at its Bulgarian plant, Aurubis CEO Roland Harings said.

BRAZIL

MoU for acid treatment of gypsum

US fertilizer producer Mosaic has signed a memorandum of understanding (MoU) with Rainbow Rare Earths to conduct a preliminary economic assessment on the extraction of rare earth elements from Mosaic's phosphogypsum stack in the Uberaba area in Brazil. The companies say that the Uberaba phosphogypsum stack – waste byproduct from phosphate manufacturing – contains valuable rare earth elements that occur as byproducts of the phosphoric acid made by Mosaic at the site. While the carbonatite does not contain rare earths in sufficient quantities to be mined for these elements alone, the plant processes it undergoes concentrate the rare earths, resulting in higher concentrations than in the original rock. Rainbow says that the benefit is that it can render the rare earths associated

1 47
2 48
3 49
4 50
5 51
6 52
7 53
8 54
9 55
10 56
11 57
12 58
13 59
14 60
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

with the phosphogypsum amenable to direct sulphuric acid leaching, which allows for a simpler hydrometallurgical process to produce separated and purified rare earth oxides. Under the terms of the MoU, Rainbow and Mosaic will look to jointly develop a process flowsheet to extract the rare earth elements from the Uberaba stack.

AUSTRALIA

Avenira looking at LFP production

Australian phosphate company Avenira says that it is looking at building a new lithium iron phosphate (LFP) cathode manufacturing plant in Darwin, Northern Territory. The plant will be linked to Avenira's Wonarah phosphate project 1,00 km away by road. Operations in both Wonarah and Darwin will be powered by a combination of solar, wind, and gas. Avenira says that within two years, it could be one of only three LFP cathode manufacturers outside of China, giving global EV manufacturers more supply and more choice of supplier of battery grade material. Avenira hopes to commence construction on the LFP plant late next year, with LFP cathode production to commence in 2025. A final investment decision is expected next quarter. Once LFP production is underway at Darwin, Avenira says that it is looking to develop a thermal phosphoric acid product from an additional processing facility at Wonarah which would then be used as feedstock for the Darwin LFP plant.

CHINA

Metals output up

Sumitomo Metal Mining (SMM) reports that China's copper cathode output in July was 925,900 tonnes, up 0.9% month-on-month, and up 10.2% year-on-year. Total output was 6.49 million tonnes from January to July, an increase of 639,300 tonnes or 10.94% year on year. Although there were seven smelters undergoing maintenance in July, a newly commissioned smelter in Shandong helped boost output. The average operating rate at copper smelters stood at 86.49% in July, flat on the month.

Primary lead output was 319,700 tonnes in July, up 9.1% month-on-month and 21.94% year-on-year; cumulative output from January to July 2023 increased by 17.63% year-on-year. Total production capacities of enterprises in the survey totalled 5.84 million tonnes. Large-scale lead smelting enterprises in Henan, Yunnan, Inner Mongolia, Shandong and other regions completed their maintenance and resumed production in July, growing output.

China's refined zinc output was 551,100 tonnes in July down 0.26% month-on-month, but a year-on-year increase of 15.79%. From January to July, the cumulative output of refined zinc reached 3.78 million tonnes, a year-on-year increase of 9.59%.

According to SMM data, China's titanium dioxide output reached 310,000 tonnes in July 2023, marking an 8.1% increase month-on-month, but a decline of 4.8% year-on-year. The total production for the first seven months of this year stood at 2.2 million tonnes, representing a year-on-year decrease of 5.3%. July saw a positive trend in the operation of domestic titanium dioxide enterprises due to price hikes, and companies that had previously reduced production resumed full operations. Consequently, the aggregate output rose by 20,000 tonnes from the previous month.

INDONESIA

Nickel Industries buys into Huayue project

Australia's Nickel Industries Ltd says that it has completed the acquisition of 10% equity interests in two producing assets from Shanghai Decent. The company has issued a Shanghai Decent affiliate 381 million shares in Nickel Industries at an issue price of A$1.02, as consideration for acquiring a 10% equity interest in the Huayue Nickel Cobalt high pressure acid leach (HPAL) project; and made a cash payment of US$75 million to Shanghai Decent, as consideration for acquiring an additional 10% equity interest in Oracle Nickel Project (ONI), increasing the company's interest from 70% to 80%. The company has also acquired options to to participate in the construction and ownership of the Excelsior Nickel Cobalt HPAL project and an option to invest in and construct a high-grade matte converter at ONI.

Nickel Industries says that the purchases establish three key pillars for it to transform its business from a historical focus on the stainless-steel market to becoming a leading producer of battery grade 'Class 1' nickel. Nickel Industries' managing director Justin Werner said: "We are very pleased to have now completed the various asset and options acquisitions outlined in our Electric Vehicle Battery Supply Chain Strategic Framework Agreement. The completion of these transactions further consolidates our strong existing relationship with Tsingshan and importantly represents an important advancement in our continuing diversification into higher margin, lower carbon forms of nickel production as we seek to become a globally significant producer of sustainable nickel."

Nickel Industries Ltd has also said that it has completed a haulage road linking its 80% owned Hengjaya Mine to the Indonesian Morowali Industrial Park in central Sulawesi, including the construction of a 70 m double lane bridge, which will allow it to begin haulage of nickel laterite ore from the company's mining operation directly to Morowali, and will allow the mine to rapidly increase total ore sales from current levels of approximately 3.5 million t/a to a targeted 10 million t/a, a run rate which is expected to be achieved by the end of 2023.

Nickel Industries' Angel Nickel site, Indonesia

PHOTO: NICKEL INDUSTRIES

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 53 54 55 56 57 58 59 60

SAUDI ARABIA

FLSmidth wins major Ma'aden beneficiation order

FLSmidth has secured a DKK 530 million contract for Ma'aden's 'Phosphate 3' project.

The Danish mining equipment company will provide major items and critical services for the construction of a large-scale phosphate beneficiation plant at the project's mine site in the Northern Province of Saudi Arabia.

FLSmidth has agreed to supply Ma'aden with key equipment for the beneficiation plant, as well as technical support services covering its design, construction, commissioning and ramp-up. The order includes: primary and secondary sizers, apron and HAB feeders, cone crushers, screens, cyclone clusters, ball mills, paste and high-rate thickeners, horizontal belt filter, slurry pumps, knife-gate valves and flotation columns.

FLSmidth has booked the order for the third-quarter of this year. It expects all the beneficiation equipment to be fully integrated on-site in Saudi Arabia during 2025.

"We are pleased to collaborate with Ma'aden on this expansion, as this order sets another strong standard for our MissionZero agenda," said Mikko Keto, FLSmidth's CEO. "In particular the incorporation of our paste thickening and dewatering technology at this important mine site plays a key role in reducing emissions and water spend from the beneficiation process."

FLSmidth's partnership with Ma'aden on this latest phosphate mine project began in 2019 with the initial laboratory testing of samples collected from the ore body. The company subsequently carried out pilot-scale tests and developed the beneficiation flowsheet.

The Kansanshi Copper Mine, Zambia

PHOTO: FIRST QUANTUM

ZAMBIA

Contract awarded for copper expansion

As part of its plans to expand the Kansanshi copper mine, Canada's First Quantum Minerals (FQM) has placed an additional order with Metso for the delivery of minerals processing equipment the stage 3 expansion of the copper mine. Metso says that the value of the order is in excess of euro 20 million, and has been booked in the Minerals segment's second-quarter orders received.

Metso's scope of delivery includes apron feeders, Nordberg® MP800™ cone crushers, TankCell® e630 and TankCell® e300 mechanical flotation cells, high-intensity Concorde CellTM units, ColumnCellTM units, HRT thickeners and a clarifier. Most of the separation equipment are part of Metso's Planet Positive offering. Last year, Metso was awarded an order for two PremierTM grinding mills with a total installed power of 50MW including Metso Megaliner™ and metallic mill linings.

"Kansanshi's flotation flowsheet combines the well-proven, energy efficient TankCell® flotation cells with the new Concorde CellTM, unlocking the potential for further improved flotation performance. Concorde CellTM high-intensity, forced-air pneumatic flotation cells allow operations to enhance fine and ultrafine particle selectivity," said Antti Rinne, Vice President, Flotation, at Metso.

The Kansanshi mine, near Solwezi in the Northwestern Province of Zambia, is one of the largest copper mines in the world. First Quantum Minerals is currently working on a $1.25 billion expansion, announced last year, including a standalone 25 million t/a processing plant that will increase copper production substantially. Africa's second-biggest copper producer, Zambia aims to increase production to 3 million t/a of copper within the next decade. The country produced 800,000 t/a of copper in 2021.

BANGLADESH

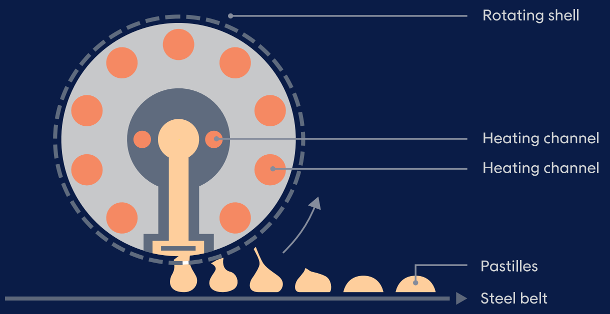
Ma'aden renews fertilizer supply deal with Bangladesh

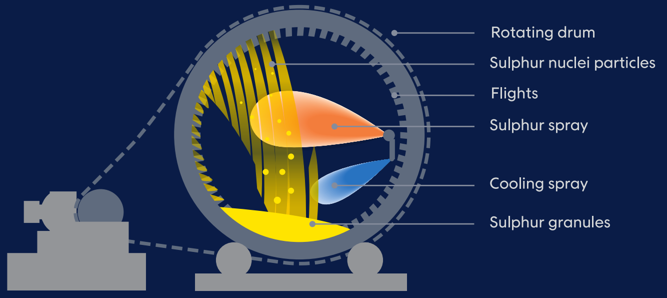
Ma'aden has renewed its agreement to supply the Bangladesh Agricultural Development Corporation (BADC) with 600,000 tonnes of fertilizers. The agreement was signed during a visit to Ma'aden's headquarters by a BADC delegation in mid-August.

The agreement means Ma'aden will continue to supply approximately 42 percent of Bangladesh's diammonium phosphate (DAP) requirement.

"We are pleased that we are able to continue working with BADC to ensure a reliable supply of high-quality fertilizer products to the Bangladesh market. We are excited to extend our near-decade-long relationship with BADC and playing a role in helping support food security efforts in the region," said Hassan Al Ali, Ma'aden EVP for its phosphate business unit.

Ma'aden is planning to increase its phosphate fertilizer production by 50 percent to nine million tonnes p.a. by implementing its 'Phosphates 3' mega project. The company is the world's second-largest exporter of phosphate fertilizers currently.


Rotating shell
Heating channel
Heating channel
Pastilles
Steel belt


Rotating drum
Sulphur nuclei particles
Flights
Sulphur spray
Cooling spray
Sulphur granules

1 47 2 48 3 49 4 50 5 51 6 52 7 53 8 54 9 55 10 56 11 57 12 58 13 59 14 60 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

People

Occidental Petroleum has appointed **Sunil Mathew** as its new chief financial officer for the next three years. He succeeds **Robert Peterson**, who served as Senior Vice President and CFO. As EVP, Peterson will now oversee the company's chemical segment. Mathew joined Occidental in 2004 and has been Vice President of Strategic Planning and Analysis since 2014, in which role he was instrumental in the company's large-scale divestiture effort of around $10 billion following the Anadarko acquisition. He has also worked for Schlumberger in the Middle East and Asia. Peterson, who has been CFO since 2020, will become executive vice president of essential chemistry at Occidental Chemical Corporation (OxyChem), a wholly-owned subsidiary.

Vedanta says that it has appointed **John Slaven** as the chief executive officer of its aluminium business and **Stephen Russel Moore** as deputy CEO for its subsidiary Cairn Oil & Gas. Slaven will begin his new appointment on October 3, 2023 for three and a half years, while Moore will take over his new role with immediate effect, the company says. Moore was previously chief operating officer (COO) of Cairn Oil & Gas, the oil and gas exploration venture of the larger Vedanta group. The company says that Slaven, "will be leading all aspects of the strategy of aluminium business' growth and strategy, including development of strategic alliances with global partners to fast-track business delivery." Slaven has earlier worked with Australian company BHP Billiton in major executive roles. Moore will be overseeing the "growth strategy and strategic business alliances with global partners to fast-track business delivery". Vedanta also plans to establish an advisory board for Cairn's business, and intends that CEO **Nicholas Walker** will play a key role in this.

Chevron has waived its mandatory retirement age of 65 to allow chief executive Mike Wirth to remain in position for the foreseeable future, during what the company describes as a volatile period for the oil and gas industry. Wirth, who turns 63 later this year, has been at the helm of the oil and gas major since 2018. The company also says that CFO **Pierre Breber** will retire next March after a 35-year career at the company. He will be replaced by **Eimear Bonner**, Chevron's current chief technology officer, who previously led its Tengizchevroil joint venture in Kazakhstan.

Australian oil and gas company Beach Energy has appointed a new Managing Director and Chief Executive Officer (CEO), effective from 21 February 2024. In the meantime, the company has selected an interim CEO, as its current CEO's tenure has come to an end. According to Beach Energy, **Morné Engelbrecht** ceased to be CEO on 9 August 2023. Beach chairman, Glenn Davis, expressed gratitude to Engelbrecht for his leadership and contribution to the company both as CEO and before that as CFO.

Engelbrecht, who assumed the role of Acting Chief Executive Officer in November 2021, stepped into the permanent CEO role in May 2022, after what Beach described as an "extensive international recruitment process" led by the firm's board of directors and external advisors. He has over 20 years of oil, gas, and resource sector experience, including the last seven years with Beach Energy.

Brett Woods will become the new Managing Director and CEO from 21 February 2024. Woods has over 25 years of experience in upstream oil and gas, including most recently ten years at Santos where he undertook a number of executive roles including Chief Operating Officer (COO), Vice President Developments and Vice President Eastern Australia business unit.

Woods began his career with Woodside Energy in the graduate programme and held senior technical roles in Australia and Africa. In 2007, he became Managing Director and CEO of African start-up Rialto Energy. Woods was responsible for growing Rialto's business through acquiring new exploration licences in Ghana and Cote d'Ivoire, raising capital and commencing two large drilling campaigns in the highly prospective Transform Margin.

In the intervening period current non-executive director, **Bruce Clement**, has been appointed interim CEO and will continue as an executive director. Commenting on the interim CEO role, Davis underlined the board's confidence in Clement's ability to continue to deliver the company's growth projects and drive operational performance. ■

Calendar 2023

SEPTEMBER

11-15

30th Annual Brimstone Sulphur Symposium,
VAIL, Colorado, USA
Contact: Mike Anderson, Brimstone
Tel: +1 909 597 3249
Email: mike.anderson@brimstone-sts.com

11-15

Amine Experts' Amine Treating & Sour Water Stripping Technical Training Course,
KANANASKIS, Alberta, Canada
Contact: Daniel Domanko, Senior Manager
Tel: +1 403 215 8400
Email: Daniel.Domanko@SulphurExperts.com
Web: AmineExperts.com

13-14

Oil Sands Conference & Trade Show,
CALGARY, Alberta, Canada
Contact: Bruce Carew, EventWorx
Tel: +1 403 971 3227
Email: marketing@eventworx.ca

18-22

Sulphur Experts' Sulphur Recovery Technical Training Course,
KANANASKIS, Alberta, Canada
Contact: Daniel Domanko, Senior Manager
Tel: +1 403 215 8400
Email: Daniel.Domanko@SulphurExperts.com
Web: SulphurExperts.com

OCTOBER

9-13

Amine Experts Amine Treating Technical Training Course,
NOORDWIJK, Netherlands
Contact: Jan Kiebert, Senior Manager
Tel: +31 71 408 8036
Email: Jan.Kiebert@SulphurExperts.com
Web: AmineExperts.com

16-20

Sulphur Experts Sulphur Recovery Technical Training Course, NOORDWIJK, Netherlands
Contact: Jan Kiebert, Senior Manager
Tel: +31 71 408 8036
Email: Jan.Kiebert@SulphurExperts.com
Web: SulphurExperts.com

NOVEMBER

6-8

CRU Sulphur & Sulphuric Acid Conference 2023, NEW ORLEANS, Louisiana, USA
Contact: CRU Events
Tel: +44 (0)20 7903 2444
Email: conferences@crugroup.com

13-16

European Refining Technology Conference,
LAGO MAGGIORE, Italy
Contact: World Refining Association
Tel: +44 (0)20 7384 8056
Web: worldrefiningassociation.com/event-events/ertc

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 53 54 55 56 57 58 59 60

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 53 54 55 56 57 58 59 60

Demand for sulphur fertilizers

Unloading fertilizer at a port.

PHOTO: PERO STUDIO / SHUTTERSTOCK.COM

While phosphate fertilizer production represents the main slice of demand for elemental sulphur and sulphuric acid, sulphur fertilizers continue to be a growing sector of demand due to changes in the way that we use sulphur.

Sulphur is a vital nutrient for plant and animal health, and is commonly regarded as the "fourth nutrient" for plants, after the big three of nitrogen, phosphorus and potassium. While sulphur is not needed in the same quantities as nitrogen, for some crops, such as oilseeds, it can be comparable in its requirement to P or K. It is essential for plants to form proteins, enzymes, vitamins and chlorophyll. In legumes it is crucial in nodule development and efficient nitrogen fixation. Protein synthesis requires large amounts of sulphur, especially for the formation of oils within the seed. As a constituent of several amino acids and vitamins in plants and animals, it is critical for determining the nutritional quality of foods. It is also essential for photosynthesis and contributes to crop winter hardiness. Crops with high sulphur requirements include legumes such as alfalfa and soybeans, as well as canola and rapeseed, but because of its effect on nitrogen uptake, it is important for crops with high nitrogen requirements such as maize and cotton. Persistent experiments show that sulphur application can increase crop yields by around 20%. Sulphur also helps the uptake of other micronutrients, such as zinc, and contributes towards helping with dealing with zinc and other deficiencies.

Elemental sulphur also has fungicidal properties, and, applied as a powder, can e.g. control growth of mildew. For high pH soils it can help acidify soils and lower soil pH, and when applied as gypsum it can be applied as a source of calcium and improve soil physical properties, for sodic soils which have high salt content. Calcium as a nutrient can be particularly beneficial for e.g. peanuts, which have a high calcium requirement.

Sulphur deficit

It is a well rehearsed argument, but one that bears repeating, that the industrialised world 'benefited' from 'free' sulphur application to soils for many decades, from two main sources. The first was that the fertilizers used often had an overlooked sulphur component. Ammonium sulphate, for example, was one of the most widely used nitrogen fertilizers in the first half of the 20th century, as it was a by-product from a number of industrial processes, such as manufacture of caprolactam for artificial fibres like nylon. It was also produced using sulphuric acid to scrub the by-product ammonia from coke oven gas – the main source of gas for lighting and heating in the late 19th and early 20th century. Likewise, the first commercial phosphate fertilizer was single superphosphate

1 47
2 48
3 49
4 50
5 51
6 52
7 53
8 54
9 55
10 56
11 57
12 58
13 59
14 60
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

(SSP), produced by reacting phosphate rock with sulphuric acid. SSP is around 12% sulphur, and ammonium sulphate 24% by weight, and this sulphur was being applied as a matter of course with the fertilizer.

However, the latter half of the 20th century saw the development of more concentrated forms of nutrient, firstly ammonium nitrate, and then urea, which gained particular popularity in the fast developing agricultural economies of Asia and South America. Urea has double the nitrogen content of ammonium nitrate by weight, and hence is more efficient to ship and apply, but of course none of the sulphur. Likewise the development of triple superphosphate (TSP) and then mono- and di-ammonium phosphates (MAP/DAP), the latter with up to 60% phosphate content, as compared to 20% for SSP, soon eclipsed the SSP market. And in the potash market, potassium sulphate (also known by its old name sulphate of potash or SoP) became less popular than potassium chloride (so-called muriate of potash or MoP).

> **“The Sulphur Institute (TSI) has calculated that the total ideal crop sulphur requirement worldwide is around 24 million tonnes S per year**

At the same time, sulphur dioxide emissions to atmosphere from various industrial processes, but in particular power generation from burning coal and vehicle emissions from burning gasoline, went largely unchecked. Efforts to tackle this were the birth of the modern sulphur industry, as sour gas producers and oil refiners were pushed to remove ever-greater percentages of sulphur from their product. In parallel with this, a switch away from burning coal in Europe and North America towards natural gas and the installation of scrubbing systems at remaining coal-fired power stations and metal smelters has progressively reduced sulphur dioxide emissions across those continents.

The extent of this has been recently document in a paper published in Nature looking at changes in soil sulphur in the US Mid-West due to falling rates of atmospheric deposition, which calculated that atmospheric sulphur deposition in the region fell by around 80% from 1985-2017. In this region of the US, this was balanced by increased application of sulphur-containing fertilizers such that the total amount of soil sulphur remained roughly constant. However, this has not been the case everywhere. The Sulphur Institute has persistently warned of a growing sulphur deficit in soils, meaning that sulphur is less available to plants and growth rates and crop quality may be affected. The Sulphur Institute (TSI) has calculated that the total ideal crop sulphur requirement worldwide is around 24 million tonnes S per year, while total application of sulphur fertilizers is around 11.8 million tS/a, or only about half of the ideal requirement. In sub-Saharan Africa this shortage is even more acute, with a sulphur deficiency of around 90%, contributing to degraded soils and increased rates of poverty and malnutrition.

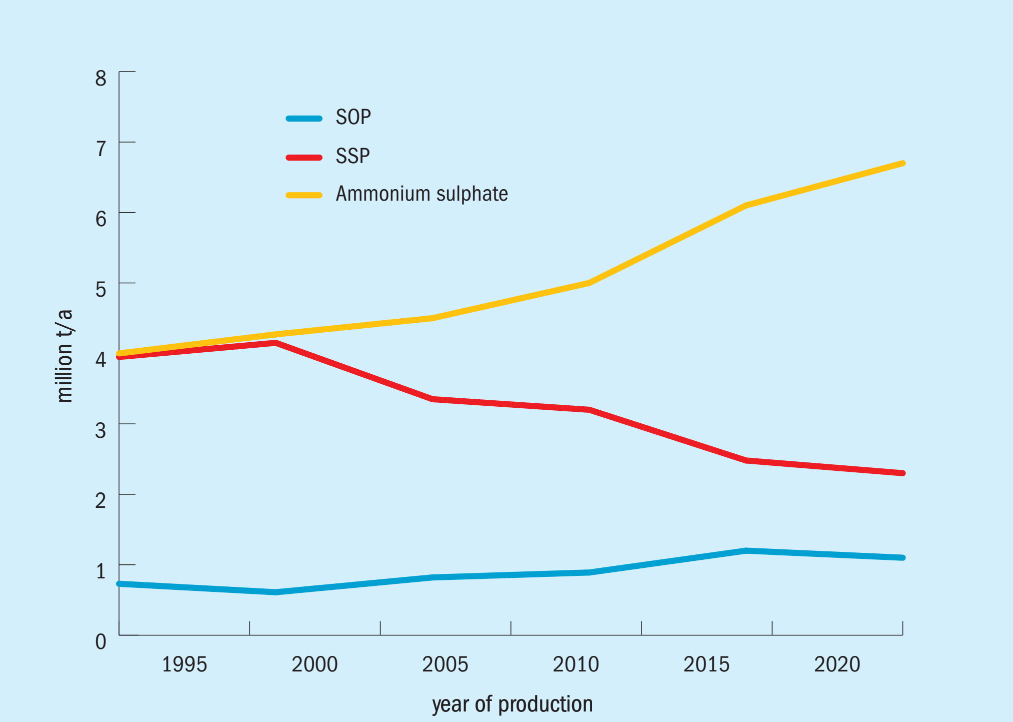
Sulphur vs sulphate

There are essentially two forms in which sulphur can be applied to soils; as elemental sulphur, or as sulphate. Sulphate is the form in which plants are able to take in the nutrient, as it is soluble and can be transported via water into the roots. Conversely, elemental sulphur must first be broken down by thiobacteria into soluble sulphates before it can become available to the plant. This process is comparable to the way that urea must be oxidized to a nitrate before plants can use the nitrogen, but the conversion process for sulphur is much slower and can take months. This process can be sped up by increasing the surface area of elemental sulphur by using it in a micronised form (particles <150 micrometres in diameter), or by breaking up sulphur granules into smaller particles. A common technique is to use 5% bentonite clay in the sulphur granule. The clay absorbs water and swells, leading to the brittle sulphur granule to fracture. Some of the major developments in the past decade in sulphur fertilization have involved greater control over sulphur particle size and dispersion in conventional fertilizers, leading to a growing range of ‘sulphur enhanced’ fertilizers.

However, as with nitrates, there are risks with the over-application of sulphate fertilizer. The main concerns are related to sulphates leaching into water courses, where the sulphate can be reduced to sulphide, which can have toxic effects on river and marine organisms.

As always the way forward is proper nutrient management, but it makes the application of sulphur fertilizers a more knowledge-intensive process than some other nutrients.

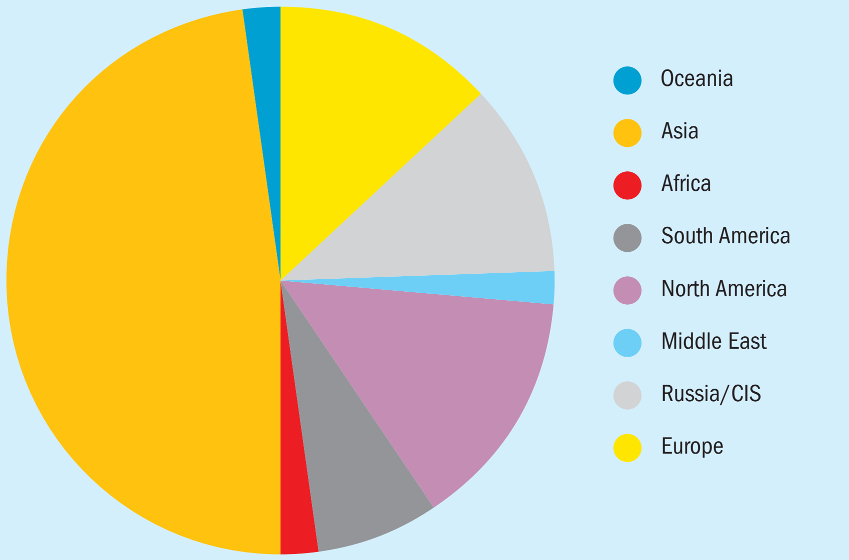
Fig 1: **Use of traditional sulphur containing fertilizers, million tonnes S per year**



Source: IFA

1 47
2 48
3 49
4 50
5 51
6 52
7 53
8 54
9 55
10 56
11 57
12 58
13 59
14 60
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

Fig 2: **World ammonium sulphate capacity by region, 2021**



Source: IFA

'Traditional' sulphur fertilizers

The three main traditional sulphur-containing fertilizer – ammonium sulphate, single superphosphate and potassium sulphate – still represent a significant majority (ca 70%) of sulphur fertilizer applications. Figure 1 shows how application rates of these fertilizers have changed over time.

Ammonium sulphate

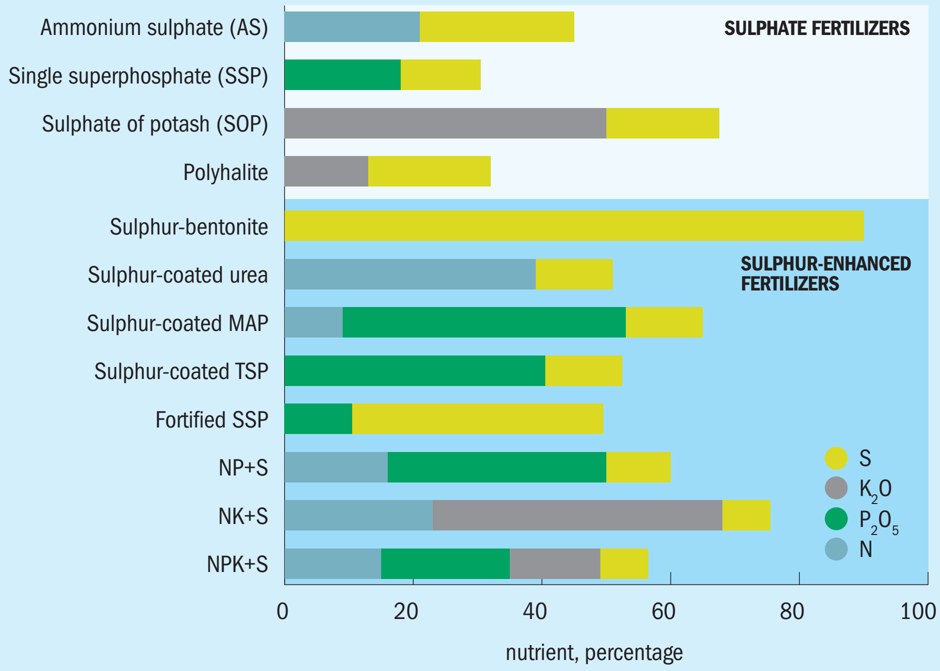
The most popular remains ammonium sulphate. Global ammonium sulphate capacity was 38.6 million t/a in 2021, or around 9.3 million tonnes S per annum. Figure 2 shows the geographical distribution of capacity. Most is in China, where there is a great deal of involuntary production as a by-product of caprolactam manufacture for nylon fibres, methylmethacrylate, acrylonitrile, methionine production etc, and this new capacity in China represents most of new AS supply over the past two decades. Around 65% of AS capacity added between 2017 and 2021 was in China. IFA estimates that 71% of AS capacity is based on by-products from other production, and in China this figure is 83%. It is also 90% in Europe and 73% in North America. However, in the Middle East, Africa and South America, the opposite is true, and on-purpose production predominates, between 75% of production (in South America) to 95% (in the Middle East). Ammonium sulphate capacity is predicted to continue to grow to 41.5 million t/a (10.0 million tS/a) by 2026, with China continuing to represent the bulk (70%) of new production, for various industrial processes. Most of the rest of new capacity will come from Russia and Turkmenistan.

As AS production is largely involuntary, it tends not to be determined by fertilizer prices but rather the markets for fibres and the other products that it is a by-product of. This ensures that AS will continue to represent the largest slice of sulphur fertilizer production for the foreseeable future. Consumption is concentrated in Asia, with the USA, Brazil, Turkey and Mexico also major consumers.

Single superphosphate

World capacity for single superphosphate (SSP) is 56.1 million t/a (6.7 million tonnes S per annum), making it the second best selling fertilizer worldwide for both P and S content. China represents 31% of capacity here, but there is also considerable capacity in India (23%) and Brazil (17%). Around 7% of capacity is in Australia, and these four markets also represent around 85% of demand for SSP; because of its relatively low phosphate nutrient content compared to diammonium phosphate, it tends to be consumed in the country of origin, and export volumes have declined due to increasing competition from more economic high-analysis phosphates. SSP capacity and production has fallen from 2015 to 2020, as Figure 1 shows, but out to 2025 is expected to remain roughly the same as 2020 figures. This masks some changes in geographical capacity, however; Chinese capacity is falling, as MAP/DAP becomes preferred, while India will have added around 700,000 t/a of SSP capacity from 2015-2024.

Fig. 3: **Nutrient content (NPK+S) of selected sulphate and sulphur-enhanced fertilizers**



Source: Various

Potassium sulphate

Potassium sulphate/sulphate of potash (SoP) has always been a niche product compared to the much more widely used potassium chloride (muriate of potash/MoP), but it is valued as a chloride-free source of potash for cash crops such as tobacco, tree nuts and citrus fruits. World capacity is around 11.3 million t/a (2.0 million tonnes S). China accounts for 70% of world capacity, and Germany another 10%. Other major producers are the US and Belgium. China also dominates consumption, with North America and Europe also major consumers.

Sulphur-enhanced fertilizers

With a growing recognition of the issue of sulphur deficiencies in soils has come a wide range of sulphur containing or enhanced fertilizers (see Figure 3). These typically use innovative technologies to incorporate elemental sulphur into higher analysis fertilizers, either within granules or as an external coating. Introducing a liquid sulphur spray to Urea, TSP, MAP or DAP during drum or pan granulation, for example, results in N and P products with a 5-20% elemental sulphur content. Sulphur-enhanced fertilizers combine nutrient availability with high use-efficiency, and also have good storage and handling properties. The market for sulphur-enhanced NP+S products has developed over the past decade, with particular take-up in the US, Brazil, India and parts of Africa. In North America, Mosaic has been selling its MicroEssentials range of fertilizers since 2008, containing 10-15% sulphur in a 50-50 mixed form of both sulphate (for initial availability) and micronised elemental sulphur to keep plants growing throughout the season. Sales of MicroEssentials reached 2.8 million t/a in 2022, according to with Mosaic. PhosAgro and OCP also have NPS products. OCP exported 1.4 million t/a of NPS products in 2021 according to company figures.

Controlled release fertilizers (CRFs) can be produced by coating highly soluble nutrients such as urea with relatively insoluble coatings. While India uses the plant fibre neem, other polymers can be used, and elemental sulphur (usually with a polymer outer coating) is also used as a coating – the sulphur breaks down slowly, eventually allowing the encapsulated to become available over a longer time period. Sulphur-coated urea (SCU) combines 77-82% urea (36-38% N) with a 14-20% sulphur coating. SCU is used for multiple nitrogen applications on sandy soils under high rainfall or irrigation conditions. It is marketed as a controlled release fertilizer for grass forage, turf, sugarcane, pineapple, cranberries, strawberries and intermittently-flooded rice.

The popularity of liquid fertilizers in North America, especially liquid ammonia and urea ammonium nitrate solution (UAN) has led to the use of soluble thiosulphates to produce sulphur enhanced liquid fertilizers. Tessenderlo Kerley, a leader in speciality liquid fertilizers, has four main thiosulphate products, with ammonium, potassium, calcium or magnesium, with a sulphur content of 10-26% sulphur.

Urea gold

The launch of new sulphur enhanced fertilizers continues. India has recently launched a new premium variety of urea coated with sulphur, which is known as 'urea gold'. It was unveiled during a visit to Rajasthan by prime minister Narendra Modi, and is being sold by one of India's major state owned fertilizer companies, Rashtriya Chemicals and Fertilizers Ltd (RCF). The sulphur-coated urea has an analysis of 37% nitrogen (N) and 17% sulfur (S), and aims to serve two primary objectives: fulfilling sulphur requirements in Indian soils and enhancing nitrogen use efficiency (NUE), as the sulphur coating allows for a slower release of nitrogen, leading to prolonged nutrient availability during the plant's growth cycle. India has low rates of NUE; only around 35% of nitrogen that is applied makes its way into crops. Urea gold is being marketed as a way of using less urea; 15kg of urea gold is equivalent to 20kg of conventional urea, according to the marketing literature. India has long struggled with overapplication of urea and lack of balanced nutrient management. As with the domestically produced neem-coated urea, the aim is also to try and make the country's existing production of urea go further, reducing import demand. According to local press reports, manufacturers of urea gold will be allowed to sell the fertilizer at a maximum retail price (MRP); a major boost for areas where soil contains less sulphur.

> **"The launch of new sulphur enhanced fertilizers continues. India has recently launched a new premium variety of urea coated with sulphur, which is known as 'urea gold'.**

Still room for growth

While reliable statistics are hard to come by, total fertilizer sulphur nutrient consumption is estimated to be 12.2 million tonnes S, against a potential global requirement of 24 million tonnes S. This ongoing sulphur deficiency in soils, especially in parts of the developing world, where attempts to tackle SO_2 pollution have been more recent and the effects are only now starting to be felt, needs to be tackled in order to achieve the kind of crop yields that the world will need in order to sustain a growing population.

Indeed, sulphur fertilizers represent a potential bright spot amid general declining or plateauing use of fertilizer. Overall fertilizer demand is slowing in most markets as they mature, and efforts are taken to correct overapplication and fertilizer leaching into water courses. Indeed, consumption is falling in many major markets. The Chinese government aimed to stabilize fertilizer application rates at 2000 levels via its Zero Fertilizer Growth policy, but in fact a combination of environmental crackdowns and overcapacity led to a 15% fall in fertilizer use from 2015-2020. EU consumption fell by several percent over the same period due to a focus on nutrient use efficiency. Recent runs of high prices have also impacted on fertilizer demand as affordability has been low; IFA estimates that global fertilizer consumption dropped by 7.6% over 2021-22, recovering only around 4% this year. Looking forward, fertilizer use is expected to grow by 1-2% year on year out to 2027. However, for sulphur fertilizer the comparable increase is expected to be 3% per year, with Asia the largest source of new demand as sulphur deficiency is increasingly recognised and tackled. ■

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 53 54 55 56 57 58 59 60

GLOBAL
ENVIRONMENTAL &
INDUSTRIAL RESPONSE

SULFURIC ACID TOWER MAINTENANCE AND NEUTRALIZATION SERVICES

Acid Tower Maintenance Services

- Tubesheet Cleaning
- Mist Eliminator/Flat Pad Removal/Install
- Header/Distribution Maintenance
- Header/Distribution Removal/Install
- Trough Leveling/Cleaning
- Structured & Saddle Packing Removal / Install
- Tower Bottom Cleaning
- Stack Cleaning
- Economizer Cleaning
- Pump Tank Cleaning
- Furnace/Boiler Cleaning
- Install/Removal of Nozzles, Thimbles, and other various components
- Distribution Circulation Inspections
- UT Metal Thickness Inspections

Neutralization and Cleaning Services

- Economizer Neutralization
- Pump Tank Neutralization
- CIL Cooler Neutralization
- Mist Eliminator Neutralization
- Demolished/Removed Plant Components
- Storage Tank Neutralization
- Other various assets that require neutralization and cleaning for proper inspection and maintenance to be performed

FOR MORE INFORMATION CALL
866-456-2368
OR EMAIL
SALES@GLOBALENVIROTEAM.COM

Other Services

- Catalyst Handling and Screening
- Hydroblasting - CIL Tube Cleaning
- Dustless Abrasive Blasting – Metal Prep / Coating Prep
- Sulfur Pit Cleaning
- Waste Handling and Transportation of Hazardous and Non-Hazardous liquids or solids (Used Catalyst, Sulfates, Low pH liquids...)
- Specialty Coatings
- Fiberglass Repairs

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 53 54 55 56 57 58 59 60

PHOTO: TESLA

Is LFP the ‘next big thing’?

Lithium ion battery production is driving major expansions in nickel and cobalt extraction, but lithium iron phosphate (LFP) battery use is growing rapidly.

Above: A Tesla Model 3, powered by LFP batteries.

The electrification of the world has driven increasing use of a number of strategic minerals, particularly copper, and with it demand for the sulphuric acid used to extract the metals from the other components of the rock that they are bound into. As electrification spreads from power grids into automotive uses, there has been a new push for nickel, cobalt and lithium. Increased copper and cobalt mining in Africa’s copper belt, the nickel high pressure acid leaching plants springing up in Indonesia and the new lithium mines being developed in the US are just three symptoms of this.

So far, the recent wave of new capacity has been based around serving new lithium ion battery production, which has been growing at astonishing rates of up to 40% year on year. But ‘lithium ion’ actually covers a range of battery chemistries, including nickel manganese cobalt (NMC) and nickel manganese aluminium (NMA). NMC has become the dominant technology for personal electronics and some electric vehicle (EV) producers, including Volkswagen and some Tesla models, and this is leading to the increased appetite for cobalt in Africa. However, a competing technology, lithium iron/ferrous phosphate (LFP), is also becoming increasingly important.

Different chemistries

Both types of battery use graphite as an anode for lightness, but differ in their cathode composition. NMC contains a mixture of lithium manganese oxide and lithium cobalt dioxide, and produces the highest energy capacity; between 150-200 Watt hours per kg (Wh/kg). By comparison, LFP ($LiFePO_4$) has an energy capacity of 90-120 Wh/kg. This is why NMC has come to be preferred for electronics that require high levels of power density like laptops, mobile phones and tablets, as well as automotive applications. However, they also have disadvantages. NMC batteries are less stable, especially in environments with higher or fluctuating temperatures. They heat up quickly and because of their oxide component have been known to experience runaway thermal reactions leading them in the worst cases to catch fire. The oxygen is released when the cell suffers an internal short circuit and heats up. Since fires require fuel, oxygen and an ignition source, robbing the fire of any of these will put it out. However, once a fire starts in a nickel-cobalt battery, it produces its own oxygen which is why these fires are so difficult to extinguish. Fire protection agencies cite lithium battery fires as the fastest growing fire risk in many countries.

LFP batteries, conversely, have excellent chemical and thermal stability. Furthermore, NMC batteries have a life cycle between 500-1,000 charging cycles, much lower than the 1,000-10,000 cycles that LFP batteries can tolerate. This makes lithium iron phosphate batteries much better

1 47
2 48
3 49
4 50
5 51
6 52
7 53
8 54
9 55
10 56
11 57
12 58
13 59
14 60
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

for applications that need to run for long periods of time without being changed.

The weight penalty of LFP batteries means that NMC is likely to be preferred for personal electronic items, but for electric vehicles that do not require the longest ranges, some EV manufacturers have preferred the better thermal stability of LFP batteries, including Ford and Tesla's Model 3. There is another factor as well; battery cost is the single largest component of EV cost, and LFP batteries are typically cheaper than NMC batteries. Both require lithium, but iron and phosphates are generally cheaper than cobalt, nickel and manganese, particularly following the price spikes in commodities after the Russian invasion of Ukraine.

Another issue is the potential scale-up required for battery production. Nickel sulphate demand has been rising at around 12% year on year, and in spite of the HPAL boom in southeast Asia, not enough high grade nickel production is coming on stream to meet projected demand. It is estimated that by 2030 there could be a shortfall of up to 400,000 t/a of nickel unless new projects are developed quickly. To achieve the estimated 3.1 million t/a of nickel required by 2040 would require around 70 new nickel projects, at a typical annual production capacity of 45,000 t/a. Phosphate, however, is already mined at 20 times the volume of nickel, and scaling up is likely to be less problematic.

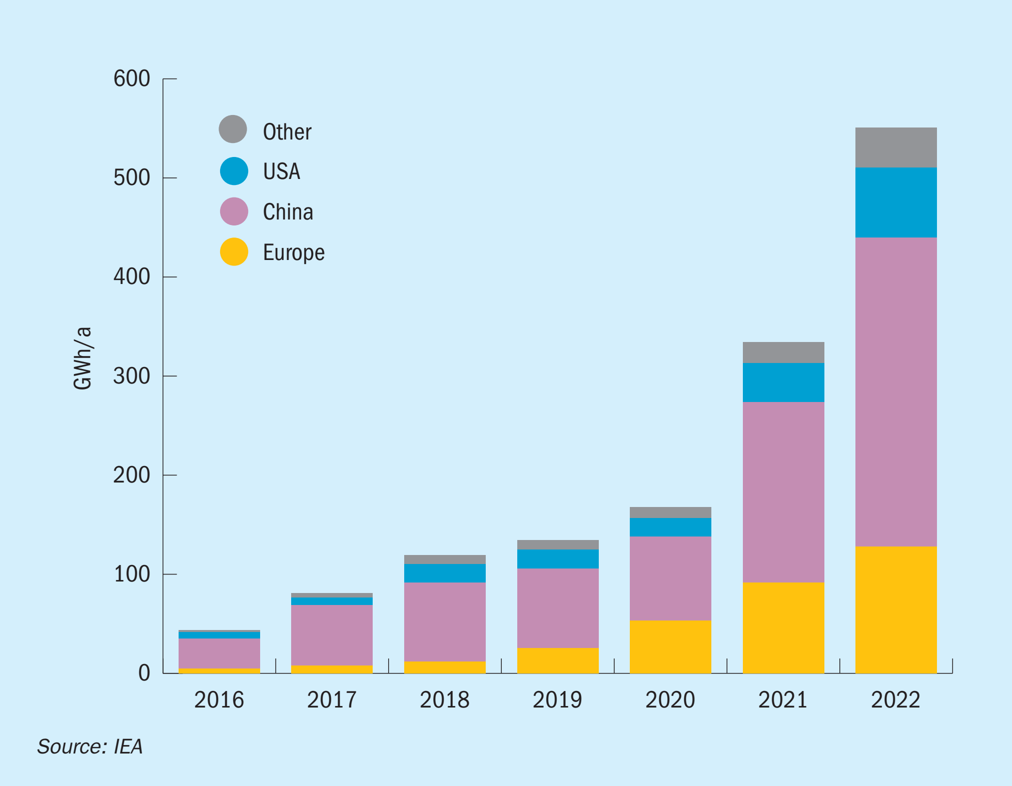
China leading demand

LPF batteries already power the majority (60%) of electric vehicles in the large and rapidly growing Chinese EV market, and they are now starting to make inroads in North America and Europe. By the end of last year, LFP batteries had already claimed one third of the global market for EV batteries, and that share seems likely to rise. While this will have a similar effect on the lithium market whether NMC or LFP batteries are produced, a preference for LFP has the potential to affect the phosphate market. To produce one tonne of LFP requires 0.73 tonnes of 85% phosphoric acid, and therefore of course a slightly higher quantity of sulphuric acid.

In 2021, China's capacity for manufacturing LFP stood at 970,000 t/a. By the end of 2022, this had reached 3 million t/a, including 370,000 t/a of capacity at Hunan Yuneng, 200,000 t/a by Longbai Group; 190,000 t/a at German Nanometer; and 100,000 tons at Longpan Technology, who acquired Changzhou Liyuan. New and planned capacity additions, according to Acuity Commodities, include another 3.1 million t/a in 2023, and 2.8 million t/a in 2024. These capacity additions include battery manufacturers such as Hubei Wanrun and Hunan Yuneng; mineral suppliers such as GEM, Huayou Cobalt and Zhongwei; and chemical phosphate and titanium dioxide manufacturers like Longbai Group, Chuanfa Lomon and Jinpu Titanium. Partnerships are forming between EV manufacturers, battery companies and raw materials suppliers in order to secure sufficient supply.

> "China's EV market grew by 80% in 2022 alone"

Fig. 1: **Battery demand by region 2016-2022**



Source: IEA

LMFP

A new wrinkle to LFP development is lithium iron manganese phosphate (LMFP), by doping iron in lithium manganese phosphate to form a solution. LMFP has a higher energy capacity than conventional LMP; up to 260 Wh/kg. However, it suffers by comparison in terms of number of charging cycles, though still better than NMC. Manganese precipitation remains a niggling problem with the technology, though iron: manganese ratios can be adjusted to mitigate this, though this also lowers the energy capacity, and there is considerable research development effort being put into solving this issue, using concentration gradients or carbon coatings. Low temperature performance can also be relatively poor. Nevertheless, China's (and indeed the world's) largest battery maker Contemporary Amperex Technology Co Ltd (CATL) has began construction of a new LMFP battery factory in June 2022, with completion due this year.

Acid demand

While the LFP capacity additions in China are spectacular, they are also running considerably ahead of demand. However, demand is increasing rapidly and will begin to catch up over the next few years. China's EV market grew by 80% in 2022 alone, and worldwide the EV market continues to evolve rapidly as shown in Figure 1. Wood Mackenzie estimates that total world demand for LFP will be 685,000 t/a this year, and that it will continue to rise at an average annual growth rate of 13-14% year on year for the next ten years. This would take it close to 2 million t/a by 2030, with a similar effect on phosphoric acid and sulphuric acid demand over that period, outside of the lithium required. ■

Sulphuric acid recycling

As producers and regulators become increasingly concerned about the ‘circular economy’, there is increasing focus on regenerating waste sulphuric acid for re-use.

A Topsoe WSA plant at Bestgrand Chemical Group, Guangdong, China. The plant processes spent acid from the neighbouring CNOOC refinery.

Environmental concerns are driving attempts to recycle and reduce consumption of raw materials, leading to the concept of the ‘circular’ economy, where materials are recycled and reused in a continuous loop. For sulphuric acid, this takes the form of regeneration or recycling of acid or acid-containing waste streams which have already been used in an industrial process.

Alkylation

One of the major sources of spent acid is refinery alkylation units. Alkylation converts light olefins into a high-quality gasoline blendstock by reacting them with isobutane. The most common is C4 alkylate, made by alkylating butylene with isobutane. However, alkylate can also be made from propylene and isobutane, or pentene and isobutane. It is particularly desirable because of its combination of properties; zero sulphur content, no aromatic content, low vapour pressure and high octane number, and is used as a blendstock in the manufacture of cleaner burning, premium quality gasoline.

It has been a mainstay of US refineries for some time, particularly since alternative octane improvers like MTBE have been significantly restricted since the 1990s, the increasing mandate of ethanol from corn has required alkylate as a balancing component, and higher-octane gasolines have been required to meet Corporate Average Fuel Economy (CAFE) standards. In the US 90% of refiners operate alkylate units, and alkylate now represents around 15% of the US gasoline pool. But while US alkylate capacity has been relatively stable over the past decade, use of alkylate as a blendstock has slowly but steadily continued to spread elsewhere around the world, particularly in Asia.

Acid is used to catalyse the alkylation reaction, and the two main ones used are sulphuric and hydrofluoric (HF) acid. Installation and operating costs are similar for sulphuric and hydrofluoric acid alkylation. Sulphuric acid is cheaper than HF but is more complex to regenerate and has higher usage rates. In the early days of the processes sulphuric acid was preferred, but during the 1980s and 90s, HF gained predominance, and by the turn of the century there was roughly a 50-50 split between their installations. However, sulphuric acid has gradually gained prominent due to concerns over the use of hydrofluoric acid. In particular, an explosion and fire at the Philadelphia Energy Solutions (PES) refinery in Philadelphia in 2019 led the US Chemical Safety Board (CSB) to call upon the Environmental Protection Agency (EPA) to review its regulation of HF in alkylation and other applications and look for substitutes. As yet no formal rulemaking has emerged on the subject, but there have been several conversions from HF to sulphuric acid or other systems, and the split between sulphuric acid and hydrofluoric acid alkylation systems is currently about 60-40.

One of the factors that favours sulphuric acid is ready access to sulphur or sulphur-containing off-gases at refineries from the sulphur recovery section. Various sulphuric acid technologies are available for dealing with SO_2 from Claus plants, such as Topsoe’s Wet gas Sulphuric Acid (WSA) process.

1 47 2 48 3 49 4 50 5 51 6 52 7 53 8 54 9 55 10 56 11 57 12 58 13 59 14 60 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

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 53 54 55 56 57 58 59 60

1 47
2 48
3 49
4 50
5 51
6 52
7 53
8 54
9 55
10 56
11 57
12 58
13 59
14 60
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

Table 1: **Installed alkylation capacity by country, 2021, '000 bbl/d**

United States	1,314
China	128
Japan	112
India	105
South Korea	86
Others	819
Total	**2,564**

Source: GlobalData

Capacity

Total US alkylate capacity is just over 1.3 million bbl/d, according to the Energy Information Association, just over half of it in the PADD 3 region (US Gulf Coast). This has been relatively stable over the past five years, but over the same period capacity outside the US has risen to almost the same amount; 1.3 million bbl/d (see Table 1), with installations at, e.g. Reliance's refinery in Jamnagar where an 83,000 bbl/d unit – one of the largest in the world – now operates. Chinese capacity now represents about 128,000 bbl/d of this, with a number of alkylation sections added to refineries over the past decade to help meet China-VI (<10ppm sulphur content) gasoline standards. Elessent alone says that it has completed seven installations of its STRATCO technology at Chinese refineries.

Between 2022 and 2026 another 39 refineries have started up or are expected to start up alkylation units, including at Vadinar in India, with 32,000 bbl/d of capacity, Al Zour in Kuwait, as well as refineries in Mexico, Brunei and Nigeria, for a total of 200,000 bbl/d of capacity. About 70% of this will be in China and India, much of it expansions at existing refineries, taking global alkylation capacity to 2.8 million bbl/d, or about 120 million t/a of capacity.

Looking to the longer term, OPEC forecasts a steady (ca 2% year on year) increase in global alkylation capacity out to 2035 to deal with ever more stringent fuel quality standards.

Spent acid

While HF functions almost as a 'pure' catalyst, for the sulphuric acid alkylation route there is a fractional conversion of acid, and hence 'consumption' is relatively high; around 10-12 kg of acid per barrel of alkylate produced at best, and potentially as high as 15-25 kg/bbl alkylate if the cracker is being run at high severity. Not all of this is pure consumption; acid concentrations must be kept high (>90%) in order to prevent acid 'runaway', where catalytic activity rapidly declines and polymerisation is enhanced, and so the acid must be continually topped up with fresh acid and spent acid removed from the system. Spent acid often has a lower concentration than a clean project and so cannot be reused until it is cleaned and concentrated again.

Dealing with this acid can be done either on-site or off-site, by a contractor. The latter is typically used for refineries that have moderate to low alkylation capacity, and the benefits are primarily reliability and an economically viable solution for SAR that helps reduce a company's environmental footprint. To achieve scale, such merchant facilities typically handle acid from a number of customers, and may also handle chemical spent acid from an electronics plant etc.

With the onsite model, a refiner can either build its own facility, or engage a third party to design, build, own and operate the facility for them. In this case, the third party can provide key sulphur management services for the refinery by processing all of its spent acid, along with all or some of its sulphur-bearing gases. This is a good option for large scale consumers of acid and can dovetail neatly with an on-site acid plant handling Claus plant gases as described above, offering more certainty about availability as well as a reduced environmental footprint, transportation and loading/unloading costs. An onsite plant can also deliver high-pressure steam back to the refinery for its use in production.

Regeneration

The regeneration process is essentially an oxidation reaction. Feed acid coming into the regeneration plant is concentrated to remove any water. This reduces the total volume of the spent stream before it enters the regeneration furnace where it undergoes thermal cracking. Spent acid is atomised and sprayed into a large furnace heated to around 1000-1200°C, where it decomposes into SO_2, water and oxygen. The fuel/air mix is controlled to maximise the yield of SO_2, with the fuel feed either natural gas or, at a refinery, potentially off-gases from refinery process streams or fuel oil. The hot combustion gases are then cooled in a high-pressure boiler or radiant heat exchanger, which recovers heat for the conversion section of the plant. The gas stream then passes to a gas cleaning section to remove any ash or solid impurities such as metals or organics from the gas, and reduce the water vapour content to the desired acid concentration. The SO_2 bearing gas is then dried by contact with weak (93-96%) sulphuric acid in a packed bed acid tower or drying tower, and passes to a contact vessel, where it reacts with a catalyst, typically vanadium pentoxide, to form SO_3. The SO_3 is dissolved in 100% sulphuric acid and added to water to produce pure sulphuric acid at the desired concentration, from 93-99%.

> **"Between 2022 and 2026 another 39 refineries have started up or are expected to start up alkylation units, including at Vadinar in India with 32,000 bbl/d of capacity ..."**

Other sources

As well as refinery alkylation, many chemical processes generate spent sulphuric acid, including electronics manufacture, pigments and dyestuffs, old car batteries and many more. Historically these have sometimes been merely diluted and discharged into water courses, leading to environmental pollution, and regulations continue to tighten on the disposal of sulphuric acid. For small scale producers, neutralisation with calcium carbonate or the like is a possibility, though this generates tailings that must also be disposed of. But for sites generating more than 2,000 t/a, regeneration becomes an option. As demand for sulphuric acid continues to increase, coupled with increasingly strict SOx emissions regulations and a growing corporate and regulatory focus on reducing environmental footprint, the use of spent acid regeneration is likely to continue to increase.

1 47
2 48
3 49
4 50
5 51
6 52
7 53
8 54
9 55
10 56
11 57
12 58
13 59
14 60
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

Sunset over the city of New Orleans.

PHOTO: LARRY GIBSON/ISTOCKPHOTO.COM

Join the debate in New Orleans

CRU's Sulphur + Sulphuric Acid 2023 Conference and Exhibition takes place at the Sheraton New Orleans, Louisiana, USA, 6-8 November. Take part in this leading annual forum for the global sulphur and sulphuric acid community to learn, connect and do business. Hear from industry leaders and subject experts from around world and across the industry.

The 39th Sulphur + Sulphuric Acid 2023 Conference and Exhibition returns this year to the history-rich and fun-filled city of New Orleans. For over 35 years this event has been the premier networking and professional development event for those involved in the production, consumption and trade of sulphur and sulphuric acid.

Commercial agenda

In 2023, you can expect an expanded market outlooks agenda, including expert insights from CRU's analysis teams on major supply and demand markets, including sulphur and sulphuric acid, plus additional industry updates from key players from across the supply chain.

In addition to the commercial agenda, the extensive technical programme will provide technical updates on the production and processing of sulphur and sulphuric acid, with industry-leading presentations covering new innovations in process technology, materials and equipment developments, as well as practical case studies highlighting operational experiences and plant improvements.

Participants will also be able to interact with speakers and SME's via live streamed panel discussions and Q&A sessions and attend troubleshooting clinics.

Interactive troubleshooting clinic

On the first day of the conference there will be troubleshooting clinics for sulphur and sulphuric acid. Both seasoned plant operators/engineers and those less familiar with these processes will benefit from these sessions which aim to address real-world challenges encountered while operating or maintaining sulphur recovery and related facilities/sulphur-burning, metallurgical, and regenerative sulphuric acid production facilities. These interactive sessions will explore common operational challenges, examine potential root causes, and collaboratively work toward practical solutions. Delegates are encouraged to share troubleshooting topics in advance and/or in person, during the session.

Exhibition

Running alongside the agenda will be an exhibition of world-class solution providers serving the sulphur and sulphuric acid industries providing the opportunity to discover new innovations the latest developments in process technology, equipment and instrumentation.

Technical programme

On the second and third days of the conference the technical programme is split into parallel streams, for sulphur and sulphuric acid.

Sulphur stream

The sulphur stream programme features 18 presentations and 4 panel sessions covering the following key topics:

- Sulphur product: Safe and effective forming and handling;
- Sulphur plant design: Challenges and solutions for new/existing facilities;
- Innovations in hydrotreating, gas treating and sulphur recovery;
- The shifting sulphur industry landscape.

In addition, there will be a special session by Motiva and panellists on a joint industry RCA success story about lowering sulphur tank emissions and sulphur pit degassing.

Sulphuric acid stream

The sulphuric acid stream programme features 20 presentations and 4 panel sessions covering the following topics:

- Future of sulphuric acid: Energy transition, circular economy and supply chain;
- Sulphuric acid plant performance: Catalyst and emissions;
- Sulphuric acid plant design: Technology and equipment;
- Sulphuric acid plant operations: Best practices, debottlenecking, reliability;
- Sulphuric acid plant energy management: Gas cooling and waste heat recovery.

Technical programme highlights

A selection of abstracts from the Sulphur + Sulphur Acid Conference technical programme.

How Keyera is handling sulphur in a challenging environment

A. Giess and S. Killian, AMECO Group

Efficient and reliable systems are essential for managing the large volumes of natural gas liquids involved in sulphur handling. The innovative AMECO reclaimer had to tackle operational problems such as reclaim rate, durability in extreme temperatures, and protection against corrosive sulphur dust. It boasts an impressive 2000 t/h reclaim rate and exceptional durability tailored for the harsh Northern Alberta environment. Automation and remote-control features minimise human intervention on-site, thereby enhancing safety.

A retrofit solution for remelting a sulphur pipeline

R. Marriott, H. Hart, L. Toonen, C. Deering, P. Davis, ASRL

Sulphur has been safely transported in sulphur pipelines several km long with both resistive skin heating (electric) and hot water (glycol) jackets. However, if the heat is interrupted long enough for the sulphur to solidify, the phase behaviour of sulphur causes challenges for any remelting process.

As many longer pipelines have very practical and efficient resistive heating, ASRL proposes incorporating a supplemental internal flow line which could be used to circulate hot glycol/water only after a freezing event. If this strategy were employed, the radial stress could potentially be relieved before re-energising resistive heating and therefore safely re-establishing flow.

New low-density titanium dioxide catalyst for improved sulphur recovery

J. Le Touze, Axens

Axens has developed a new titania-based catalyst called CRS 41, which has a much larger porosity than Axens' benchmark titania catalyst CRS 31. Thanks to a proprietary binder used during catalyst manufacturing, the porosity of CRS 41 is increased while the required mechanical resistance for loading is preserved. The large porosity of CRS 41 results in a significant improvement in product performance, allowing customers to achieve higher COS/CS_2 conversions by reducing the reactor size or the titania requirement by 10%.

The new CRS 41 features a reduced sock loading density of 700 kg/m³, which makes it ≈20% lighter than CRS 31. Thus, the cost-to-fill is more attractive than with CRS 31 without compromising performance and pressure drop.

Living with hotspots at the SRU thermal oxidiser combustion chamber due to refractory failures since 2010

M. Badaruddin, M. Azahar Ahmad, M. Akram Safiq, M. Noor Azmi, PETRONAS

Malaysian Refining Company Sdn Bhd's (MRCSB) sulphur recovery units were revamped in 2009 to increase the sulphur processing capacity. However, both newly revamped SRU trains experienced repetitive hotspots caused by refractory failures. The plant operation team managed the SRU trains with hotspot conditions, executing shutdown activities for both SRU trains alternately every 12 months since their commissioning in 2010.

The presentation will cover the problems faced by MRCSB, efforts performed to identify the root cause of the problem and current efforts being taken to eliminate the hotspot issues.

Enhancing durability of equipment through innovative redesign of the economiser in sulphuric acid production

A. Putro, A. Arifin Nasution, PT Petrokimia Gresik

This presentation details the inventive redesign of an economiser at the 1,800-t/d sulphuric acid DCDA plant at Petrokimia Gresik. The original configuration led to significant corrosion and 21% tube inactivity within 6 years, impairing thermal efficiency and increasing the SO_3 gas outlet temperature to the intermediate absorption tower. This caused sudden shock cooling, resulting in acid mist that triggered corrosion of the mist eliminator and gas-to-gas heat exchanger tube and finally impacted SO_2 emission and plant performance.

A unique redesign was introduced which significantly reduced the average SO_3 gas temperature at the IAT inlet, decreasing acid mist production and prolonging the operational lifespan of the mist eliminator and eliminating acid condensation in the economiser.

Case study for the replacement of the upper part of a co-current flow quench tower

G Floyd, Eco Services Operations Corp. and R. Günther, STEULER-KCH GmbH

Eco Services, Dominguez Plant, operates a spent acid unit in Los Angeles, California. After the spent acid furnace and the waste heat boiler the waste gas has to be cleaned and cooled down in a co-current flow quench tower. Due to the high thermal- chemical- and mechanical stress in the quench tower the acid resistant brick lining system was frequently damaged during operation, necessitating lengthy and costly repairs in each shutdown.

STEULER-KCH recommended using a new, workshop-fabricated, acid- and heat-resistant brick lining system. In the shutdown the damaged, existing upper part of the quench tower was removed and the new pre-brick lined equipment installed. The quench tower has been running without damage since 2020.

How to avoid living with an "ex-con" – Making smart converter selection choices

S. Puricelli, W. Mutler, EXP

This presentation will look at converter design considerations ranging from stacked, staid and catenary configurations, will delve into cost/benefits of upgraded materials, will discuss when an internal heat exchanger is a good choice and how various configurations affect reliability and maintenance.

The new normal in project implementation: learnings from Covid times

C. Bartlett, H. Storch, A. Klein, Metso

The Covid pandemic has changed engineering and project implementation and it is highly unlikley that we will return to pre-Covid ways of working. The impacts can be seen in many areas of the business, including new ways of working based on digital tools, the hybrid office and ways of communicating with one another.

Metso will discuss the learnings from the pandemic and will also focus on further post pandemic refinements of project implementation based on digital tools and virtual teams that will take place to potentially cope with the future challenges such as supply chain bottlenecks and regionalisation versus globalisation strategies. ■

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 53 54 55 56 57 58 59 60

Unlocking the power of sour gas reserves

TarT technology, one of 8 Rivers' decarbonisation technologies, shows promise as an economical, efficient, sour gas sweetening process with near-zero carbon dioxide emissions, and may be key to unlocking access to the world's sour gas reserves.

Gigaton-scale, affordable, and decarbonised solutions are needed to support the world's growing energy demand while facing our climate crisis. To avert the climate crisis, technologies that can meet the scale and access needs while averting billions of tonnes of carbon dioxide (CO_2) not thousands, will create a key bridge to the energy transition.

It is essential that we explore and adopt pragmatic, affordable, and immediate solutions to make the 2050 net-zero emissions goal set by the United Nations Coalition[1] realistic, as a delay in adopting these solutions only adds to future challenges. One such opportunity is the need to scale ultra-low carbon natural gas. As a displacement to coal, greater access to ultra-low-carbon natural gas can reduce global emissions by over 15%.

Natural gas as a decarbonisation pathway

Under current market conditions, natural gas is the most effective gigaton-scale fossil fuel-based solution available today. Per an IEA report, 98% of natural gas consumption has a lower emissions intensity than coal in power or heat applications[2]. Switching from coal to gas is expected to reduce greenhouse gas emissions by 50% when producing power and 33% when producing heat. Across the developed world, the shift is already underway: as coal plants retire (in many cases, earlier than originally scheduled), utilities replace them with a combination of gas and renewables. In the developing world, where governments' first priority is expanding energy access, the battle is less over existing coal-fired power plants than planned ones. As cost-conscious developing countries industrialise, meeting socio-economic growth and decarbonisation plans will depend on delivering the economic case that gas is the more affordable option to prevent future coal infrastructure from construction.

Whether decarbonisation plans include retiring existing coal plants or averting the construction of new ones, cost, access, and security of energy will be at the centre of an effective and equitable energy plan. Countries that have taken advantage of low-cost fuels and energy to grow their economies have the ability to invest in more speculative options to decarbonise. Developing countries must regularly weigh decarbonisation against fundamental infrastructure pillars, such as education, healthcare, and energy investments. Furthermore, while developed countries bear the brunt of the impact from historical emissions, it is the economic growth and stability of developing economies that will shape 21st-century emissions. Unlike the expensive energy storage systems needed to make renewables dispatchable, natural gas can deliver reliable baseload power with tremendous emissions reductions in a manner affordable without subsidies.

Decarbonisation case study: The American (shale) revolution

Recent history underlines that reductions in natural gas pricing can deliver significant emissions impact. In 2008, innovations in fracking technology unlocked large swathes of previously inaccessible United States gas reserves. As US access to proximate, abundant, affordably-produced natural gas grew, prices fell. And as prices fell, so did the carbon emissions.

Between 2005 and 2021, US carbon emissions fell even as the nation's overall energy consumption rose (see Fig. 1). Even as state and federal governments, locked in partisan gridlock, struggled to enact climate policy, its emissions reductions soared past those of far "greener" Germany, as well as Japan and the UK. Meanwhile, rapidly industrialising China saw its emissions skyrocket as it built out its coal capacity, even as it increased its renewables investments[3].

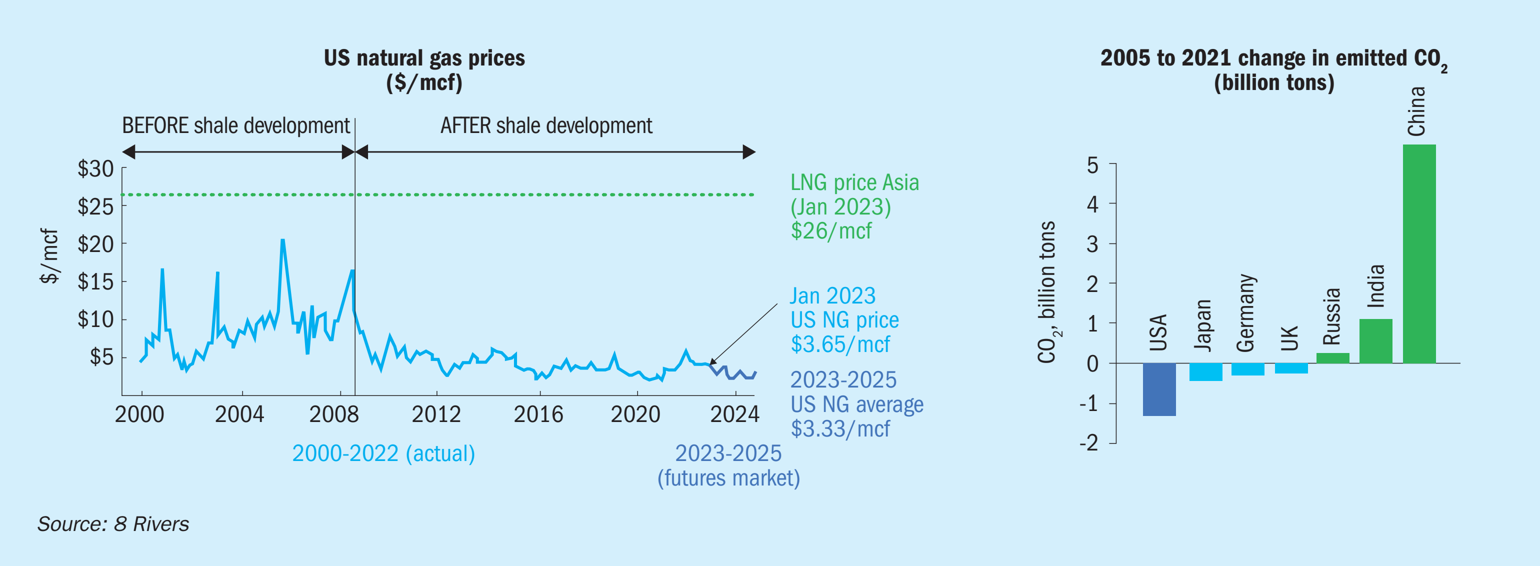
The fact that areas with lower natural gas prices saw emissions drop significantly despite greater electricity generation, while areas with high natural gas prices saw the reverse, suggests that lowering the cost of natural gas is a key short-term decarbonisation lever.

To catalyse a similar scale of cost (and, ultimately, emissions) reductions worldwide, we need a similar stimulant to access underutilised natural gas supplies. Thankfully, the pathway to access this resource is straightforward: more efficient sour gas processing with inherent carbon capture.

Sour gas processing: the next "revolution" in natural gas access

More than 40% of the world's natural gas reserves contain enough sulphuric contaminants to qualify as sour, but processing it poses operational complexity that affects the final product's cost intensity[4]. These high costs, combined with other technical hurdles, render billions of cubic feet of sour gas impractical globally. Consequently, a technology that can sweeten gas more economically could have a game-changing impact on the next several

Fig. 1: **Effect of natural gas pricing on emissions impact in the US**



Source: 8 Rivers

decades of emissions reductions by reducing the cost of natural gas for those deposits.

Historically, sour gas processing has faced economic and environmental barriers. On the economic side, challenges include high processing cost, high cost of acid gas reinjection, poor scalability, and an oversupplied elemental sulphur market. On the safety and environmental side, challenges include H_2S toxicity, high carbon intensity, harmful SO_2 emissions, and difficulties around carbon capture integration presented by conventional processing technologies.

Despite these ongoing challenges, the sour gas processing industry has been static. “Most innovations I’ve seen in recent decades have been associated with incremental improvements in the conventional sour gas treating process, and new types of sulphur recovery tail gas treating processes to drive regulation-mandated efficiency gains,” says Angela Slavens, Managing Director of UniverSUL Consulting. “For example, when I started my career, Sulphur recovery units needed 99% efficiency. Now, tail gas treating requirements demand >99.9% efficiency, so we’ve seen technologies respond.” But those gains stemmed mostly from regulation, not from a perceived market need.

However, a changing environment (figuratively and literally) means the industry is poised for a shakeup. “Recently, the industry is changing so much [thanks to] the move toward decarbonisation. [It] is definitely changing the way people look at new opportunities. I’ve seen a lot more appetite for new technology. Whether organisations move quickly on it, I don’t know. But I think people will be most interested in new technologies proven to save money, reduce carbon footprint, and demonstrate staying power throughout the energy transition,” Ms. Slavens says.

Highly sour processing capability can secure sulphur’s future

The industry’s increased emphasis on efficiency isn’t only for decarbonisation. It’s also to increase access to sulphur in a future where natural gas may, eventually, pose a lower proportion of the overall energy mix. Ms. Slavens says the future may well incentivise seeking out extremely sour wells to ensure sulphur access: “For example, in the early 1990s, when sulphur was briefly in short supply, Shell tapped an Alberta gas reserve with over 90% H_2S content to prove that they could extract high levels of sulphur from such wells if needed.”

Eventually, Ms. Slavens predicts, such a need may arise – meaning that the sour gas processing “technology of the future” must not only be lower-emissions and more efficient but able to handle extremely high levels of H_2S. “Since the start of the shale gas revolution in the US, I’ve been speculating about when we may eventually need to prioritise such highly sour gas to meet sulphur demand, though no one knows on what timeline. I just hope it happens before I retire. If not, I’ll have to come out of retirement, just to see sulphur having its heyday,” she laughs.

Twofold need for processing innovation

Overall, the case is clear: economic sweetening of highly sour natural gas is important for two reasons. First, it advances decarbonisation by providing cheaper natural gas, which can then accelerate the transition away from coal. And second, it helps to secure the future supply of sulphur, an ingredient in key industrial products from fertilizers to pharmaceuticals. And after years of seeing only small modifications to sour gas processing technology, Ms. Slavens thinks the appetite for change is here: “A sour gas sweetener that operates more efficiently with lower emissions would make a huge difference to the industry,” she says.

Indeed, 8 Rivers’ forecasts estimate that reducing the cost of sweetening could achieve significant impact, and has developed its TarT technology to deliver these economic and decarbonisation gains.

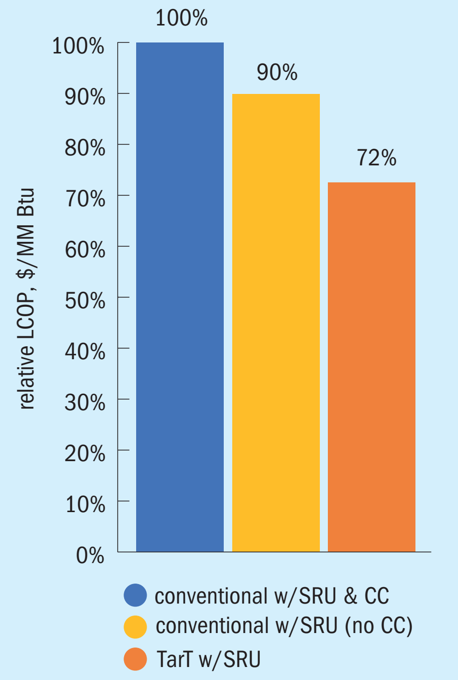
TarT: ultra-economical sour gas processing with inherent carbon capture

8 Rivers has designed a cryogenic sour gas sweetening technology, TarT, that achieves both efficiency gains and emissions reduction.

TarT originated at a conference in the Middle East after 8 Rivers presented NET Power, an 8 Rivers-born legal entity to market the Allam-Fetvedt cycle for carbon-free power generation using natural gas. Attending energy organisations, mindful of the Middle East’s magnitude of sour gas, asked whether the zero-emissions power cycle would work with high H_2S content. At the time, the answer was no. But 8 Rivers’ culture of entrepreneurship and ingenuity wouldn’t let the answer stay “no” for long. After a company-wide competition, TarT emerged – an affordable, zero-emissions sour gas processing solution compatible with the zero-emissions Allam-Fetvedt power cycle and other systems that utilise natural gas as a feedstock or fuel, so long

1 47
2 48
3 49
4 50
5 51
6 52
7 53
8 54
9 55
10 56
11 57
12 58
13 59
14 60
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

Fig. 2: **Comparison of the LCOP of sweet gas production for TarT relative to conventional technology**



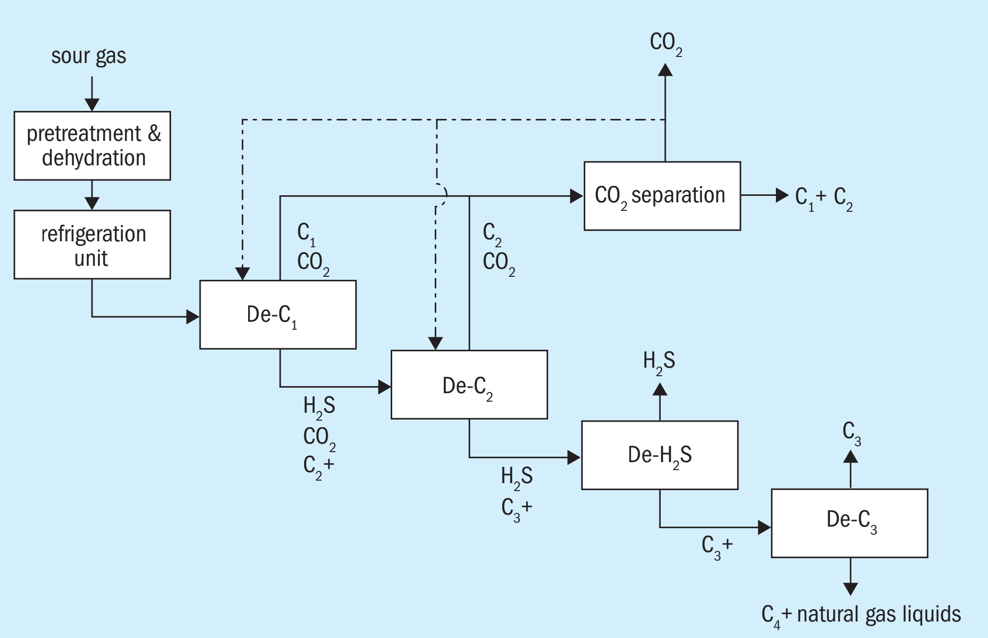
Source: 8 Rivers

as any resulting CO_2 is captured from its utilisation.

TarT deploys liquid carbon dioxide's properties as a solvent to achieve best-in-class efficiency and inherent carbon capture. While engineers may find it counterintuitive to deploy a contaminant as the first step in a purification process, the carbon dioxide input is key to TarT's success.

TarT processes sour gas high in H_2S at lower costs than conventional amine-based technologies, with none of their associated environmental concerns, such as emission of volatile organic compounds (VOCs). Furthermore, TarT's inherent carbon capture makes it even more cost-competitive when compared with conventional amine processes paired with costly, inefficient back-end carbon capture technologies. A case study was performed by 8 Rivers comparing TarT to a conventional amine-based sweetening process with carbon capture and natural gas liquid (NGL) recovery. The feed gas studied had an H_2S and CO_2 content of 16 and 8 mole percent, respectively. TarT was demonstrated to have a 28% reduction in its levelised cost of sweetened natural gas production (LCOP) relative to the conventional amine process with a carbon capture retrofit (see Fig. 2). The TarT technology displayed an 18% reduction in natural gas LCOP relative to the conventional process with no carbon capture as well. This improvement is displayed in Fig. 2. The amine used in this study was DEA and a sulphur recovery unit was included for both technologies. The TarT process inherently performs NGL recovery and carbon capture (CC), so these units had to be added to the conventional technology to perform a uniform comparison.

Fig. 3: **Process overview: TarT's cryogenic extractive distillation systems**



Source: 8 Rivers

Additional benefits include a modular, skid-mounted design that can be easily scaled up or down, making it more feasible for deployment to small, remote reserves that might otherwise be stranded. Recent announcements by governments can further incentivise and facilitate investment into concurrent H_2S and CO_2 technologies, such as TarT, compared to other less efficient carbon removal technologies.

Regardless of these incentives, the best way to understand TarT's standout effectiveness is to examine its process and emergent features in more detail.

Process overview

By reimagining what others see as a waste stream to see its potential as a feedstock, TarT integrates sour gas sweetening with carbon capture, NGL recovery, and acid gas enrichment. TarT's cryogenic distillation system leverages liquid CO_2's properties as a natural solvent to enable inherent CO_2 capture. Where other technologies vent sour gas's embedded carbon dioxide to the atmosphere, TarT captures it for sequestration or utilisation. The resulting low-CO_2 sales gas (<2 vol-%) can qualify as "low-carbon" natural gas, making it a cost-effective feedstock for clean ammonia synthesis, especially when paired with 8 Rivers' ultra-low-emissions hydrogen production technology, $^8RH_2$. And importantly, TarT has no upper limit for H_2S and CO_2 content. So if Ms. Slavens' "drilling for sulphur" hypothetical does come to pass, TarT will be up to the challenge.

Fig. 3 shows the main process steps for the base configuration of the TarT process in which pipeline quality natural gas, LPG, C_4+ NGL blend, and high-pressure high-purity H_2S and CO_2 streams are generated. There is an option to run the process in a C_2 recovery configuration, generating a pure ethane stream. This requires a few additional process steps. By looking at the arrangement of equipment in Fig. 3, one can conclude that the TarT process relies on equipment that is all commercially available. In fact, there are several decades of experience in the oil, gas, and petrochemical industries that can be beneficially used to design a TarT sweetening and NGL recovery plant. The functionalities of the main process steps for the base configuration of the TarT process (Fig. 3) are described in Table 1.

The coldest sections of the plant in the base case configuration of the TarT process are the overhead condensers in the De-C_1 and De-CO_2 towers, which are nominally set to -55°C. This provision minimises the risk of the formation of solid CO_2 and H_2S during transient and steady-state operations that may otherwise occur in other similar low-temperature natural gas treatment

1 47
2 48
3 49
4 50
5 51
6 52
7 53
8 54
9 55
10 56
11 57
12 58
13 59
14 60
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

Table 1: **Description of main process sub-systems for the base configuration of TarT process**

Process sub-system	**Functionality**
Pretreatment and dehydration	Reduces the dew point of the feed stream to avoid ice formation in low temperature sections of the plant and the formation of hydrates. If present, mercury is also removed in this step.
Refrigeration unit	This system mainly comprises heat exchangers and a refrigerant compressor. It accommodates the required refrigeration loads of the various streams and condensers and recovers cold energy from product streams.
Demethaniser (De-C_1) tower	All sulphur species in the sour feed including H_2S are separated from C_1 with the help of liquid CO_2 in this column. The overhead vapour from this column typically contains nearly all the C_1 in the feed, less than 4 ppmv H_2S, plus varying amounts of CO_2 and C_2 depending on the condenser pressure and temperature. In the base configuration, the condenser pressure and temperature are 40-50 bar and -55°C.
Deethaniser (De-C_2) tower	The feed into this tower is composed of mainly C_2+ hydrocarbons and H_2S as well as a varying amount of CO_2. Liquid CO_2 is used as a solvent in this column to separate CO_2 and C_2 from H_2S entering the column and to generate the overhead C_2/CO_2 mixture that meets sulphur specifications for sales gas. In the base configuration, this stream is compressed and mixed with the overhead vapour from the De-C_1 tower.
CO_2 separation	The distillate streams from the De-C_1 and De-C_2 towers contain varying amounts of CO_2, which needs to be reduced to meet pipeline specifications (<2 mol-%). This is achieved by using a single-step membrane followed by further purification of the compressed permeate stream in a CO_2 stripper (De-CO_2) column. This configuration reduces the compression energy requirement and methane loss in the CO_2 product as compared to a two-stage membrane configuration.
H_2S separation	The De-H_2S tower separates H_2S from C_3+ hydrocarbons. A stream of light naphtha is introduced into the top of this column to break the C_3/H_2S azeotrope within the column and facilitate the separation. The overhead vapour can contain up to 99% H_2S at circa 16 bar.
Depropaniser (De-C_3) tower	This tower is a conventional depropaniser that produces C_3 or LPG distillate. The bottom product can be sold as C_4+ NGL blend or further fractionated as desired.

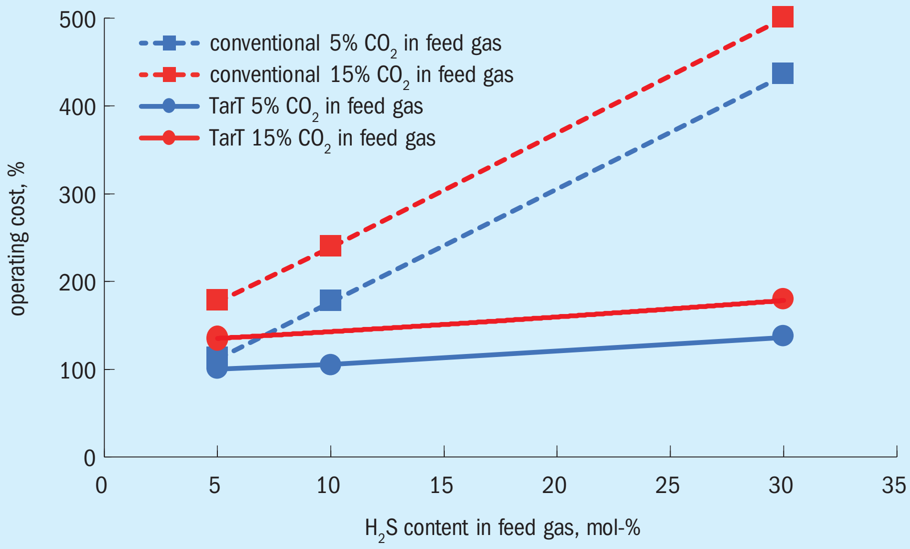
Source: 8 Rivers

processes, which tend to operate at temperatures below the triple point of CO_2 at -56.6°C. In addition, it also eliminates the need of using costly equipment such as that employed in the controlled freeze zone (CFZ) process[5]. Furthermore, the use of a membrane for additional CO_2 removal eliminates the need to generate the colder temperatures, around -90°C, which are required in some other low-temperature techniques, as well as the much higher thermodynamic inefficiencies of a refrigeration loop at such low temperatures[6].

The TarT process also resolves one of the main challenges in the low temperature separation of sour gas species by using liquid CO_2 to enhance the separation of C_2 from H_2S in a De-C_2 column and to maximise C_2 recovery from such processes. Historically, when C_2 is available in the sour gas and a low-temperature process is used for CO_2 separation, H_2S eventually ends up with the C_2 and an additional step of H_2S separation from the C_2 stream is required. This leads to additional processing costs and typically results in low C_2 recovery, or to choosing conventional sweetening processes such as amine-based technologies and its associated cost and energy efficiency penalties.

In practice, when a high-pressure CO_2 product for enhanced oil recovery or sequestration is desired from a gas processing plant, the maximum allowable H_2S in the CO_2 product may be as low as 10 ppmv. Using the conventional amine process, this would require an additional amine train for selective removal of H_2S from either sour gas or the resulting CO_2/H_2S mixture from the first amine unit. For example, DEA solvent can be used in the first amine unit for selective removal of H_2S from sour gas with minimum CO_2 co-absorption followed by a DGA amine unit to remove the remaining CO_2 in the sour gas. This CO_2 can be dehydrated and pressurised for EOR application or sequestration. This configuration generally increases both the capital and operating cost of the conventional technology option, as demonstrated in Fig. 2. In contrast, the TarT process inherently generates separate CO_2 and H_2S streams with high purities and at desired pressures. The resulting high-pressure H_2S stream can be

Fig. 4: **Opex comparison of TarT relative to conventional technology as a function of H_2S content in feed gas**



Source: 8 Rivers

converted to a value-added sulphur product or safely and permanently sequestered in a depleted oil/gas field or a permeable saline aquifer.

The TarT technology has a very flexible process configuration that allows for optimisation based on the composition of the sour gas feed, desired product output, market conditions in the relevant jurisdiction of deployment, and the specification and characteristics of the site. It economically sweetens even the sourest natural gas reserves, captures the natural CO_2 present in the gas, enriches the H_2S, and recovers the natural gas liquids.

Opex-advantaged with highly sour gas

TarT enables access to gas reserves whose acid gas content would be economically inaccessible with conventional amine technologies. Plus, its edge in opex advantage over amine-based sweetening increases in tandem with H_2S content (see Fig. 4). And, while not included in the chart in Fig. 4, TarT is even more cost-effective once you factor in the price of carbon capture, for operators who choose it, on conventional amine technologies.

Deployable to remote fields

But TarT's reduced sensitivity to H_2S content in feedstocks is not the only way it makes "economically inaccessible" reserves accessible. Its modular construction enables each block to be designed and built independently, which drives down capex due to economies of scale and learning effects. Thanks to its more flexible size, TarT can also operate more economically at smaller scales than conventional processes, a feature which boosts its ability to handle small, remote reserves that might otherwise be stranded assets.

Conclusion: Unlocking decarbonised fuels through unconventional thinking

While "purification by contamination" may not be a strategy in engineering textbooks, the resulting savings in cost and carbon attest to the value of thinking outside of the box. To meet mid-century decarbonisation goals, the energy industry will require much more innovative thinking. It is imperative not only to dream up futuristic, "moonshot" solutions but to reimagine practical ways to decarbonise by deploying the technology already on hand.

Given natural gas's potential to accelerate global decarbonisation, and the proportion of sour gas in the world's gas reserves, the sulphur industry will be an integral player in the fight to achieve emissions reductions by replacing coal with gas. 8 Rivers looks forward to collaborating with sour gas processors and the broader sulphur industry in this endeavour. ■

References

1. United Nations. (n.d.). Net zero coalition. United Nations. https://www.un.org/en/climatechange/net-zero-coalition
2. IEA. (2019). The Role of Gas in Today's Energy Transitions. IEA. https://www.iea.org/reports/the-role-of-gas-in-todays-energy-transitions
3. EQT Corporation. (2021, December 7). The honorable Elizabeth Warren December 7, 2021... – EQT Corporation. https://www.eqt.com/wp-content/uploads/2021/12/ResponseLetterSenWarren.pdf
4. Cook, P. Z. a. G.: "CCS roadmap for industry: High-purity CO_2 sources (Sectoral Assessment – Final Draft Report)", Carbon Counts Company (UK) Ltd (2010).
5. Kelley, B. T., et al.: "Controlled Freeze Zone™ for developing sour gas reserves." Energy Procedia 4: 824-829 (2011).
6. Ryan, A. S. H. M.: "Cryogenic distillative separation of acid gases from methane", US4318723A (1982).

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 53 54 55 56 57 58 59 60

Keep your sulphur recovery unit online and efficient

Comprimo and Ametek now offer the Analyser Air Control Technology (2ACT) Solution to the industry in which the information for the SRU air control is available 6-7 minutes earlier with the installation of an acid gas feed analyser-based feed forward control. This improvement to conventional SRU combustion air control systems enables operating companies to control their assets closer to design capacity at higher recovery efficiency and with fewer unscheduled outages.

Marco van Son, Gerton Molenaar and Ines Hernandez-Virla (Comprimo, part of Worley)

Worldwide, there are more than 2,500 individual sulphur recovery units (SRUs) installed, predominantly at refineries and natural gas processing facilities. Given the stoichiometric nature of the H_2S conversion to elemental sulphur in every SRU, the precise and quick control of the combustion air to the main burner is key to maintaining high sulphur recovery efficiencies (SRE) and low SO_2 emissions. This is particularly challenging when the compositions of the acid gases feeding the SRU changes, as it can lead to increased SO_2 emissions and negatively impact refinery/gas plant throughput. Especially in refineries dealing with two acid gas streams, amine acid gas (AAG) and sour water acid gas (SWAG), with the SWAG typically experiencing more hydrocarbon carry-over events, the impact can be more pronounced.

With the emerging greater application of bio feedstocks in refineries, whether through full conversion or co-processing, there is a growing need to improve prediction and better control the emissions from SRUs. The introduction of bio feedstocks is leading to requirements to operate SRUs at much lower capacities than originally designed and with almost continuously fluctuating acid gas compositions. These changes have a detrimental effect on the ability to control the SRU with fixed air-to-acid-gas-ratios and feed-back correction from the tail gas analyser. Consequently, there is a higher risk of upsets in the SRU, which could potentially result in environmental violations.

In addition, there is an increasing emphasis on decarbonisation and sustainability within the refining industry, leading to a shift in the approach to maintaining emission standards. The inability to properly maintain the air demand of an SRU during upsets can result in higher fuel gas demands and shorter operating windows, which all can be reported as a larger CO_2 footprint. It is therefore essential to maintain stable operation in an SRU and to avoid unplanned shutdown and restart events.

In gas plants, a noticeable trend is the reduction of H_2S concentration in the acid gas due to the depletion of the wells feeding the plants. As a result, meeting sulphur recovery efficiency requirements may become more challenging. This places greater importance on ensuring tight control of the unit's air demand to address this potential challenge effectively.

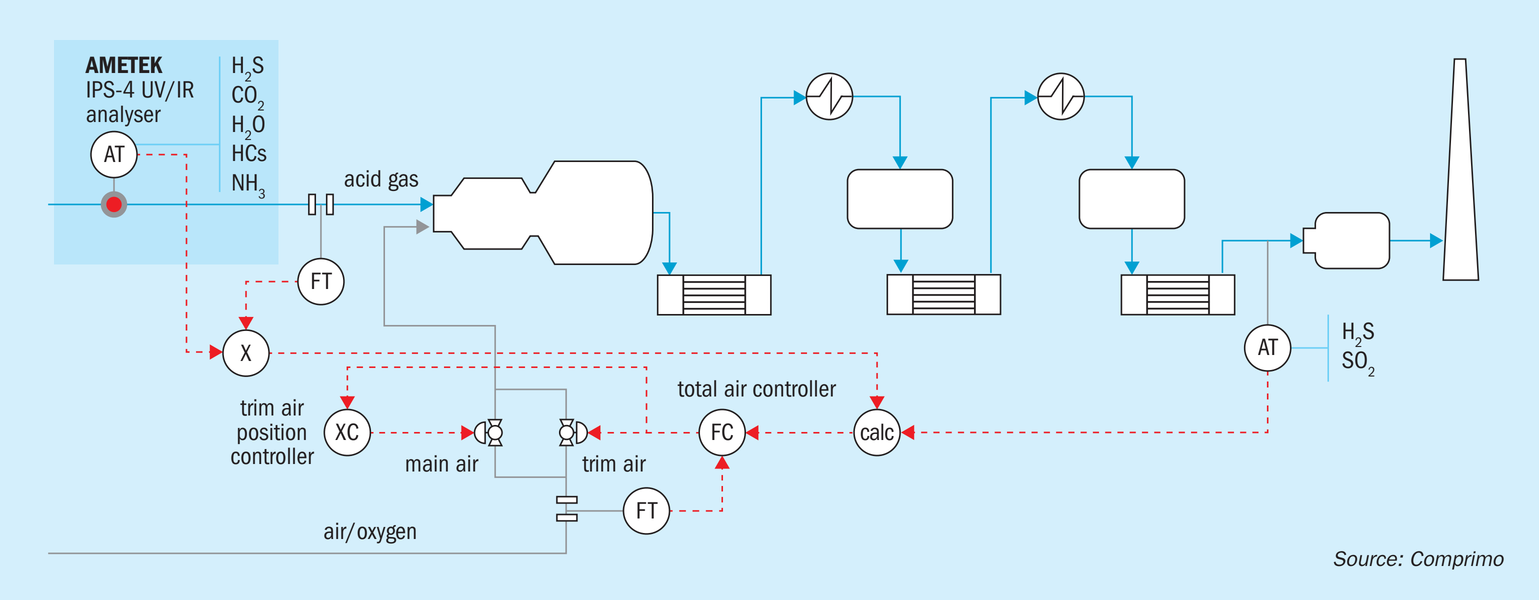
Conventional SRU control and Comprimo's ABC

Comprimo's Advanced Burner Control (ABC) and conventional SRU control both manage feed gas flow rate variations via feed-forward ratio control, but not in the same way. Conventional SRU control uses the main and trim air valves fully independently; the main air valve is controlled in direct ratio to the SRU feed gas flow, while the trim air valve is only controlled by the tail gas quality controller. Some variations of this philosophy may exist in the industry, such as tying the trim air control valve to the sour water acid gas supply, but the fundamental principle remains the same – each valve acts independently. The drawbacks of this strategy, such as slow and inaccurate feed gas ratio control via the main air valve and limited tail gas quality control capacity via the trim air valve, are overcome by the different strategy Comprimo's ABC applies.

ABC controls both the main and trim air valves simultaneously and utilises each valve's specific strength in the best manner; it provides rapid and accurate total air response to any change in acid gas feed flow rates combined with enough tail gas quality control capacity. While the total air flow controller manipulates the small (thus rapid) and accurate trim air valve in response to any air demand change, the main air valve is continuously adjusted to ensure that the trim air valve stays within its operating capacity. Shortly after that response has been provided, the trim air valve returns to its optimal position to wait for new air demand changes.

If no measures are taken, as in conventional SRU control, the air flow response is non-linear in an SRU, especially for main air

Fig 1: **Process flow scheme for the 2ACT Solution**



Source: Comprimo

control. ABC takes this into account using proprietary functions to establish linear responses at any plant load and repositions the trim air valve to its optimal position. Where conventional SRU control uses separate main and trim air flow transmitters, ABC utilises only a common air flow transmitter, thereby reducing engineering, hardware, and maintenance costs, while providing a more accurate combustion air flow. Ultimately, ABC outperforms conventional SRU control in maximising sulphur recovery efficiency through its superior tail gas quality control optimisation.

2ACT™ Solution

Although Comprimo's ABC is an important improvement over conventional SRU control, it still lacks the ability to react to rapid changes in feed gas composition. The feed-forward part of both ABC and a conventional combustion air control system takes the acid gas flow rate into consideration, but not its composition. Both ABC and the standard control designs rely solely on feed-back from a tail gas analyser that is typically located after two or three Claus stages. As a result, there is a significant time delay between a change in feed at the front end of the system and its subsequent impact to the tail gas.

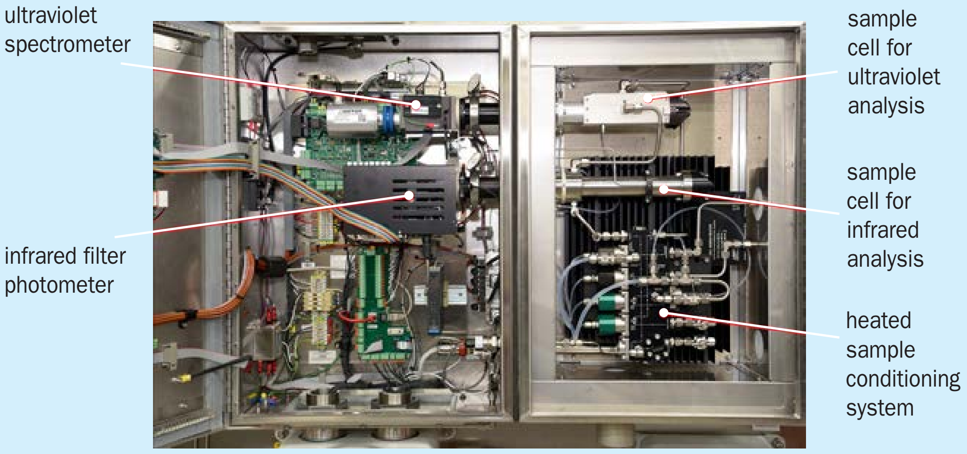
The 2ACT Solution, represented in Fig. 1, addresses this problem by enhancing ABC with the addition of an AMETEK IPS-4 UV/IR analyser upstream of the SRU. This analyser monitors all the acid gas feed components (H_2S, CO_2, H_2O, hydrocarbons, NH_3) by continuously sampling the acid gas. This revolutionary development determines and uses dynamic air-to-acid-gas-ratios and improves the existing feed gas flow compensation by adding molecular weight compensation to precisely provide the required air supply to the SRU main burner. As a result, the required combustion air quantity to the SRU main burner is continuously calculated within seconds and adjusted through ABC, in direct response to all possible changes the feed gas can encounter, such as flow, temperature, pressure and composition. This results in a more accurate air-to-acid-gas-ratio control and improved SRU control robustness. For a typical SRU, this means that the impact of changing acid gas compositions can be managed up to 6-7 minutes quicker with the 2ACT Solution.

The 2ACT Solution, formerly known as ABC+, has undergone further developments to simplify the probe and sample conditioning system, overall analyser integration and system safeguarding, leading to its rebranding.

With the implementation of the 2ACT Solution, the SRU achieves exceptionally stable control without requiring any operator intervention, even in the following scenarios, based on actual 2ACT Solution installations:

- Hydrocarbons carry-over at a rate of:
  - 2.0 mol-% total hydrocarbons (CH_4 equivalent) per 10 seconds
  - 2.8 mol-% total hydrocarbons (C_4H_{10} equivalent) per minute
- H_2S and CO_2 acid gas concentration changes of 15 mol-% at a rate of 4.0 mol-% per minute
- Changes in air demand (air-to-acid-gas-ratio) of 10–15% within seconds.

Fig 2: **AMETEK IPS-4 UV/IR analyser (open)**



Source: AMETEK

1 47
2 48
3 49
4 50
5 51
6 52
7 53
8 54
9 55
10 56
11 57
12 58
13 59
14 60
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

AMETEK IPS-4 acid gas feed analyser and HAG probe

The AMETEK IPS-4 analyser, shown in Fig. 2, is a built for purpose analyser for the 2ACT Solution. It uses two technologies to measure the key components in acid gas streams in a single analyser, without cross-interference. The ultraviolet spectrum is used to measure H_2S and NH_3 and the infrared spectrum is used to measure CO_2, H_2O, total hydrocarbons (THC) and also NH_3. Each analyser is configured to automatically zero the analyser by flushing the measuring cell with nitrogen. The analyser can be manually spanned if required with calibration gases.

The IPS-4 acid gas feed analyser is installed with a heated acid gas (HAG) sampling probe. The HAG probe is a fully integrated, electrically heated sample handling probe assembly designed for this purpose. It is equipped with double block integrated shut-off valves that allow servicing without removal from the process. The probe has a serviceable membrane filter to capture entrained liquid. The probe (and sample line) is temperature controlled to ensure that no sample condensation occurs which is key to reliable gas composition measurement. High and low temperature alarms are incorporated for the probe and the sample line.

The HAG Probe provides the motive force required to circulate the sample through the analyser system and only requires a single process tie-in point/connection. Preferably nitrogen is used to drive the built-in aspirator.

Ideally, the sample probe is installed as far upstream from the SRU main burner as possible, where it can accurately sample the acid gas stream compositions that are processed in the SRU. Typical locations for the sample probe are anywhere downstream of the amine regenerator and sour water stripper reflux drums. Another option, but less favourable, is downstream of the knock-out drums.

Field results from case studies

Over the last 15 years, Comprimo has designed and implemented the 2ACT Solution for 14 SRUs around the world, in both refineries and gas plants, in brownfield revamps as well as greenfield projects.

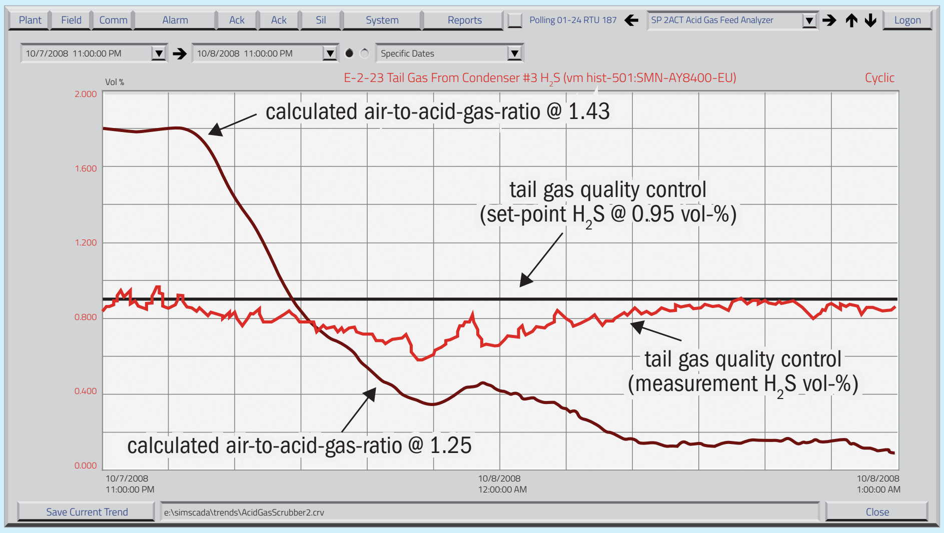
In this section, three case studies are presented showing the performance of the 2ACT Solution during process disturbances, for a refinery SRU and two gas plant SRUs.

Case study 1

Gas plant: 2+1 SUPERCLAUS® – one single train

The initial version of the 2ACT Solution (formerly known as ABC+) was installed at the Simonette gas plant in Alberta, Canada in 2008 and operated successfully for ten years until the SRU (two Claus reactors followed by a SUPERCLAUS® reactor) was decommissioned in 2018 as part of the conversion to acid gas injection. The Simonette gas plant was an example of a challenging SRU control application.

Fig 3: **The 2ACT Solution maintaining control while shutting in a raw sour gas feed**



Source: Comprimo

The plant processed gas from over 65 wells using four main pipelines, including one as long as 110 km. In the various raw feed gas streams, the H_2S content ranged from 2% to 16%.

To recreate process disturbances, during the first week of start-up after the 2ACT Solution went online, tests were carried out by purposely creating changes in the acid gas feed composition. These changes in H_2S, CO_2 and THC content were obtained by shutting down or introducing variant raw gases to the plant.

A frequently occurring change in acid gas composition was caused by the exclusion of raw gas with high H_2S concentration (approx. 16%), which was caused by pigging of pipelines or compressor station failures. A change in H_2S content in the acid gas from 65% to 50% in about 30 minutes was a very common occurrence, in combination with changes in flow rate and THC.

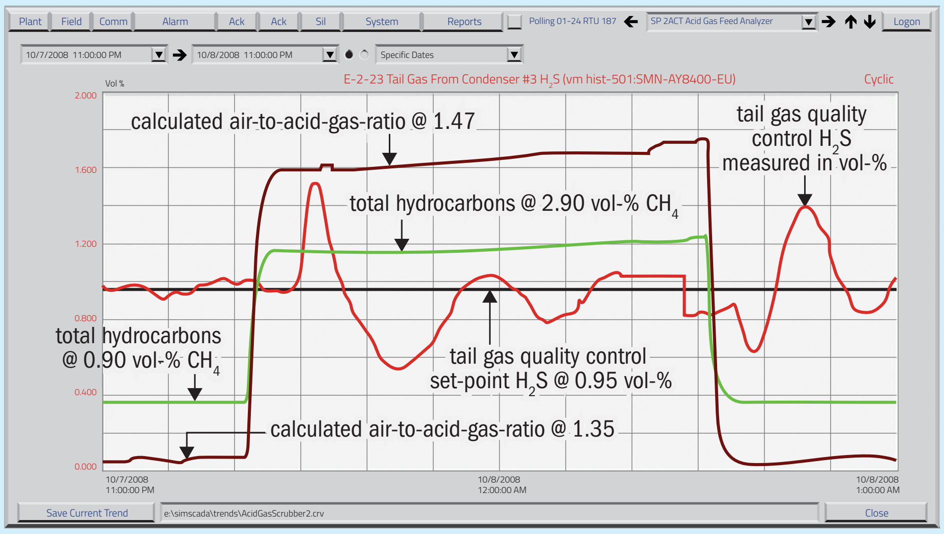
Before implementing the 2ACT Solution, this phenomenon caused frequent SUPERCLAUS® reactor bypass trips due to high H_2S resulting in SRE losses and non-compliance with regulatory SO_2 emission requirements. Panel operators were unable to efficiently determine the precise timing or the amplitude of the upset to be expected, and thus could not take countermeasures.

The control response of the 2ACT Solution to this commonly occurring change in acid gas composition is illustrated in Fig. 3. It can be seen that the H_2S concentration in the tail gas (red line) stays very close to the set-point at 0.95 vol-%, (straight black line) even though the air-to-amine-acid-gas-ratio (brown line) is changing significantly and rapidly from 1.43 to 1.25. This is equal to a change in air demand of 13%. It should be noted that the time involved in the process to shut off the incoming pipeline is quite different than the time required to open it again (24 minutes versus 6 minutes); during both events the control system managed to control the tail gas quality, without initiating a high or low DCS alarm, let alone activating the high high H_2S trip.

Another change in acid gas composition was obtained by introducing natural gas to the upstream amine regenerator. The THC content in the acid gas feed was increased from 0.9 vol-% to 2.9 vol-% within ten seconds which is illustrated in Fig. 4. As a result, the calculated air-to-acid-gas-ratio immediately showed a significant increase

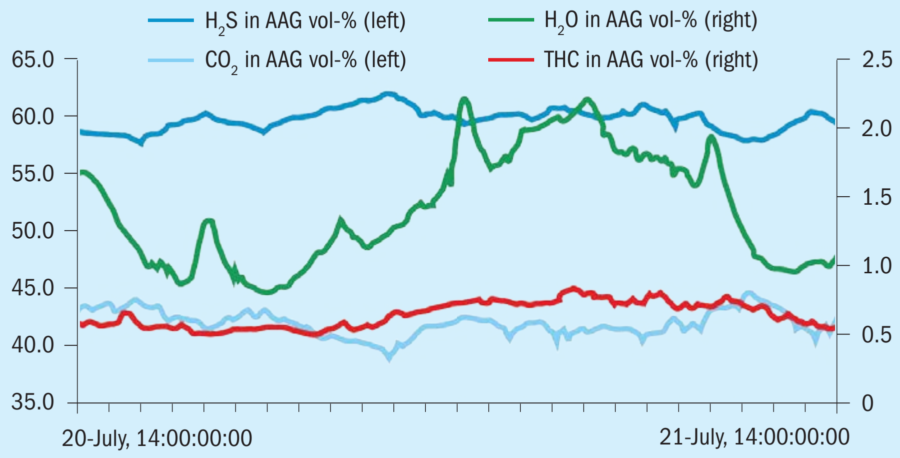
1 47
2 48
3 49
4 50
5 51
6 52
7 53
8 54
9 55
10 56
11 57
12 58
13 59
14 60
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46

Fig 4: **The 2ACT Solution response to a hydrocarbon carry-over upset**



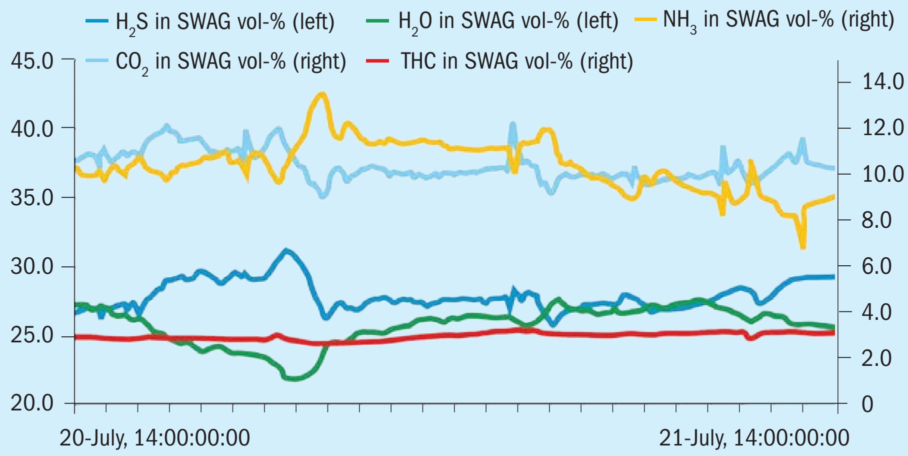
Source: Comprimo

Fig 5: **AAG feed concentrations**



Source: Comprimo

Fig 6: **SWAG feed concentrations**



Source: Comprimo

in air demand of 9%. After an initial modest H_2S concentration spike at the tail gas analyser, the response of the control system was very satisfactory as within several minutes the H_2S concentration returned to its set-point. Also at the reverse upset, where THC content was rapidly decreased again, an identical response was observed. Conventional control systems are not able to respond to these changes adequately and timely. In fact, a hydrocarbon carry-over of this magnitude would cause major upsets causing acid gas flaring and emission violations.

Case study 2

Refinery: 3+1 EUROCLAUS® – two trains

The first 2ACT Solution at a refinery was implemented in 2013 in the United Kingdom for two identical parallel SRUs. Both SRUs are based on Comprimo's EUROCLAUS® technology with two Claus reactors and a hydrogenation reactor, followed by a common selective oxidation reactor. The two SRUs are fed with amine acid gas (AAG) from two parallel amine regeneration units (ARU) and sour water acid gas (SWAG) from a sour water stripper unit (SWSU), fed by a fluid catalytic cracker unit (FCCU). The tail gas from the hydrogenation reactors is routed to the common selective oxidation reactor.

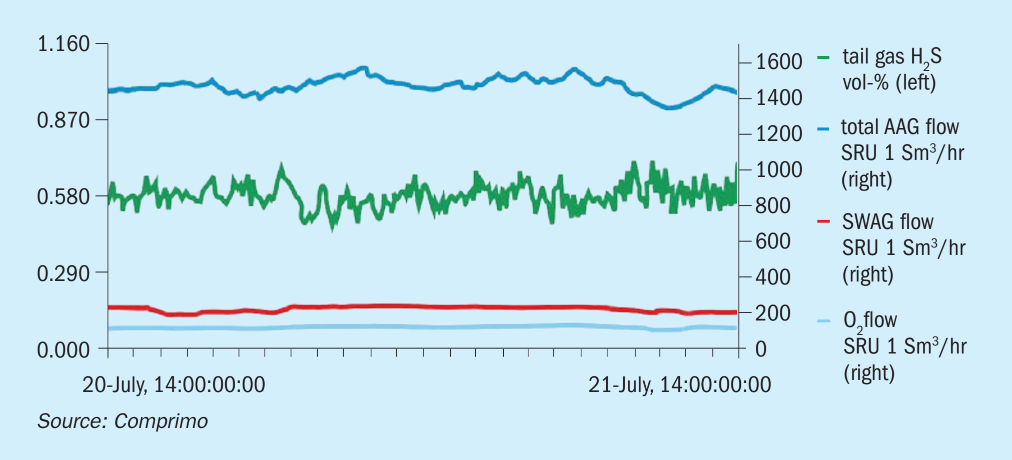
The customer's expectations were met when the 2ACT Solution was implemented, showing very precise and stable tail gas H_2S control at set-point +/- 0.05 vol-%. The 2ACT Solution has been running with excellent online time (> 95%) and satisfactory performance for both AAG and SWAG for ten years.

The following figures, captured on one specific day of operation (July 20, 2014), show three trends indicating important operating variables. The variations in acid gas composition measured by both AAG and SWAG feed-forward analysers are depicted in figs 5 and 6, followed by Fig. 7, which shows the variations in AAG, SWAG and O_2 flow, together with the tail gas H_2S concentration.

Despite all sorts of fluctuations in AAG and SWAG feed composition (particularly for H_2S, CO_2, NH_3 and water) and flow, the 2ACT Solution manages to maintain the tail gas H_2S concentration in a narrow bandwidth around the optimum tail gas operating set-point of 0.58 vol-% H_2S. This installation shows that the 2ACT Solution provides high SRE as well as high online reliability for SRUs in refinery applications.

1 47
2 48
3 49
4 50
5 51
6 52
7 53
8 54
9 55
10 56
11 57
12 58
13 59
14 60
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

Fig 7: **AAG, SWAG, O_2 flows and tail gas H_2S concentration**



Source: Comprimo

Case study 3

Gas plant: 2 Claus + 2 CBA – two trains

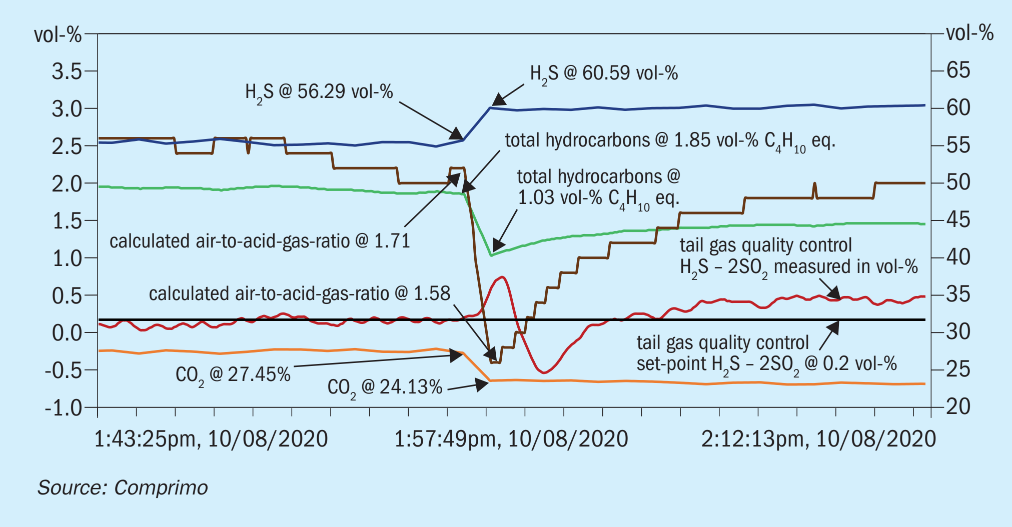
In 2020 the 2ACT Solution was implemented in a gas plant in Texas with two identical SRUs consisting each of two Claus reactors followed by two Cold Bed Absorption (CBA) reactors. The gas plant is part of an enhanced oil recovery (EOR) asset. The required SRE for the facility was set to increase in 2020, and the plant preferred to avoid the installation of a high capital investment new tail gas treating unit (TGTU). In order to meet the new SRE requirements, the customer was therefore interested in implementing the 2ACT Solution to improve the controllability of the facility, to improve the SRE and decrease SO_2 emissions.

As part of the optimisation project, a new AMETEK IPS-4 acid gas feed analyser was installed at the outlet of the acid gas KO drum in each SRU. To integrate the 2ACT Solution the existing air control system was modified, in order for the on-line measured acid gas composition to be used to automatically calculate and modify the air-to-acid-gas-ratio. The 2ACT Solution went online in 2020 and shortly after, tests were carried out by fully opening and fully closing the acid gas feed from one of the upstream units to one of SRUs, purposely creating changes in the acid gas feed composition.

Fig. 8 shows the performance of the 2ACT Solution to the compositional changes in the acid gas feed to the SRU during one of the process upsets. The H_2S concentration increased at a rate of 4.4 mol-% per minute, while the CO_2 concentration and the THC content decreased at rates of 3.7 mol-% and 0.82 mol-% per minute, respectively. The 2ACT Solution responded rapidly decreasing the air demand by 7.6%, to maintain the tail gas H_2S – $2SO_2$ process value in a narrow bandwidth around its set-point of 0.2 vol-%.

This facility was able to meet the required sulphur recovery efficiency of 98.8+% on a continuous and long-term basis with this improvement of the SRU air control system. The 2ACT Solution provided a low-cost solution and prevented significant capital investment for a new TGTU to meet regulatory SO_2 emission requirements.

Fig 8: **Response to upsets in feed gas composition by the 2ACT Solution**



Source: Comprimo

Conclusions

There are a multitude of different Claus based technologies that are being used in sulphur recovery units to meet specific emission targets. One commonality between all the technologies is that good control of the air demand is essential for minimising emissions as well as to protect the process from upsets. This may include SO_2 breakthroughs in amine-based tail gas units that can lead to fouling and reduced performance and on-line availability of the system. With the tail gas analyser at the back of the unit, conventional control systems are unable to respond adequately and promptly to changes in feed compositions.

By implementing SRU air control based on acid gas composition measurement, such as with the 2ACT Solution, the impact of fluctuating acid gas feed compositions can be greatly reduced. The 2ACT Solution is a complete low-cost solution and by preventing even one SRU upset that would result in reduced gas plant/refinery throughput it can provide an immediate return on investment. The various installations in both refinery and gas plant applications globally, illustrate that the following benefits can be expected from its installation:

- reduced SO_2 emissions and prevention of SRU incinerator stack regulatory SO_2 violations;
- protection of TGTU catalyst, quench system and amine system;
- prevention of unplanned downtime or reduced throughput;
- closer operation to SRU nameplate capacity;
- reduced flaring;
- less operator intervention required;
- safer, easier and faster SRU start-up as typically the acid gas composition is not known during start-up;
- instantaneous monitoring of varying AAG and SWAG feedstocks including varying co-processing rates and ratios of potential future bio-feedstocks for operational confidence and troubleshooting or debottlenecking of the SRU. ■

References

1. Molenaar G. and Henning A.: “Cutting edge SRU control”, Brimstone Vail Sulfur Symposium (2009).
2. Henning A.: “Next generation SRU control also for SWAG”, Sulphur 2014 Conference, Paris (Nov 2014).
3. Henning A., Simmonds S. and Hauer R.: “Analysers and next generation SRU control”, *Sulphur Magazine* 356 (Jan-Feb 2015).

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 53 54 55 56 57 58 59 60

1 47
2 48
3 49
4 50
5 51
6 52
7 53
8 54
9 55
10 56
11 57
12 58
13 59
14 60
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

Protecting your assets with PFA

In this case study **Johannes Derfler** of AGRU Kunststofftechnik reports on how a new condenser design, engineered by OMV and INWA AG using PFA sheets from AGRU, was implemented at OMV refinery in Austria to address maintenance problems due to corrosion of the wet sulphuric acid (WSA) condensers and the follow-up units. As a result of the renovation, maintenance costs have been cut in half, while both maintenance intervals and overall operational safety has increased.

OMV, the largest industrial company in Austria refines fuel products and petrochemicals at its site in Schwechat Austria. In the refining process, crude oil and natural gas are processed into high-quality fuels, oils and other special products such as paraffin, heating oil, bitumen, sulphur and sulphuric acid. The aim of all these processing steps is to achieve a high added value product from the raw material, to work economically as a company, all while operating to sustainably protect dwindling resources and the environment. In the end, all the residual products from the processes are fed into a combined heat power plant to produce steam, electricity, district heating and other products through combustion energy. A downstream flue gas cleaning system (SNOx) cleans the flue gases and allows the burning of high-sulphur fuels in the power plant. Due to the high sulphur content in the fuels, SO_2 is produced during combustion which is then used for the production of concentrated sulphuric acid. Sulphuric acid is the most commonly used acid in the world, and there is a global interest in this product as it is essential for a variety of applications. As a result, a contaminated flue gas is turned into clean exhaust air and a saleable industrial product.

In the first step of the flue gas cleaning system, dust is filtered via electrostatic precipitators. Afterwards the NOx is removed in a catalytic process in a second step. The remaining SO_2 gases are then oxidised via converters to SO_3. In the last step of the converters, the majority of the SO_3 reacts with H_2O to form H_2SO_4 vapour. The vapour is transported to the heat exchanger, in which the gaseous sulphuric acid is condensed to liquid H_2SO_4 with a concentration >94%. The condensing droplets of sulphuric acid are formed on the surfaces of the heat exchangers (acid condenser) and the surrounding equipment.

The dew point of the flue gases depends on its composition and is typically reached if the gas temperature drops below approximately 250°C. The condensation of acid droplets on metal surfaces leads to so-called “dew point” corrosion, in which regular steels and stainless steels are rapidly destroyed. In order to achieve sufficient resistance to the highly aggressive application conditions, a multilayer structure is often used, consisting of the following materials: a chemical stone lining, a foam glass layer, non-welded PTFE plates, a chemical protection layer and a carbon steel tank.

This lining system was also used at OMV. However, due to the significant increase of maintenance work over the years, the associated operational downtimes and repair costs that occurred, the economic efficiency of the SNOx plant decreased considerably over time. It was apparent that the multilayer structure did not create a long-term leak-proof lining system. This resulted in corrosion of the carbon steel tank by the condensing sulphuric acid. To ensure safe operation it was necessary to remove the lining system, which was already soaked with acid, and to refurbish the steel structure before applying a new corrosion protection lining system.

Due to the apparent downtimes and the increasing repair costs OMV decided to fundamentally redesign the condenser area. The design objectives were defined as follows:

- production capacity and product quality at least equal to the current system;
- increased reliability, availability and safety;
- extension of maintenance intervals;
- lower maintenance costs due to easier repair.

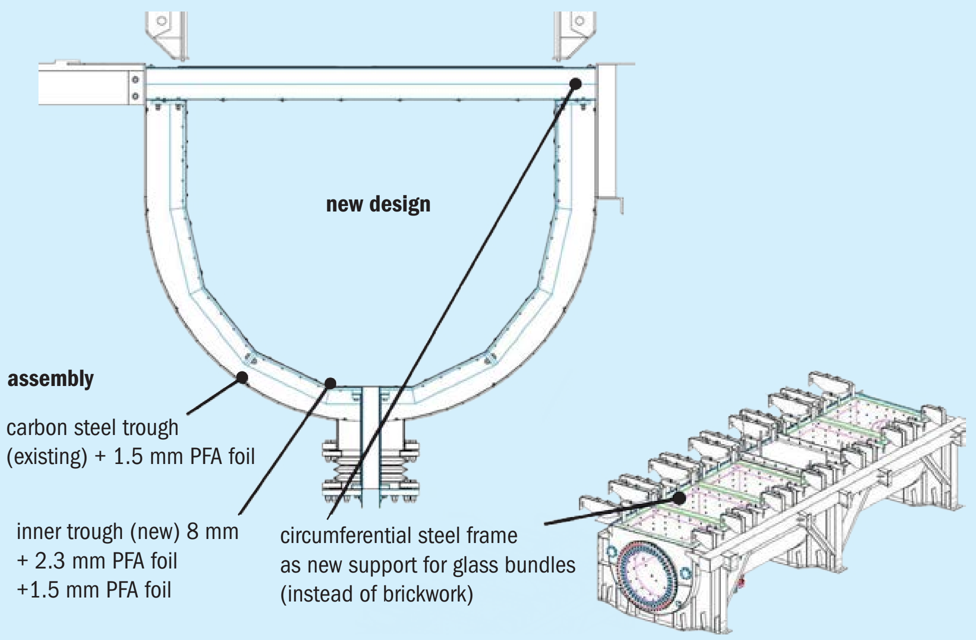
In the course of the design work, detailed solutions were worked out, that made it possible to shut off certain parts of the SNOx plant, so that the plant could be operated under partial load during its maintenance. In addition, a two-layer structure already patented by OMV was developed, to allow the process to be permanently checked for leaks via a monitoring system. However, the focus of the development was the selection of a lining system that would withstand the harsh operating conditions and meet the specified project objectives. In the selection process, eight different lining systems were evaluated and analysed. Due to experience in the field of PFA linings for sulphuric acid condensers INWA AG was able to provide long-term references demonstrating the functionality of this lining system in similar applications. In addition, AGRU placed an order with a Swedish testing institute to expose AGRU PFA sheets for one year at temperatures and concentrations that exceeded the operation conditions. The results clearly showed that no significant changes to the product properties occurred at 260°C and 98% sulphuric acid after one year. Based on the available long-term references and the investigation carried out, the PFA fixed point lining system was specified as the optimal lining system by OMV. INWA AG was awarded the contract to start with the refurbishment of the first of four plant sections in 2018. Fig. 1 shows the new tank design, which consists of a double layered steel tank, both layers lined with PFA.

Compared to the old design, the chemical protection layer now consists of two PFA sheets located on top of each other, whereby the PFA sheet at the bottom was simply installed for additional operational safety. The steel tank at the bottom, which is not in contact with the medium during normal operation, was also lined with a PFA sheet in order to provide comprehensive corrosion protection even in the event of leakages.

PFA fixed point lining

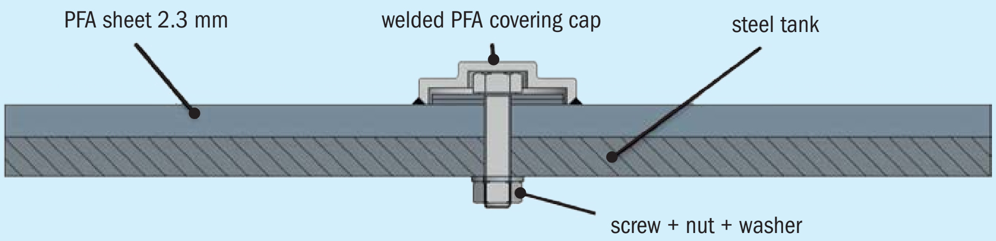
With the PFA fixed point lining, a PFA sheet is fixed to a steel structure by a mechanical fastening using bolts or screws. This system is mainly used in flue gas applications and desulphurisation plants up to 260°C (see Fig. 2).

Fig 1: **Detailed view of the new condenser design**



Source: OMV

Fig 2: **Sketch of mechanically fixed PFA sheet and injection moulded cover cap**



Source: Source AGRU


PHOTO: OMV

Fig. 3: PFA lining and welding work in the sump area

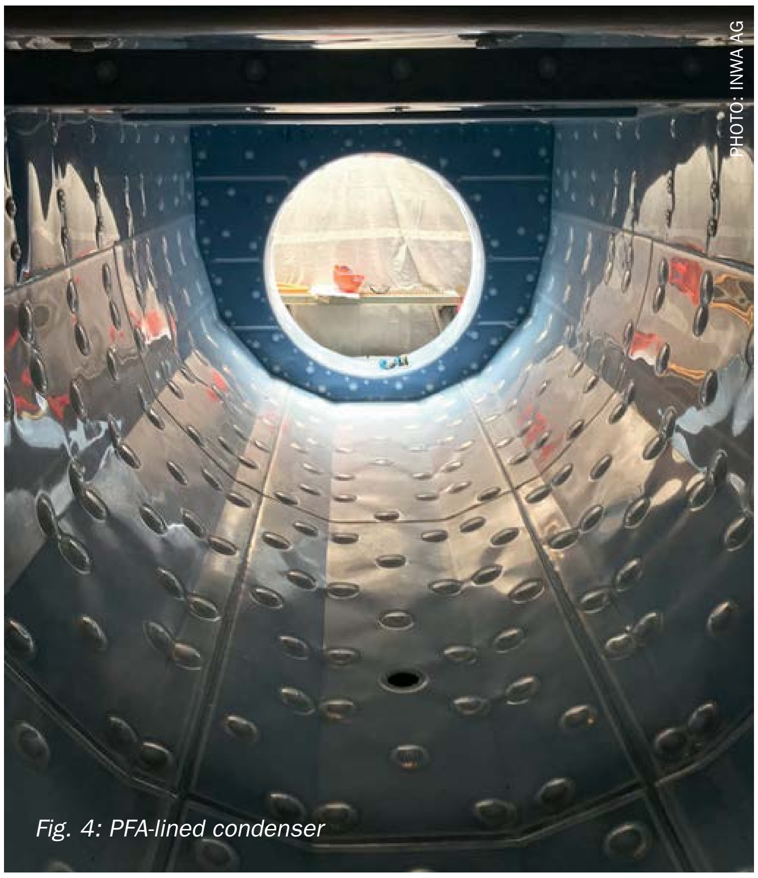


PHOTO: INWA AG

Fig. 4: PFA-lined condenser

1 47 2 48 3 49 4 50 5 51 6 52 7 53 8 54 9 55 10 56 11 57 12 58 13 59 14 60 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

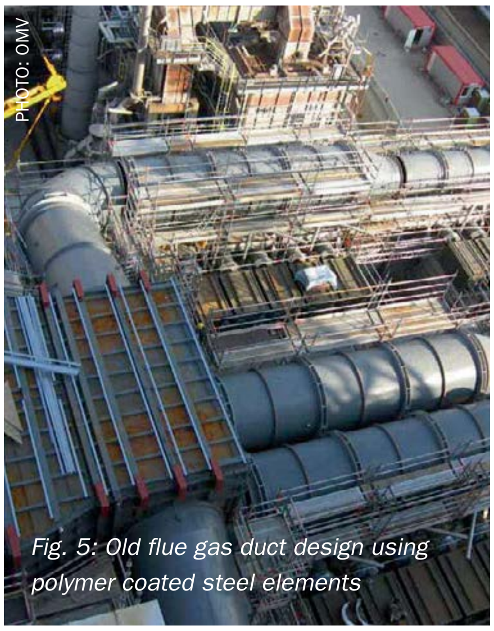


PHOTO: OMV

Fig. 5: Old flue gas duct design using polymer coated steel elements

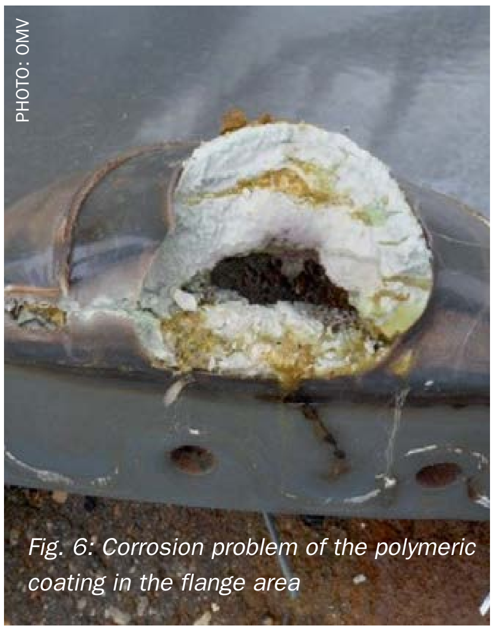


PHOTO: OMV

Fig. 6: Corrosion problem of the polymeric coating in the flange area

The PFA fixed point lining offers simple repair possibilities since the sheets can be welded again after proper preparation in the case of damage. In future, time-consuming special repair work with dissimilar materials will no longer be necessary, thus reduced downtime is expected.

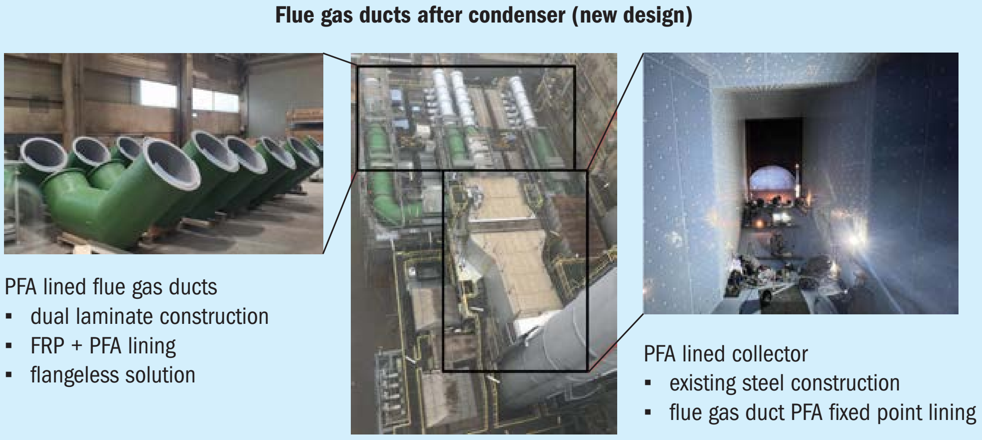
Between 2018 and 2022 all four condensers were relined using this patented lining concept. Since the PFA products are used under very aggressive operation conditions, the PFA production was inspected and controlled by INWA AG and OMV through regular audits. As a system supplier, AGRU was able to produce all the required PFA products, thus making an important contribution to the realisation of this project.

Fig. 3 shows the installation and welding work of the AGRU PFA sheets in the sump area and Fig. 4 shows the final lined condenser, before being placed into operation.

Fig 7: **Cross section through the wall section of a PFA–FRP dual-laminate tank**

Source: Source AGRU

Fig 8: **Overview of the new flue gas duct system**



Source: Source AGRU

Flue gas ducts

The flue gases cleaned by the condensers are then collected in the clean gas ducts so that they can leave the plant via the chimney system, see Fig. 5. In the old design, the clean gas ducts were made from steel components with a thin polymeric coating for chemical resistance. Due to the low thickness and the large number of flange joints required for this type of installation, many corrosion problems and leaks were present, see Fig. 6. As a result, it was decided to completely replace the pipes using a combination of PFA FRP dual-laminate pipes and a PFA fixed point lining.

FRP dual-laminate construction

By using the FRP dual-laminate construction the chemical resistance of the PFA material is combined with the mechanical strength of the FRP reinforced plastic. A fabric backing system in the polymer lining is used to provide a bonding between both materials, see Fig. 7. The refurbishment of the clean gas ducts was conducted in 2022. An overview of the new plant components and linings is shown in Fig. 8.

Conclusion

In the course of a routine inspection carried out in 2022 no damage or abnormalities were detected on the PFA condenser lining installed in 2018. Mr Ronald Hoffer, the person responsible for this project for OMV concluded after inspection of the plant area: “Despite the highly aggressive application conditions, the PFA lining shows no noteworthy damage or changes after an operating period of three years. It seems that sheets have just been installed”.

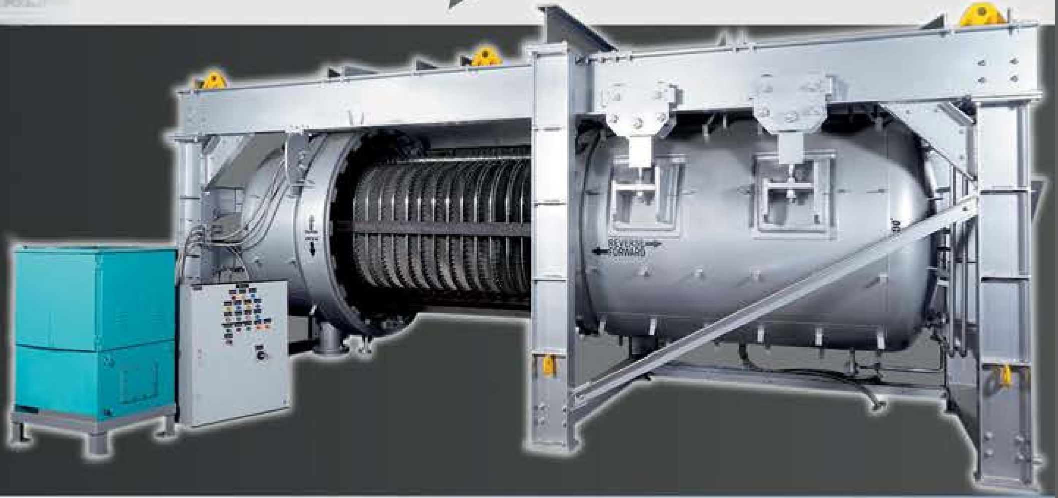
Thanks to the successful development and the completed reconstruction, OMV and INWA AG were able to apply for a patent for this double layer lining system. In addition, the specified project goals were achieved:

- increase in reliability, availability and safety;
- 50% reduction in maintenance costs;
- 75% reduction of downtimes;
- patented leakage monitoring system enables permanent control of the plant components;
- increased operational safety due to installation of an additional tight lining system.

1 47
2 48
3 49
4 50
5 51
6 52
7 53
8 54
9 55
10 56
11 57
12 58
13 59
14 60
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

Sharplex®

MOLTEN SULPHUR FILTER



Advantages

- Quick opening and closing by hydraulic
- Full jacketed design of vessel
- 5 layer bolted leaf design can handle high pressure
- Large leaf spacing allows higher thickness of cake build up and permits easy cleaning
- Overhead frame design can be offered
- Scrapper plates are provided to remove the residual molten sulphur from the inside of vessel
- More than 50 installations

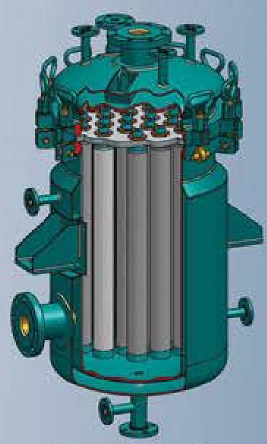
FILTRATION AREA
from 5 m^2 to 200 m^2

Sharplex have supplied several filters for molten sulphur filtration in sulphuric acid & sulphonation plants. Sharplex offers horizontal pressure leaf filter for molten sulphur filtration in Shell retraction design and Bundle retraction design.

Both the versions are operated (for opening and closing of filter) hydraulically for easy of operation.

FOR EFFECTIVE SULPHUR FILTRATION

CARTRIDGE FILTERS FOR SULPHUR POLISHING



Cartridge type polishing filters are installed after main molten sulphur filters to remove traces of fine suspended particles ash and filteraids escaped from main filter, which may choke the downstream equipments in the plant.
The removal of these fine solids will help in running the downstream equipments smooth without interruptions. This will result in reducing the downtime of the plant to great extent.

SHARPLEX FILTERS (INDIA) PVT. LTD.
R-664, T.T.C. Industrial Area, Thane-Belapur Road, Rabale, MIDC,
Navi Mumbai - 400701, India; **Tel :** +91-91-3692 1232/39,
+91-22-27696339/6322/6325. **E-mail :** sales@sharplexfilters.com
Website : www.sharplex.com

signsmith/sfpl/0919

TGU catalyst poisoning and deactivation

With the aid of a rigorous kinetic model for TGU hydrogenation reactors, incorporating catalyst deactivation mechanisms, designers and operators can forecast the life expectancy of reactor catalyst beds.

Michael A. Huffmaster (Consultant), Prashanth Chandran, Nathan A. Hatcher, Daryl R. Jensen (Optimized Gas Treating, Inc.)

Catalyst deactivation is the loss over time of catalytic activity and/or selectivity. It is a problem of great and continuing concern in the practice of industrial catalytic processes. Costs to industry for catalyst replacement and process shutdowns total billions of dollars per year, and in sulphur recovery, TGU catalyst expenses account for at least \$50 million per year plus the cost of unloading and loading. This does not include lost profit from downtime for unplanned outages, which can exceed \$1 million per day at a sulphur constrained facility.

Time scales for catalyst deactivation vary considerably; for example, with cracking catalysts, longevity is measured in seconds; in ammonia synthesis the iron catalyst may last for 5-10 years. However, all catalysts inevitably decay. In TGUs, typical life is 5-6 years, although many operators can use the same catalyst charge through two turnaround cycles, and some have successfully operated for 10-12 years. Severe cases of deactivation have life shortened to a few months. There are two known remarkable longevity records – 18 and 20 years.

TGU catalysts are largely cobalt and molybdenum on an alumina support, a support which is used widely in the process industry and for the Claus process. This body of knowledge is a strong reference regarding deactivation. Argyle and Bartholomew[3] provide a comprehensive reference. TGU catalysts are not specifically included in this reference so experience as informed by sulphur recovery industry experience and research is presented.

Deactivation can be classified by stress type: chemical, thermal, and mechanical. Mechanisms are multiple: poisoning, coking, fouling, thermal degradation/sintering, vaporisation or sublimation, metal/support interactions, and attrition/crushing. Activity loss in a well-controlled process happens slowly. However, process upsets or poorly designed hardware can bring about rapid failure.

Many are the paths for heterogeneous catalysts to decay. For example, a solid catalyst may be poisoned by any of several contaminants in the feed. Its surface, pores, and voids may be fouled by hydrocarbon-related processes. Oxygen or chlorine in the feed gas can lead to deleterious effects. Similarly, changes in the oxidation state of the active catalytic phase can be induced by reactive gases such as O_2 or SO_3 in the feed. Furthermore, the process environment causes aging by the very exposure to process gas, moisture and normal operating temperature.

Hydrothermal aging

Hydrothermal aging causes irreversible loss of surface area of alumina and titania supports. The mechanism is the transformation of the surface structure from water interacting with hydroxyl groups on alumina. Surface area and activity are lost in the first days to weeks of operation, depending on the temperature and water concentration. This is a form of sintering driven by water vapour and temperature, but at lower temperatures.

The surface of fresh catalyst has a large area and numerous active sites. Reformation occurs early in operation, ultimately reducing the surface area by about 30%. The surface then becomes stable, declining slowly over years. In this way, γ-alumina is converted to β-$Al(OH)_3$ (boehmite, bayerite or gibbsite)[5]. Surface hydroxyls can also condense, dehydroxylating the surface. Further, diffusion of surface Al atoms results from the breakage and reestablishment of surface Al-O-Al bonds. Loss of specific surface area lowers catalyst performance as the number of Al-OH surface sites drops in proportion to the loss.

The mechanical coalescence of smaller particles forming larger spheroids as well as trapped voids (rather than catastrophic structural collapse) reduces surface area. The process progresses by establishment of filets at contact points, then gradual reformation and merging. For example, coalescence of eight micro spheres into one results in a single particle with twice the radius and half the surface area.

Active metals can also migrate or undergo crystallite growth under hydrothermal conditions, reducing the active site number density. Water vapour promotes sublimation and migration, which act to grow larger crystallites or slabs with fewer sites, reducing dispersion and lowering activity. The sulphide form is less volatile and more resistant to migration than the oxide.

Generally, fresh TGU catalyst has a specific surface area of 300–350 m^2/g, which rapidly declines to 240–260 m^2/g, then is relatively stable, declining over years until “spent” at approximately 120 m^2/g. Catalyst activity also declines with aging, and spent catalyst expresses about half of the activity of fresh catalyst. Hydrothermal aging tends to occur uniformly throughout the catalyst bed and activity declines over the useful life.

Thermal degradation and sintering

Sintering is a thermal process which causes fairly rapid agglomeration of base (micro) particles into substrate, or of active metals into fewer, larger crystallites. The sulphide form of the active metals is fairly stable and provides some resistance to sintering

because sublimation temperatures are higher than for the oxides. Temperature exposure that causes sintering (500–1,000°C) is well above the normal operating range for a TGU, but can be experienced in some units under upset conditions, especially upon introduction of oxygen.

Thermally-induced catalyst deactivation results from (1) loss of surface area caused by crystallite growth of the catalytic phase, (2) loss of support area from support collapse and of catalytic surface area from pore collapse on crystallites of the active phase, and/or (3) chemical transformations of catalytic to non-catalytic phases. Supported metals sintering and redispersion has focused on the dynamics of metal crystallites: (1) crystallite migration, (2) atomic migration, and (3) (at very high temperatures) vapour transport.

Steam and thermal deactivation are believed to occur by separate mechanisms, differing primarily in the mode of mass transport. With steam, surface- or vapour-phase diffusion predominate; whereas, thermally, bulk- and grain-boundary diffusion predominate. It has been suggested that voids-trapping within catalysts steamed to low surface areas can be considerable[3].

Aging from thermal cycling has a mechanical aspect. Expansion and contraction of the catalyst induced by temperature changes in the presence of water vapour causes permanent destruction of the microporous structure. This is a normal aging process and occurs over an extended period owing to the inherent character of fixed-bed configurations used in TGU applications. The crush strength is reduced and fines are produced by attrition.

The effect of temperature on metal and oxide sintering depends on the driving forces for dissociation and diffusion of surface atoms: both are proportional to the fractional approach to the absolute melting point temperature (T_{mp}). Thus, as temperature increases, the mean lattice vibration of surface atoms increases; when the Hüttig temperature ($0.3T_{mp}$) is reached, less strongly bound surface atoms at defect sites (e.g., edges and corner sites) dissociate and diffuse readily over the surface, while at the Tamman temperature ($0.5T_{mp}$), atoms in the bulk become mobile. Accordingly, sintering rates of a metal or metal oxide are significant above the Hüttig temperature and very high near the Tamman temperature[4]. The data in Table 1 are for compounds of cobalt and molybdenum, active metals in TGU catalysts. For reference, the operating temperature of a TGU reactor is 200–300°C (473–573K).

Promoters and impurities affect sintering and redispersion, affecting metal atom mobility on the support; in the latter case, dissociation and migration decreases at high melting points. Similarly, support surface defects or pores impede surface migration of metal particles – especially micropores and mesopores with pore diameters about the same size as the metal crystallites.

Sintering rate data were historically fitted to a simple power-law expression (SPLE):

$$\frac{d\left(\frac{D}{D_0}\right)}{dt} = k_s\left(\frac{D}{D_0}\right)^n$$

where k_s is the sintering rate constant, D_o the initial dispersion, and n is the sintering order (3–15 for typical catalyst systems). The SPLE assumes surface area or dispersion ultimately reaches zero when, in fact, for a given temperature and atmosphere, a non-zero value is observed. The general power-law expression (GPLE) adds a term to account for the observed asymptotic approach:

$$\frac{d\left(\frac{D}{D_0}\right)}{dt} = k_s\left(\frac{D}{D_0} - \frac{D}{D_0}\right)^n$$

This gives a limiting dispersion D_{eq} at infinite time. The order of sintering, m, is found to be either 1 or 2 as shown by Fuentes and coworkers[5,6] and by Bartholomew and coworkers[7-9].

Sintering rates are exponentially dependent on temperature, fitting the classic Arrhenius relationship. The references cited above give example rates and activation energies on alumina and other supports, although TGU catalysts are not explicitly included. E_{act} varies from 30 to 150 kJ/mol and decreases with increasing metal loading and increase in the following order with the atmosphere: $NO < O_2 < H_2 < N_2$[7-12]. Metal–support interactions are weaker (bond strengths of 5–15 kJ/mol); with few exceptions, thermal stability for a given metal decreases with support in the order $Al_2O_3 > SiO_2 >$ carbon. Extending this approach to lower temperature operating ranges in TGUs provides reasonable representation of observed aging-rate-related deactivation.

In oxidising atmospheres, γ-alumina and silica are the most thermally stable carriers; in reducing atmospheres, carbons are most stable. Steam accelerates support sintering by forming mobile surface hydroxyl groups that are subsequently volatilised at elevated temperatures. Chlorine similarly promotes sintering.

Table 1: **Tamman and Hüttig temperatures for compounds of Co and Mo**

Compound	Tmp / K	Tamman T / K	Hüttig T / K
Co	1,753	877	526
CoO*	2,206	1,103	662
CoS	1,468	734	440
$CoCl_2$	1,008	504	302
Mo	2,883	1,442	865
MoO_3	1,068	534	320
MoS_2	1,458	729	437
Mo_2Cl_{10}	467	233	140

**Cobalt also forms a mixed oxide, Co3O4 with Tmp = 1250K*

Sulphur condensation

If the reactor is operated at or below the sulphur dewpoint, liquid sulphur can accumulate within the catalyst pores. This is typically associated with a problem in the upstream SRU coalescer operation or a blocked rundown line. It is also notable that sulphur condensation within the micropore structure is possible because the bulky S_8 molecule formed is larger than some of the micropores.

Whereas SO_2 is converted to sulphur and water on Co/Mo active sites, the resulting sulphur remains on the Co/Mo sites and is hydrogenated to H_2S.

However, if SO_2 conversion is achieved via the Claus reaction on alumina, it produces a S_6 or S_8 molecule which must desorb, diffuse and re-adsorb on Co/Mo to be converted to H_2S. The S_8 molecule can effectively become stuck, unable to vacate the catalyst pore, so condenses and blocks it. This can be reversed simply by increasing the temperature in the bed and re-vaporising the condensed sulphur. Sometimes, this is easier said than done. For example, the designer may have failed to provide enough margin to the preheater to cover this operating scenario or is restricted to using condensing steam which limits the temperature.

Excessive sulphur entrainment from upstream SRU condensers and coalescers or blocked sulphur rundown lines can also increase the likelihood of reaching the sulphur dewpoint within the TGU catalyst bed (not just in the catalyst pore). SulphurPro® evaluates the dewpoint temperature margin within the catalyst bed, which is crucial to predicting deactivation by this mechanism.

Fouling

Fouling is the physical deposition of species onto the catalyst surface that causes activity loss from blockage of sites or pores. Examples include mechanical deposits of carbon and coke in porous catalysts as well as condensation of sulphur. Carbon- and coke-forming processes also involve chemisorption of different kinds of carbon or condensed hydrocarbons that may act as catalyst poisons. Carbon can be a product of CO disproportionation, while coke is produced by decomposition or condensation of hydrocarbons on catalyst surfaces and typically consists of polymerised heavy hydrocarbons. Nevertheless, coke forms may vary from high molecular weight hydrocarbons to primarily carbon such as graphite, depending upon the conditions under which the coke was formed and aged.

Coking and sooting

Carbon and coke formation on supported metal catalysts can restrict access via build-up on active metal sites or support, or blind active metal sites. Carbon may (1) chemisorb strongly as a monolayer or physically adsorb in multilayers, blocking access of reactants to metal surface sites, (2) completely encapsulate a metal particle and thereby fully deactivate it, and (3) plug micro- and mesopores, denying access of reactants to many internal crystallites.

Deactivation of supported metals by carbon or coke can occur either chemically from chemisorption or carbide formation, or physically and mechanically from blocking surface sites, metal crystallite encapsulation, and pore plugging. Destruction of catalyst pellets by carbon filaments occurs in other applications but has not been observed in TGUs. Blocking of catalytic sites by chemisorbed hydrocarbons, surface carbides, or relatively reactive films is reversed by regeneration with controlled oxidation. Regeneration of TGU catalysts is seldom practiced because of poor success controlling the required mild oxidising atmosphere in the plant environment.

Coking is accelerated on super acid sites that result from SO_2 adsorption or sulphate formation in the upper portion of the bed before SO_2 is extinguished. The biggest effect is when aromatics, heavy hydrocarbons or olefins are present.

Known promoters of coking, sooting and carsul formation include:

- olefins from refinery gas as fuel or poor-quality hydrogen makeup;
- refinery hydrogen (e.g., reformer) containing aromatics or BTEX and chlorides;
- acid gas enrichment streams containing BTEX.

In addition to hydrocarbon structure and reaction conditions, both the extent and rate of coke formation depend on the acidity and pore structure of the catalyst, increasing with acid strength and concentration. Thus, coking is driven by SO_2, therefore, coking will be more severe in the top of the bed and at the first active reaction front. Coking in TGU catalyst beds proceeds from top to bottom but can also occur thoroughout the bed to some degree.

Sooting commonly occurs when sub- or near-stoichiometric natural gas firing is used in SRU start-ups and shutdowns, or by improperly operating the inline reheat burners or reducing gas generator (RGG). Sooting is minimised by using a good quality high intensity swirl type burner for RGG, or avoided completely with an indirect TGU preheater.

Fine soot particles accumulate on the surface of catalyst and fill interstitial areas, restricting diffusion from the bulk to the catalyst surface and increasing pressure drop through the bed. Soot can even block macropores and restrict access to mesopores and micropores. This type of deactivation typically occurs at the top (inlet) of the catalyst bed and can create a rigid crusty structure.

1 47
2 48
3 49
4 50
5 51
6 52
7 53
8 54
9 55
10 56
11 57
12 58
13 59
14 60
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

It causes loss in catalyst performance and also increases pressure drop through the catalyst bed, thus lowering hydraulic capacity,

Another cause of sooting is the deposition of carbon within the catalyst pores from disproportionation of carbon monoxide:

$$2CO \rightleftharpoons C_{graphite} + CO_2$$

This effectively blocks the metal sites and reduces activity. Hydrogen and water vapour inhibit the path, although hydrogen partial pressure is quite low under TGU conditions. Disproportionation proceeds slowly under TGU low pressure conditions, and because CO is considerably reduced through the bed, it occurs mostly in the upper portion of the bed, advancing as catalyst is poisoned, and the reactive front moves down the bed.

Poisoning

Poisoning is the strong chemisorption of reactants, products, or impurities on sites otherwise suited for catalysis, operationally a species whose adsorption strength is higher than other species competing for catalytic sites. Adsorbed poisons such as sulphate may induce changes in the electronic or geometric structure of the surface. Poisoning can be reversible or irreversible. An example of reversible poisoning is the deactivation of acid sites by nitrogen (ammonia, cyanide) in the feed. Regardless of reversibility or irreversibility, the poison's effects are the same. Many poisons occur naturally in feed streams that are treated in catalytic processes.

Sulphation

Sulphation results from the interaction of SO_2 and H_2O on the catalyst surface, causing gradual build-up of sulphate, and reducing the effective surface area. In the TGU, SO_2 concentrations are low and SO_2 is fully converted across the reactor bed. The strong chemisorption of SO_2 is generally reversible. While sulphate on alumina is key to Claus catalysis, this inhibits hydrolysis of COS and CS_2. With oxygen slip, SO_2 forms sulphate, which is permanent, and If SO_3 is present it will sulphate the alumina.

A significant impact of SO_2 is raising the acidity of alumina which promotes coking. Chemisorbed sulphate has a strong interaction with electron distribution on the alumina surface, creating super acid sites. Hydroxyls on the catalyst surface serve as weak Brönsted acid sites with acid strength inversely proportional to the O-H bond strength. Sulphur dioxide additionally pulls electron density away from the O-H bond, making the H sufficiently acidic to catalyse coking or carsul formation.

Carsul

Carsul is akin to coking coincident with polymerisation, adding another dimension to hydrocarbon contamination. When C_{3+} hydrocarbons enter the TGU reactor they can crack on the catalyst's acid sites and combine with sulphur across the catalyst surface[3]. A tenacious carbon-sulphur polymer is formed called Carsul, which coats the catalyst and builds up, potentially blocking the macropores and preventing access to catalyst interior. Cracking tendency is worst at high temperatures, especially above 450°F (232°C). BTEX is particularly nasty in this regard as the cracking occurs deeper in the catalyst pore structure. High acidity and the presence of SO_2 drives this reaction; sulphur is required, so it tends to form at the reactor inlet, moving progressively down the bed.

Deactivation by Carsul is permanent, but it is completely preventable by keeping precursor hydrocarbons out of the feed. Certain streams are known to contribute to this headache, including using reformer hydrogen as supplemental hydrogen, using refinery gas as fuel for the RGG, and processing acid gas enrichment off-gas (AGE) because it usually contains heavier hydrocarbons and BTEX. Also, sulphur plants which process BTEX can pass those species to the TGU, especially with lean acid gas because of difficulty to generate high enough thermal reactor temperatures to destroy BTEX. Historically, activated carbon and silica gel beds have been used to scavenge BTEX from lean acid gas feeds to the SRU.

Reaction to produce inactive phases

Refinery units process crude oil which contains sulphur and metals, such as vanadium, nickel, arsenic, phosphorous, selenium, and zinc that act as catalyst poisons in many petroleum refinery processes. They can enter off gas streams from those units and make their way into refinery gas or the acid gas removal units. Although most of these metal poisons wind up on the catalysts in the units where they are processed, some migrate or are entrained into the vapour phase and can make their way into the acid gas and the SRU and TGU.

Dispersed metal sulphides are catalytic phases in TGU applications. If the metal catalysts are oxidised or reduced, by prolonged exposure to hydrogen without hydrogen sulphide, it will lose essentially all its activity. These chemical modifications are closely related to poisoning, although the distinction is loss of activity due to the formation of an altogether new phase, e.g., oxide or metal, rather than via the presence of an adsorbed species.

Metal loss through formation of volatile compounds, e.g., metal carbonyls, oxides, sulphides, and halides in CO, O_2, H_2S, and halogen-containing environments, can be significant over a wide range of even mild conditions. Carbonyls are formed at relatively low temperatures but high CO partial pressures; halides will form at relatively low temperatures and low concentrations of the halogen. However, the conditions under which volatile oxides are formed vary considerably with the metal.

Reaction of SO_3 with γ-Al_2O_3 produces aluminium sulphate $Al_2(SO_4)_3$ and is a serious cause of deactivation of alumina-supported catalysts in several catalytic processes. It leads to support breakdown and pore plugging.

Summary of deactivation mechanisms

Poisoning and thermal degradation are generally slow processes, while fouling and some forms of chemical and mechanical degradation can lead to rapid, catastrophic catalyst failure. Some forms of poisoning and many forms of fouling are reversible; hence, they can be regenerated, but this is seldom practiced for TGU catalysts. Conversely, chemical, mechanical, and thermal forms of catalyst degradation are rarely reversible.

It is often easier to prevent rather than cure catalyst deactivation. Some poisons and foulants can be removed from feeds using guard beds, scrubbers,

■ Contents ISSUE 408 SULPHUR SEPTEMBER-OCTOBER 2023 BCInsight

and/or filters. Fouling, thermal degradation, and chemical degradation can be minimised through careful control of process conditions, e.g., effective destruction of ammonia in the SRU, avoiding feeds with BTEX to the SRU or TGU, avoiding reformer hydrogen as make-up (BTEX + Cl), using natural gas instead of refinery gas for burner fuel (O_2 slip, soot, olefins and heavy hydrocarbons, temperature excursions from changing stoichiometry) and avoiding SO_3 formation in SRUs. Effective control of air or oxygen to maintain tail gas $H_2S:SO_2$ ratio with some benefit for control at elevated 4–6:1 $H_2S:SO_2$ ratio. Avoiding SO_2 breakthrough or operation without hydrogen (coking) are vital.

Mechanical degradation can be minimised by careful control of heat-up rates and minimising thermal cycles. Proper catalyst handling during loading, avoiding mechanical shock from high velocity impact, is important to prevent breakage and attrition. Catalyst design addresses choice of carrier materials, impregnation techniques, catalyst particle forming methods, and calcining. ■

References

1. Huffmaster, M. A.; Chandran, P.; Hatcher, N. A.; Jensen, D. R.; Weiland, R. H.: "Kinetic model for TGU hydrogenation reactors: Part 1 – Model development", PTQ Q1, 43–49 (2023).
2. Huffmaster, M. A.; Chandran, P.; Hatcher, N. A.; Jensen, D. R.; Weiland, R. H.: "Kinetic model for TGU hydrogenation reactors: Part 2 – Catalyst model validation", PTQ Q2, 55–61 (2023).
3. Argyle, M. D.; Bartholomew, C. H.: "Heterogeneous catalyst deactivation and regeneration: A review", Catalyst (2015).
4. Moulijn, J. A.; van Diepen, A. E.; Kapteijn, F.: "Catalyst deactivation: Is it predictable?: What to do?", Appl. Catal. A, 212, 3–16 (2001).
5. Fuentes, G. A.; Catalyst deactivation and steady-state activity: "A generalized power-law equation model", Appl. Catal., 15, 33–40 (1985).
6. Fuentes, G. A.; Ruiz-Trevino, F. A.: "Towards a better understanding of sintering phenomena in catalysis". In Catalyst Deactivation 1991 (Studies in Surface Science and Catalysis); Bartholomew, C. H., Butt, J. B., Eds., Elsevier: Amsterdam, The Netherlands, 68, 637–644 (1991).
7. Bartholomew, C. H.: "Model catalyst studies of supported metal sintering and redispersion kinetics". In Catalysis (Specialist Periodical Report); Spivey, J. J.; Agarwal, S. K.; Eds.; Royal Society of Chemistry, Cambridge, UK, 10, 41–82 (1993).
8. Bartholomew, C. H.: "Sintering kinetics of supported metals: new perspectives from a unifying GPLE treatment", Appl. Catal. A, 107, 1–57 (1993)
9. Bartholomew, C. H.: "Sintering kinetics of supported metals: Perspectives from a generalized power law approach". In Catalyst Deactivation 1994 (Studies in Surface Science and Catalysis); Delmon, B.; Froment, G.F.; Eds.; Elsevier, Amsterdam, The Netherlands, 88, 1–18 (1994).
10. Clark, P. D.; Dowling, N. I.; Huang, M.; Kijlstra, S. W.: "How do Claus catalysts really work?", Laurance Reid Gas Conditioning Conference, Norman, OK, February (2002).
11. Bartholomew, C. H.: "Sintering and redispersion of supported metals: Perspectives from the literature of the past decade". In Catalyst Deactivation 1997 (Studies in Surface Science and Catalysis); Bartholomew, C. H.; Fuentes, G. A.; Eds.; Elsevier, Amsterdam, The Netherlands, 111, 585–592 (1997).
12. Baker, R. T.; Bartholomew, C. H.; Dadyburjor, D. B.: "Sintering and redispersion: mechanisms and kinetics". In stability of supported catalysts: Sintering and redispersion; Horsley, J. A.; Ed.; Catalytica: Mountain View, CA, USA; pp. 169–225 (1991).

Monitoring for refractory failure in Claus reactors

The possible failure of refractory in a Claus unit is a concern to both licensors and operators of Claus units. **Bob Poteet** of WIKA discusses a novel and easy way to monitor the shell temperature of the Claus thermal reactor using proven technology and highlights the benefits a purge-less thermocouple system for high temperature measurement.

For many operators of sulphur recovery units (SRUs), the detection of refractory problems in the Claus thermal reactor is a concern. If the refractory starts to fail, then you can find yourself in a position where the hot gases hit the carbon steel shell and damage or lead to failure of the wall of the reactor. Many ways to detect this have been tried but all have had limitations. Some have tried thermal imaging, but then the problem with rain shields, cowlings and insulation can be a real barrier.

The problem

The industry standard has been to attach thermocouples, but nobody knows how many to put on. The question is big enough that many don't even put any on at all. The thermocouple can indicate the temperature at a specific point, but temperature excursions in other areas will go undetected. If you cover the reactor with thermocouples, then the cost spirals up. API states that an "accurate shell temperature measurement system under the shroud should be included in the ETPS design" and then recommends routine thermal imaging of the external shell to spot check the thermocouples. This can be a maintenance headache if followed as it is intended.

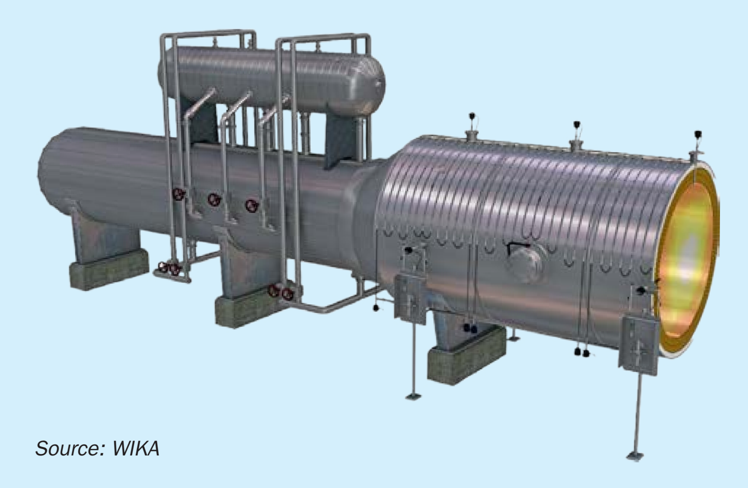
The solution

No real answer is clearly defined, but the problem really is. WIKA has acquired a very special technology where it can provide much better detection of hot spots at a reasonable cost. The heart of the system is a special sheath that in many ways resembles a thermocouple. The big difference is that instead of sensing at the tip, the readout records the hottest point anywhere along the sheath. This technology has been successfully running, monitoring a Claus unit for over 12 years at a major refinery in Italy. The refractory detection system (RDS) is run along the outside of the Claus thermal reactor along seams in the refractory (Fig. 1). This provides the best chance of seeing the temperature rising as this would be the likeliest place of failure.

The readings

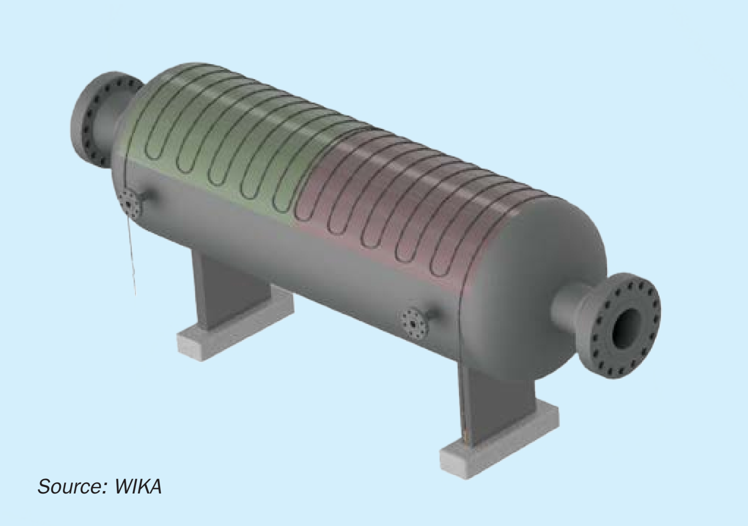
The system is installed on a Claus reactor by first dividing it into zones that will be monitored by the detection system. There can be anywhere from one to six zones in most Claus units (Fig. 2 shows a reactor with two zones). It all depends on the licensor or operator and what makes them comfortable. The readout from each zone will be like a type K thermocouple, but it is only the hottest area in a zone. It won't

Fig 1: **The top third of the reactor is monitored where failure is most likely**



Source: WIKA

Fig 2: **The unit is divided into zones**



Source: WIKA

pinpoint where in the zone the hotspot is, but you will know that there is one and then appropriate actions can take place.

Limitations

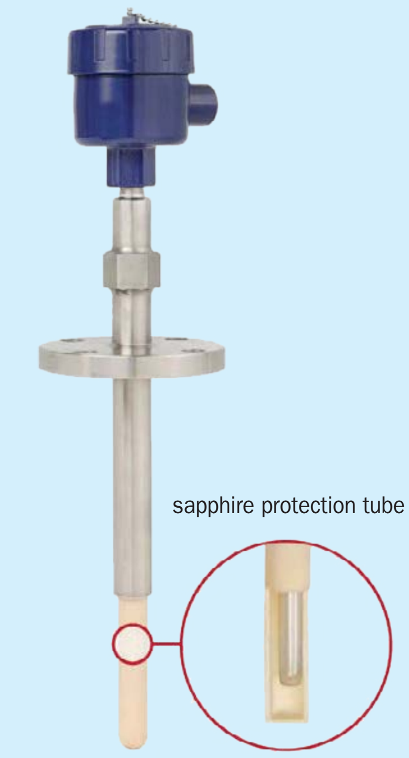
A couple of points should be noted:

- This is not a thermocouple. Modern transmitters have self-diagnostics built in and the readings below 120°C are not reliable. WIKA can prove the system is working at installation, but the unit will have to be started without a stable reading. WIKA can offer older transmitters that read to below 0°C, but careful consideration would need to be made in the evaluation process.
- Above 400°C, the readings again will lose their reliability, but they have done their job. No damage to the system will occur until getting to 900°C.

Installation

The refractory detection system is installed by trained field crew. Nelson studs are applied to the reactor and the system is held down by galvanised steel channels that are attached to the Nelson studs. This system will ensure that good contact is made between the RDS and the shell of the reactor. A six-zone unit, on a larger Claus reactor, took a three-man crew five to six days to completely install.

Fig 3: **Calitum with sapphire**



Source: WIKA

Customer feedback

The Italian refiner that has had this system for the last 12 years agreed to answer a few of WIKA's questions. During this session he reported that he knew of no other system that could give him the coverage and protection that he was looking for. He really liked the reliability of the system. He had four zones and he lost a couple of zones over the years because of contractors cutting it, but it has still been very reliable. WIKA enquired if the system had ever alarmed over the 12 years and he reported that it had twice. In neither case did the hotspot get to the point that he had to shut down, but during the next routine maintenance they were able to see that in the zones where the alarm occurred, they did indeed have some refractory problems.

Temperature measurement of the Claus thermal reactor

Temperature measurement inside the Claus thermal reactor is something that is not well understood by many instrument engineers.

Most units operate with a pyrometer and two thermocouples. Several myths that many refineries follow are:

- The temperature from the thermocouple is only for the start-up process, it is sacrificial. The problem is that the process engineers then come back asking if the pyrometers are reading correctly. One major analyser representative reported that it was common that they know from the analysers the temperature is off and the refinery can only report that this is what they see.
- The purge is only for safety reasons, it is to make sure that if the ceramic breaks there is no risk of leaks. The purge is there for a totally different reason!

Why purge?

The operating range of a Claus thermal reactor is typically 1,300°C or higher. A type K thermocouple that is typically used in plants can't operate at this elevated temperature, so Type S, R or B thermocouples are used. These are expensive platinum and rhodium thermocouples that work well at these temperatures but are very susceptible to hydrogen migration. As illustrated, the purpose of the purge is to take the hydrogen away.

Capex and opex of a purge

In a new project, purging is not something that comes without cost. Engineering is required to get the purge to the thermocouple, lines need to be installed, and then there is the cost of a purge panel. All these costs really do add up.

From an opex point of view, the purge is a maintenance problem. If the purge is too high, then the thermocouple will read low. If the purge is too low, then you lose the thermocouple prematurely. API states that daily inspection of the purge should be performed.

Some history

In 2015, WIKA acquired a technology that is used in gasifiers globally. Some of the patents go back to the early 2000s. Like a Claus unit, the gasifier is a high hydrogen and high temperature unit, but it is also high pressure unlike a Claus unit. This technology was applied to several Claus reactors, and one is known to be running successfully for ten years and another was replaced after nine years. In 2020, a redesign was done to optimise this technology for the Claus application.

How it works

The heart of the system is a mono crystal sapphire. This is a sapphire that is grown, so it has no real crystalline structure. This allows it to slow down hydrogen migration. The same technology of the sapphire and the acquired understanding of how to seal it were used in the new Calitum (Fig. 3).

The Calitum

The Calitum is designed to give secondary containment which is pressure tested at 100 bar to ensure that no leakage from the process can occur if the primary containment or ceramic is broken. One benefit is that even if the ceramic is lost due to refractory movement, the unit will continue to read unless the nanocrystal sapphire is lost.

The Calitum can easily replace existing purged units and the life and reliability of Calitum can also bring profit to those currently operating without a purge. ■

A novel combustion solution

A new burner design for the combustion of natural gas with either combustion air or pure oxygen as the oxidiser has been developed by CS Combustion Solutions. The new Oxijet®-Burner has been designed to perform both start-up and main operation functions with one burner. The key objectives, challenges, and burner design considerations are discussed.

The background to the development of the new Oxijet®-Burner started with a request for the supply of natural gas burners for a new greenfield spent acid regeneration plant for both the start-up process and the main operation. However, the main operation of this plant was to be designed as a pure oxygen firing case to increase the efficiency of the combustion process.

Initially, one start-up air burner and two main oxygen burners were requested. However, this setup would lead to complications during the main operation due to the start-up burner not being in operation in the hot chamber (damage to the burner). Also, cooling the burner with air or removing it after the start-up process was not ideal, due to the loss of efficiency of the overall process and the potential danger to personnel working close to the hot chamber and sealing of the big opening after burner removal.

Challenges

The main challenges were:

- Dry-out and start-up process:
  - ❍ maximum required heat input 11 MW;
  - ❍ cannot be done with natural gas and oxygen as oxidiser due to wet flue gas;
  - ❍ needs to be done with combustion air as oxidiser for proper dry-out.
- Main operation:
  - ❍ maximum required heat input for main operation 32.8 MW;
  - ❍ to be done with oxygen as oxidiser to maximise efficiency.
- Required space on front wall of chamber for burners to be minimised (number of burners and placement).
- Find a feasible solution with a dedicated start-up burner and two main burners or cover both operation cases with one or multiple burners.
- Ensure a feasible turn-down ratio for both operation cases, with at least 1:10 for the main operation case.

Aims

After brainstorming about the issues with a dedicated start-up burner, which would not be in operation during the main operation, CS discarded the idea, regarding it as not sensible for a new plant. The goal was therefore to design a burner system, which would be capable of operating with both combustion air and/or oxygen as the oxidiser for the combustion of natural gas.

A new burner design

In order to find the best solution, different burner designs were analysed and the operating conditions were reviewed.

The typical design of oxygen burners and air burners offered on the burner market are inherently different. Oxygen burners are typically jet-type burners with high nozzle velocities to induce the recirculation of flue gas back to the flame. Air burners are usually bigger and operate with lower nozzle velocities and often with swirl bodies to ensure good mixing of fuel and oxidiser. Operating an air burner with oxygen would not be sensible as oxygen reacts very fast with the fuel and would lead to unstable flame conditions and likely damage the burner. On the other hand, a jet-type burner operated with combustion air instead of oxygen would not be feasible due to flame instability and eventual blow out of the flame. However, finding a way to stabilise the flame would provide a viable design approach.

Designing the burner with only one fuel stage for both the start-up and the main operation case would lead to a poor turn-down ratio during the start-up case, but splitting the load and designing the burner with multiple stages would help to support a higher turn down ratio for both operating scenarios.

Lastly, deciding between one big central burner or multiple smaller burners was concluded by reviewing that jet-type burners have slim long flames, and it therefore makes most sense to spread out the heat load via two burners. In this way, proper heat distribution in the chamber can be ensured, while simultaneously minimising the required space on the chamber head.

CFD analysis of the burner design

Multiple CFD analyses were done to verify the dual-fuel stage design of the two burners. The images in Figs 1 and 2 show the temperature and SO_2 distribution of the burner design at different sections of the chamber.

Close to the burners is the hottest part of the chamber with good recirculation of flue gas back to the burner flames. Secondary oxygen and spent acid are injected in the first part of this chamber from the top and sides, respectively. At the end of the chamber the temperature distribution is almost completely homogenous at around 1,100 °C.

The results

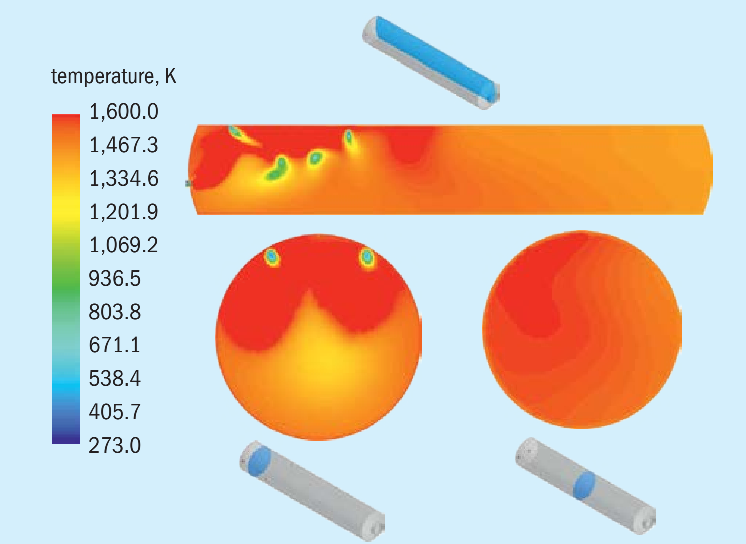
As a result of the burner design review and CFD analyses a completely new burner design was developed for combustion of natural gas with either combustion air or pure oxygen as oxidiser.

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 53 54 55 56 57 58 59 60

New Oxijet®-Burner

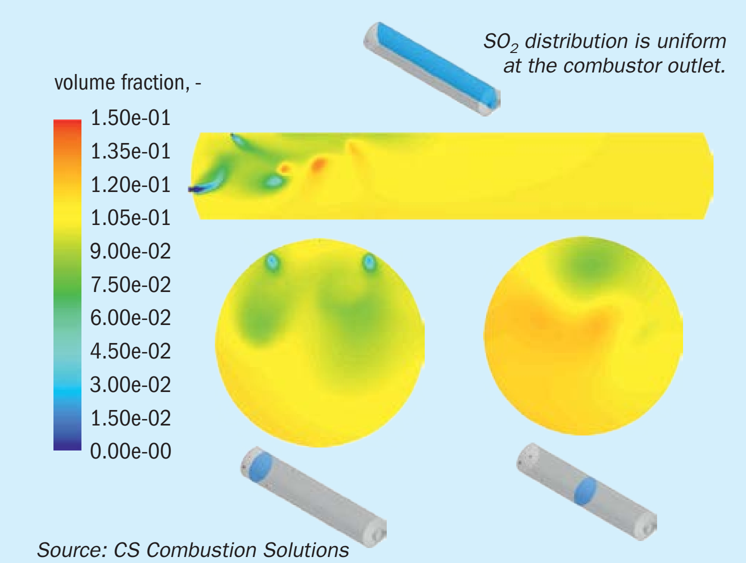
PHOTO: CS COMBUSTION SOLUTIONS

Fig 1: **CFD analysis showing temperature distribution in different sections of the burner chamber**



Source: CS Combustion Solutions

Fig 2: **CFD analysis showing SO_2 distribution in different sections of the burner chamber**



SO_2 distribution is uniform at the combustor outlet.

Source: CS Combustion Solutions

The burner can also be operated with enriched air, making it a viable solution for existing plants to reduce operating costs or increasing production capacity. Removal of the burner after start-up procedure is not necessary. The burner has a simple and low maintenance procedure with an exchangeable lance design. Flame monitoring is performed via three UV and IR flame scanners installed on the burner. ■

Advertisers' Index

Advertiser	Page	Website
Argus Media	51	argusmedia.com
BCInsight	IBC	bcinsight.com/sulphur
BCInsight	37	bcinsight.com/sulphur
Chemetics	IFC	worley.com
CRU Sulphur+Sulphuric Acid Conference 2023	29	sulphurconference.com
EVONIK Corp	53	evonik.com
Global Environmental & Industrial Response	23	globalenviroteam.com
Howden	9	howden.cloud/SID
HUGO PETERSEN GmbH	OBC	hugo-petersen.de
IPCO	15	ipco.com/sulphur
OPTIMIZED GAS TREATING, INC	49	ogtrt.com/
Paqell B.V.	17	paqell.com
Prayon SA	19	technologies.prayon.com
SAVINO BARBERA SRL	57	savinobarbera.com
Sharplex Filters	47	sharplexfilters.com
SulGas 2024 Conference	33	sulgasconference.com
Sulphur Recovery Engineering (SRE)	43	sulfurrecovery.com
Topsoe A/S	5	topsoe.com
Weir Minerals	27	global.weir

Next issue: November/December 2023

Distribution: SulGas 2024 Conference

- **Sulphur forming project listing**
- **Is sulphuric acid facing oversupply?**
- **The future of phosphate production**
- **Sulphuric acid plant operation and maintenance**
- **Sulphur plant revamps to meet future challenges**

Closing date for advertisement space booking is 23 October 2023
For further information and to book advertisement space contact:
Marlene Vaz, Advertisement Manager
Email: marlene.vaz@bcinsight.com Tel: +44 (0)20 7793 2569

Editor: RICHARD HANDS
richard.hands@bcinsight.com

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

Contributors: MARIA MOSQUERA
maria.mosquera@argusmedia.com
LILIANA MINTON
liliana.minton@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
marlene.vaz@bcinsight.com
Cheques payable to BCInsight Ltd

Advertising enquiries:
MARLENE VAZ
marlene.vaz@bcinsight.com
Tel: +44 (0)20 7793 2569

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:
TIM STEPHENS,
DANI HART

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

Published by: BCInsight Ltd
China Works, Unit 460,
100 Black Prince Road,
London SE1 7SJ, UK
Tel: +44 (0)20 7793 2567
Web: www.bcinsight.com
www.bcinsightsearch.com


HUGO PETERSEN
Verfahrenstechnischer Anlagenbau
WE STAND
FOR LIFECYCLE