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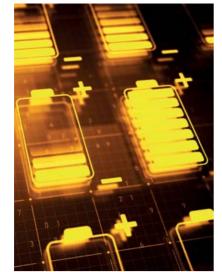
42

44

43

45

46



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Base metals

A pivot from China



Carbon free energy

Different forms of energy export from acid plants

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CONTENTS

Advances in sulphur battery technology

Lithium sulphur batteries have many advantages over conventional lithium ion batteries in terms of energy density, and they also avoid the use of costly cobalt, but they deteriorate rapidly and cannot be recharged as frequently. However, recent advances in Li-S batteries could overcome this problem and lead to widespread adoption.

20 Metals markets after China's slowdown

China has been the major market for base metals, including copper, nickel, lead and zinc over the past two decades as the country rapidly industrialised. But with China's growth slowing due to demographics and market saturation, where are metals markets and production of/demand for sulphuric acid likely to go next?

24 **Controlling SO₂ emissions**

Most processes involving sulphur, from smelting to refining, produce sulphur dioxide as a by-product. Regulations continue to tighten on industrial SO_2 emissions worldwide, leading to greater recovery of sulphur and sulphuric acid at these sites.

26 SulGas Mumbai 2023

SulGas 2023 took place as a live event 1-3 February 2023, providing participants with a platform to interact with experts in the field, share best practices and troubleshooting tips with fellow refiners, and discuss advanced technologies and operating procedures with technology providers, vendors and licensors.

28 A better understanding of SRU ammonia salt formation

Sulphur Experts Inc. combines new learnings, historical data, and recent onsite experience from operating companies to show what factors really impact ammonia plugging risk and what can be done to control it in order to allow for a wider operating range for SWS processing in the refinery SRU.

Sulphuric acid plants as a source of carbon free energy export

The sulphuric acid process is virtually carbon free and, as such, it is important to consider the energy requirements of the associated industrial complex before deciding upon what form the energy should be exported from the acid plant. Metso Outotec uses case studies to exemplify the need to fully analyse the local conditions at site before a decision is taken on a specific flowsheet.

39 Improving the performance of the SRU thermal incinerator

Blasch Precision Ceramics reports on the deployment of VectorWalls[™] to improve the performance of the SRU thermal incinerator and provide benefits such as lower fuel gas consumption and lower CO₂ emissions.

Sneaky SO₂ breakthroughs

SO₂ breakthroughs remain an ever-present threat to the successful operation of reductive, quench amine-based tail gas clean-up units. Optimized Gas Treating presents a case study which demonstrates how SulphurPro's detailed reactionkinetics and mass-transfer-rate model can be used to analyse intervention techniques and mitigation methods.

Life cycle of a sulphur melting plant

Sulphurnet discusses the importance of a whole life cycle cost analysis at the conceptual design phase when making investment decisions about new sulphur processing facilities.

REGULARS

- **Editorial**
- **Price Trends**
- **Market Outlook**
- 10 **Sulphur Industry News**
- 12 **Sulphuric Acid News**
- 17 People/Calendar



3 49

50

51

6 52

7

8

9 10

11 12

13 14

15 16

17

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19 20

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23 24

26

27

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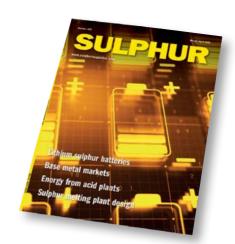
43

44 45

46

Editorial

Trouble in bulk



A sudden decline of the BDI can indicate a recession."

s it is an involuntary product, sulphur tends to be sold at whatever price the producer can get for it. This means that one of the major determinants of the sulphur price is the cost of transporting it to the customer, and in this regard one of the key indices is the Baltic Dry Index (BDI), which measures the cost of shipping dry bulk goods around the world, reported daily by the Baltic Exchange in London. The BDI has been on quite an excursion over the past couple of years - perhaps not as wild as the period from 2004-2009 when everyone wanted to ship goods to and from China, there was a shortage of vessels to carry it, and oil prices were at record highs - but eye-catching nevertheless.

In recent years the BDI has generally tended to remain low, reflecting a hangover of excess capacity in the shipping industry dating from before the 2008-09 economic crisis. Covid of course had a massive impact in 2020, first a huge decline in shipping rates because of a drop in demand, and then, by the second half of 2021, a surge, as lockdowns eased and there was pressure to return shipping capacity to the market. The BDI peaked at over 5,000 in September 2021, and although it fell back as the tight shipping market eased, two things have conspired to cause another spike in the BDI in 2022; firstly the IMO's sulphur regulations, effective from 2020, which restricted shipping fuels to less than 0.5% sulphur content globally (and <0.1% in Emissions Control Areas), and then of course the Ukraine war. The IMO regulations had already led to a premium on very low sulphur fuel oil (VLSFO), and Russia was a major supplier of VLSFO to Europe. As a result, VLSFO prices roughly doubled, from an average of \$540/t in 2021 to over \$1,000/t for much of 2022. The high fuel prices in turn led to an increase in 'slow steaming' - reducing vessel speeds to make their fuel use more efficient, which in turn lowered capacity and increased freight costs, as well as advantaging those shippers who had installed exhaust scrubbing systems instead, allowing them to take advantage of low prices for high sulphur fuel oil (HSFO).

But at the start of this year, the BDI took a turn in a different direction; dropping 60% to just 530 in February, its lowest level since the onset of covid (which was itself a historical low point for the index). The BDI is often regarded as an indicator of global economic trends, since it involves the earlier stages of global commodity chains rather than end prices to consumers. A high BDI index generally indicates tight shipping supply due to high demand, while a sudden decline of the BDI can indicate a recession, since producers have reduced demand, leaving shippers to reduce their rates in turn in an attempt to attract cargo. Since then there has been a recovery in the BDI in March to 1,500, reflecting better weather and a pickup in Chinese demand, but the outlook for the rest of the year remains uncertain. The Maritime Forecasting and Strategic Advisory (MSI) forecasts a modest 1.8% increase in shipped volumes this year, but a 1% decline in overall tonnage demand due to more efficient sailing, and a 3% increase in total fleet capacity, indicating a slack market for shipping. Weak economic conditions in North America and Europe and an uncertain year for China all add to the potential for recession.

Low freight rates are of course good news in the short term for sulphur consumers, but if the BDI is indeed signalling that we are in for rough economic times ahead then this could be a difficult year for everyone.

Mule

Richard Hands, Editor

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42

41

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44 45

46

Price Trends



MARKET INSIGHT

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

SULPHUR

Global sulphur prices softened between February and March following a small uptick as buyers entered the market. Sluggish activity in the processed phosphates market has underpinned this trend. While demand emerged in some markets, including China, buyers have had limited appetite to accept higher prices. This slowdown in purchasing has added downward pressure to major benchmarks in March. Price recovery is not expected until June, with further softening expected as second quarter contract negotiations gear up, with initial indications pointing to bearish factors underlying price direction in major regions.

Average monthly Middle East prices decreased by around \$3/t over the first quarter, down to \$135/t f.o.b. by mid-March, over \$270/t lower on prices a year earlier. Qatar's state-controlled Muntajat set its March Oatar sulphur price at \$33/t f.o.b. Ras Laffan/Mesaieed, up by \$9/t from the February QSP of \$124/t f.o.b. The March QSP level implies delivered pricing to China of \$155-161/t c.fr at freight rates, which estimated at \$22-24/t to south China and at \$26-28/t to Chinese river ports for a shipment of 30,000-35,000t. Kuwait's KPC set its March Kuwait sulphur price (KSP) at \$136/t f.o.b. Kuwait, reflecting an increase of \$12/t on the February price. Meanwhile Abu Dhabi's state owned

ADNOC set its March official sulphur price (OSP) for liftings to India at \$134/t f.o.b. Ruwais, up by \$7/t from the February price.

In supply news, KPC loaded the first sulphur export shipment of 40,000t from its new Al-Zour refinery in March. Going forward, sulphur is likely to be offered under spot tenders, but as operations increase and supply becomes more predictable fixed contract arrangements are likely. Higher output from the refiner is expected to increase Kuwait's sulphur exports alongside the recent ramp up of its Clean Fuels Project. Total sulphur capacity in Kuwait is expected to reach 2.8 million t/a in the medium term because of the new refining projects.

Indonesian nickel producers led the recent upward price momentum but now appear to be well covered for the short term. Buyers re-entered the market in early March to secure around 30,000t of sulphur for delivery in the April-May period. Prices ranged between \$163-167/t c.fr, levels not expected to be achieved again until late in the second quarter. The short term sulphur requirement for nickel high pressure acid leaching projects is a key driver for trade in 2023-2024 as new burner capacity is brought online. Indonesian sulphur imports totalled 2 million t/a in 2022 for the first time, a significant rise on just over 1 million t/a imported a year earlier.

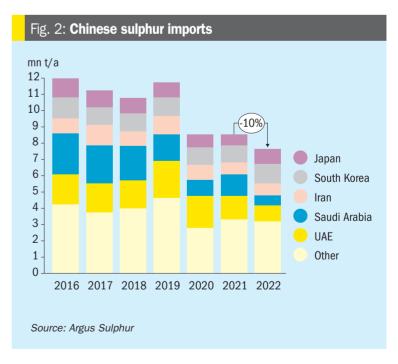
The drive for battery materials to meet growing demand in the electric vehicle sector

is a key focus for the sulphur and sulphuric acid markets. Outside of Indonesia, further developments are expected to impact the longer term view for sulphur consumption. Canada-based mining firm Lithium America has started construction at its Thacker Pass lithium project. First lithium carbonate production is targeted to start in the first half of 2026

Russian sulphur has continued to trade at a discount to other exporting regions and is moving to markets such as Egypt and Turkey, a trend Argus expects will continue in the short term. Market potential for Russian tonnes remains limited owing to the ongoing conflict in Ukraine and associated financial and economic sanctions. Constrained Russian exports are not expected to have significant impact on the market however as capacity is growing in the Middle East and Asia, offsetting this loss. We assume there is considerable stock build going on in Russia as production levels grew in 2022 on 2021 levels while exports were estimated at around 1 million t/a for the year.

Demand from Moroccan processed phosphates producer OCP was largely muted through the first quarter of the year. Argus data shows sulphur arrivals will be lower than a year earlier. An increase in Moroccan demand is expected this year compared with 2022 following demand destruction in the phosphate fertilizer market. There is a risk to the potential for this rebound because of continued downward pressure on DAP prices. Sulphur import demand in Morocco is expected to increase from the second quarter onwards to meet expected levels of phosphoric acid production.





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Sulphur 405 | March-April 2023

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Over in China, spot market activity is expected to be limited throughout April as rising domestic supply limits the need for short term requirements from international suppliers. Port inventories as of 10 March were at 1.6 million tonnes. Further price softening may encourage buyers to the market, but demand will likely hinge on the widely anticipated lifting of export restrictions on processed phosphates exports. The subsequent expected downturn in Chinese DAP prices will limit price potential for sulphur. The recent erosion of sulphuric acid export prices to negative values in parts of northeast Asia may temporarily slow acid exports from China, with the potential to supply domestic buyers. This would further pressurise sulphur import demand and pricing potential.

SULPHURIC ACID

Global sulphuric acid prices have softened so far in 2023 because of ample supply in the market, as many regional buyers moved to the sidelines of the spot market. Asian fob prices dropped into negative territory, at \$-10/t f.o.b. on the low end on 9 March. according to Argus assessments. There is potential for further price erosion in the short term before a floor is reached. Global acid demand will see a strong rebound this year, providing support for a recovery in pricing from the second quarter onwards. Phosphoric acid-based demand will see a boost this year following demand destruction in 2022.

Average prices out of Northwest Europe decreased by \$25/t between January and March, assessed by Argus at \$9/t f.o.b. at the midpoint. Supply is a key focus in the region with smelter operating rates expected to be higher this year. The Ecobat lead smelter in Stolberg, Germany, was due to resume operations in March.

In supply news, Chile's senate has passed a law allowing state copper miner Codelco to close its aging Ventanas smelter in the Valparaiso region. The law passed on 7 March enables national mining company Enami, which supports small- and medium-sized miners, to process copper concentrates at other smelters run by Codelco. Within 90 days of the law's publication, the mining ministry will have to present a report to congress containing proposals to increase Chile's state copper smelting capacity. Codelco's board announced on 7 June 2022 it would advance closure of the smelter, which has capacity to treat approximately 400,000 t/a of concentrates, rather than invest to improve its environmental performance. Acid capacity at the smelter is estimated at 650,000 t/a.

Spot demand in Chile was muted in March with ample supply. Some acid tanks were reported to be at capacity and price ideas in mid-March were \$100/t c.fr, down around \$27/t on average prices in January. The Ventanas port in Chile started resuming operations from the second half of February after a major fire on 22 December, with copper concentrate exports from the world's largest copper producer gradually increasing, according to market participants. Blockades at a key mining highway

in the world's second-largest copper producer Peru were temporarily lifted. The highway is a key transport route for Swiss resources firm Glencore's Antapaccay and Chinese firm MMG's Las Bambas mines. It has been blocked by protests against newly-elected Peruvian president Dina Boluarte since January.

Demand from Latin American buyers should emerge for the second quarter, with lower pricing expected to encourage buyers to the spot market. The continued downturn in processed phosphates pricing will likely put a ceiling for acid. Average acid prices in the Brazilian spot market were assessed at \$112/t c.fr in mid-March, down by \$27/t on the start of the year. Acid imports to the country are expected to be stable in 2023 on last year at around 850,000t.

Global acid demand growth in 2023 and 2024 combined is expected to boost consumption by over 18 million t/a. Phosphoric acid is expected to lead demand growth in 2023, adding over 4 million t/a on 2022 levels. This marks a recovery following demand erosion in the sector last year. Meanwhile, demand from the metals sectors is expected to add about 1.6 million t/a in 2023 from 2022 levels. On the supply side we expect capacity across all sources to total over just over 13 million t/a between 2022 and 2023. Smelterbased capacity is expected to see a boost at 2 million t/a. China remains the main driver of smelter capacity additions in the short term but project developments in India and Indonesia will also impact the balance going forward.

Price Indications

Cash equivalent	October	November	December	January	February
Sulphur, bulk (\$/t)					
Adnoc monthly contract	103	139	180	160	134
China c.fr spot	165	179	195	170	158
Liquid sulphur (\$/t)					
Tampa f.o.b. contract	90	90	90	125	125
NW Europe c.fr	123	123	123	123	13:
Sulphuric acid (\$/t)					
US Gulf spot	150	150	150	135	9:

Sulphur 405 | March-April 2023

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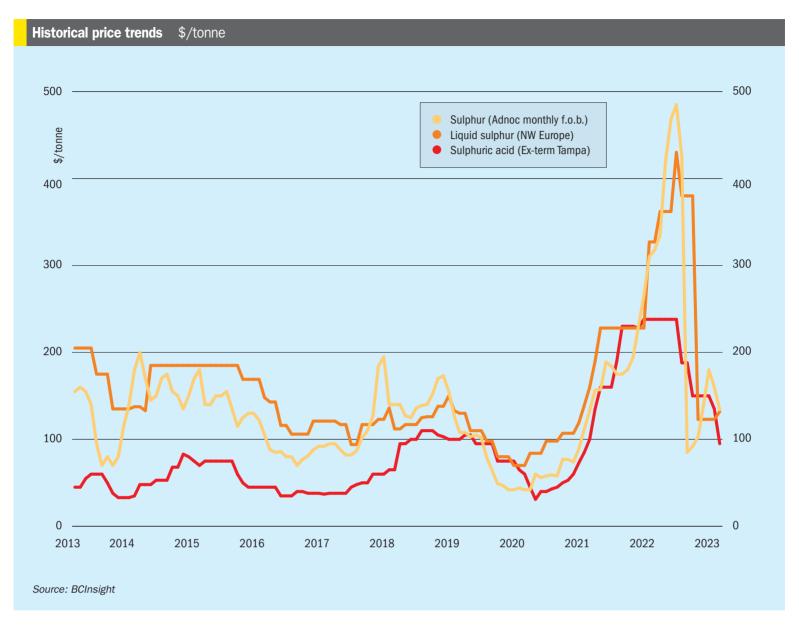
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Market Outlook



SULPHUR

- Chinese domestic sulphur supply growth remains strong. Production is expected to rise in 2023, putting pressure on import demand potential. In 2022 total imports were 7.6 million tonnes, with a stable view for the year ahead.
- In the processed phosphates market, the consensus view is that exports from China will begin to normalise in April-May with restrictions eased and the domestic season ended, but there has been no official confirmation of this. The expected increase in Chinese supply and concern over the pricing of DAP is a bearish factor for the market.
- New sulphur supply is expected online in Oman with commissioning and testing of the Duqm refinery under way, ahead of the start of commercial operations at the end of the year. Sulphur capacity is expected to ramp up between 2024-25. The Middle East region will add over 1.6 million t/a of new capacity this year,

- leading to an uptick in export availability.
- Sulphur supply from Canada to offshore markets is expected to be supported by additional forming capacity with the expected start-up of the South Cheecham project in Alberta later this year.
- Outlook: Prices are expected to continue to soften in the short term with limited spot demand emerging while second quarter contract negotiations are underway. The global market is expected to be broadly balanced later in the second quarter, with the potential for sulphur prices to recover in June if demand rises as expected.

SULPHURIC ACID

 High energy costs continue to impact some downstream sectors for acid.
 BASF has announced the permanent closure of its caprolactam plant and associated fertilizer facilities at its Ludwigshafen site in Germany. Energy costs added an additional pressure on margins and competitiveness.

- Indonesian nickel high pressure acid leach operations have been active in the acid spot market, a trend expected to continue for the short term. Halmahera Persada Lygend booked four cargoes for mid-late April shipment. Tsingshan also booked volumes for April-May delivery.
- Base metals prices declined in March with huge uncertainty in financial markets caused by the failure of two US banks spooking investors. Efforts towards stabilization allayed anxiety slowing price drops on 16 March.
- Outlook: The price downturn is expected to turn to stability by the second quarter with incremental recovery expected. With sulphur prices stable to soft in the short term, this may encourage buyers to the acid market during this period. The rate and pace of Chinese smelter acid capacity additions will be a key influence for the short term outlook as well as the return of China to the processed phosphate export market.

Sulphur 405 | March-April 2023



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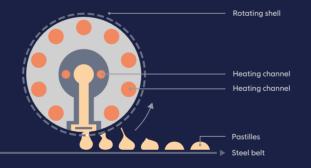


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46

Sulphur Industry News

UNITED KINGDOM

CRU to enter formal partnership with UniverSUL consulting

CRU, a leader in sulphur industry market analysis, price assessments, consultancy and events, and Abu Dhabi-based UniverSUL Consulting LLC, dedicated to providing unbiased technical expertise in sour hydrocarbon production and sulphur recovery, have announced a formal partnership aimed at enhancing the value of industry events for the sulphur industry.

Both companies have long histories in the sulphur industry and together recognise the importance of more meaningfully uniting the sulphur community in today's changing times, as the energy transition reduces sulphur supply while population growth continues to drive demand for this vital resource. These phenomena, and other future developments, will necessitate new discussions around the changing global supply/demand balance and corresponding continued requirements for effective knowledge-sharing, lessons learned capture, and discussions/ debates around best operating practices and innovative technological developments.

In this partnership, CRU will continue to deliver market-leading events, such as the Sulphur + Sulphuric Acid Conference, the world's longest running sulphur conference, which takes place annually and alternates between North America and Europe, while UniverSUL's Angie Slavens will serve in a technical principal role, responsible for developing conference technical themes

and for facilitating the growth/nurture of the technical community, based on the most relevant industry conversations of the time. The two companies will continue collaborating on their joint venture event, the Middle East Sulphur Conference (MEScon), established in 2022 in the Middle East, the new world focal point for sulphur supply, which will be further strengthened by their broader cooperation.

"The pairing of CRU's deep commercial knowledge, event production expertise and industry connections with UniverSUL's technical industry knowledge and relationships, across all of CRU's sulphur events, creates a powerful partnership which will enhance the value of sulphur gatherings for participants around the world," said Nicola Coslett, CEO Events, CRU.

"After working with CRU in an informal capacity for 20 years, I am excited to formalise this partnership, which is intended to provide greater value for contributors along the entire sulphur value chain. CRU has long-provided events highlighting the importance of sulphur and connecting key industry contributors; together, UniverSUL and CRU hope to create an environment that is even more conducive to initiating networking opportunities, providing big-picture perspectives, and encouraging community stewardship, for the betterment of the sulphur industry, for years to come" said Angie Slavens, Managing Director, UniverSUL Consulting LLC.

SOUTH AFRICA

Joint venture for sustainable aviation fuel

Topsoe has signed a memorandum of understanding (MoU) with Sasol to establish a joint venture that will produce sustainable aviation fuel (SAF). The venture will develop, build, own, and operate ventures producing SAF based on Sasol's Fischer-Tropsch technology and Topsoe's SAF technologies. Topsoe says that it is also part of its ongoing commitment to help achieve net-zero emissions and accelerate the decarbonisation of hard-to-abate sectors.

At this early stage, the companies say that they have not explored details such as which feedstock to use, precise timeline or production capacity. The next step will be to work towards establishing the company, including business plan development, setting up the JV structure and organisation, and finalising the JV agreement.

Roeland Baan, Chief Executive Officer at Topsoe, said: "We are very excited to announce this MoU, as it underlines our ambition to help decarbonise some of the most critical sectors in the world. If we are to reach net zero on a global scale by

2050 in order to fight climate change, all solutions need to be put into play. Creating a low carbon aviation sector is an important piece of the puzzle, and we're excited to extend our partnership with Sasol to help speed up decarbonisation. Combined. we have the technologies, capabilities and willingness to take the lead."

KUWAIT

Al Zour to ramp up oil product exports in 2023

Kuwait is set to ramp up refined oil product exports from its new Al Zour refinery in the second half of 2023 to ease shortfalls in Europe resulting from the embargo on Russian products, as well as to serve new demand in Asia and Africa. The 615,000 bbl/d refinery has been much delayed but started up its first 205,000 bbl/d crude distillation unit in September 2022, and is now expected to start up the remaining two CDUs in March/April 2023 and August 2023 respectively in order to reach full capacity.

Kuwait's exports of refined products reached an all-time high of 17 million barrels in January, up 30% year on year, as Al Zour shipped more fuel oil to the Singapore Strait, diesel and jet fuel to Europe, and naphtha to China, South Korea and Japan. Annual diesel exports could reach up to 7 million tonnes (143,000 bbl/d) from Al Zour, and jet fuel 4.5 million t/a (97,000 bbl/d) once the refinery reaches full capacity. Most of the diesel supplies will be directed towards Europe, which has a shortfall of around 3 million tonnes per month (745,000 bbl/d) of Russian diesel after the EU embargo.

KAZAKHSTAN

Gas processing plant to start-up in 2025

Work has recommenced on a new 1 billion cubic metre per year gas processing plant in the Atyrau region, 12 km northeast of the existing onshore Bolashak oil and gas treatment complex, to accommodate associated gas production from giant offshore Kashagan oil field. The plant was originally backed by private company GPC Investment LLC, and work began in September 2021, but it has now been transferred to the responsibility of state-owned OazagGaz. formerly KazTransGas. QazaqGaz then conducted financial, technical, and legal audits that revealed critical engineering errors

Sulphur 405 | March-April 2023

10 www.sulphurmagazine.com

47

7 8

9

12 13

14 15

16

17 18

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21 22

23 24

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46

in the design of the project, pushing the expected completion date back to 2025.

Once complete, it will have the capacity to process 1 bcm/year of associated sour gas from the Kashagan field to produce 815 million m³/year of commercial gas, 119,000 t/a of LPG, 35,000 t/a of condensate, and 210,000 t/a of sulphur. It will allow oil production from Kashagan field to increase by 450,000 bbl/d, as associated gas production at the site to date has inhibited higher crude production rates.

QazaqGaz has agreed with Kashagan project operator the North Caspian Operating Company (NCOC) to increase gas processing capacity in three phases, of which this plant will be the first. Two further plants, each with a capacity of 2 bcm/ year of sour gas are now planned, to allow further increases in oil production. The Kazakh government says that it intends to adopt a detailed roadmap for the new gas plants in the near future.

UNITED STATES

Analyser for H₂S breakthroughs in renewable natural gas production

Renewable natural gas (RNG) is a pipeline quality gas interchangeable with conventional natural gas. Historically methane produced from locations such as landfills, livestock operations, or wastewater treatment plants was lost to the atmosphere. However, as regulators update emission rules and implement renewable fuel standards, RNG has become a rapidly growing segment of next generation renewable fuels. In fact, a study published by the National Association of Clean Water Agencies suggests that potentially 12% of electrical production in the United States could be generated from RNG sourced from wastewater treatment plants.

However, before gas generated from renewable sources is released to pipelines, it first must be upgraded to meet the pipeline specifications. This typically involves removing components such as CO₂, H₂O, and H₂S. Hydrogen sulphide is a particularly challenging component for operators to remove, but common processes like amine or selexol units are not economical given the scale for most RNG facilities. Instead, operators rely on packed columns which selectively remove H₂S using sorbents. While these systems can reduce H₂S levels from several thousand parts per million down to approximately four parts per million, they need to

Sulphur 405 | March-April 2023

be periodically changed as the sorbents become saturated.

Operators rely on process analysers to detect hydrogen sulphide breakthroughs and swap to a new column. However, most analysers on the market either lack the sensitivity to detect the hydrogen sulphide at the levels and pressures leaving the packed columns or require costly carrier gases that must be continuously replaced for the analyser to keep functioning.

To resolve this issue Applied Analytics has developed its new Zeta[™] spectrometer, to be used in conjunction with the OMA-300 process analyser. When equipped with a Zeta[™] spectrometer, the OMA-300 UV ZETA can measure low levels of H₂S found at these facilities without the need for expensive reagents that need replacing. As an added benefit this system uses a solid-state design which does not contain moving parts that can fail or would otherwise require replacement.

DENMARK

Topsoe to license waste to biofuel process

Topsoe has signed a global licensing agreement for Steeper Energy's Hydrofaction[™] technology, used for converting biomass to renewable biocrude oil, enabling Topsoe to offer a complete waste-to-fuel solution via the production of advanced biofuels produced from waste biomass such as residues from forestry and agriculture. The end-products include Sustainable Aviation Fuel (SAF), marine biofuel, and renewable diesel from waste biomass. With this agreement, the parties are working towards the first commercial scale deployment of Hydrofaction technology.

Hydrofaction uses hydrothermal liquefaction (HTL), which applies supercritical water as a reaction medium for the conversion of biomass directly into a high-energy density renewable biocrude oil. Steeper's process subjects wet biomass to heat and high pressure, with process conditions carefully chosen to promote reaction pathways that favour high yields of high-quality renewable oil. Hydrofaction can convert up to 85% of incoming biomass on an energy basis, making it one of the most effective conversion technologies available.

Peter Vang Christensen, Senior Vice President, Clean Fuels & Chemicals -Technology, Topsoe, said:

"We are excited to work with Steeper and to combine our technological capabilities. This will make it easier for refineries and project developers to access the technology they need for advanced biofuels. It will also allow them to access new renewable feedstocks while supporting decarbonisation of the transportation sector, not least aviation and shipping."

CANADA

Midstream Solutions buys KANATA



The Simonette gas plant, Alberta.

Calgary-based CSV Midstream Solutions Corp says that it has completed its acquisition of the KANATA Energy Group, including majority stakes in the Valhalla and Simonette sour gas gathering and processing plants near Grande Prairie, Alberta, in the heart of the Western Canadian Sedimentary Basin. CSV already owns three natural gas assets in the Grande Prairie region: the Resthaven Gas Processing facility 80 km northeast of Grande Cache; the South Pipestone Compressor Station and Liguids Processing Facility 40 km southwest of Grande Prairie; and the Karr Gas Plant 60 km south of Grande Prairie. A proposed sour gas processing project called Albright is also in the works by the Company and will be located northwest of Grande Prairie in the Valhalla area. The KANATA assets add over 150 million cfd day net processing capacity to CSV, for a total capacity of 470 cfd.

CSV's President. Rick Staples said: "Today's announcement reinforces the continued application of CSV's disciplined growth strategy. The Valhalla and Simonette gas plants consolidate our presence in the prolific Montney, Charlie Lake, and Spirit River plays in northwestern Alberta, allowing CSV to provide reliable midstream services to our new partners and an increasing array of producers in this active corridor."

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9

19

34

45

46

Sulphuric Acid News

AUSTRALIA

Chemetics to provide sustainable acid technology

Arafura Rare Earths Ltd has awarded Worley subsidiary Chemetics Inc the contract to install Chemetics CORE-SO2™ sulphuric acid technology at its Nolans Project in the Northern Territory of Australia. The scope of the contract is to deliver the detailed engineering and supply of the sulphuric acid plant plus associated oxygen plant on a lump sum basis. The acid plant at Arafura's Nolans Project will be designed to meet future emission performance and clean energy transition goals, utilising CORE-SO2's high turndown capability and the potential to idle the plant while keeping the catalyst warm for extended periods of time, allowing the acid plant to operate with 95% reduced SO₂ emissions when compared to traditional double contact double absorption (DCDA) plants. High pressure steam production within the process will allow CO₂free electrical power to be generated. By removing the use of a diesel or natural gas start-up burner, further greenhouse gas emissions will be prevented.

Additionally, being 60% smaller in size than traditional sulphuric acid plants, the plant will low internal gas flows and fewer pieces of equipment, enabling modularisation. This will minimise construction and assembly work for the remote mine site at the Nolans Pro-



A computer rendering of the Nolans project site.

ject, leading to increased workforce safety and improved cost-efficiency.

"With this project, we will assist in Arafura's goal to be a trusted global leader and supplier of choice for sustainably mined and processed rare earth products. With each year of plant operation, more than 700 tonnes of SO₂ will be converted to usable sulphuric acid rather than emitted into the atmosphere." Chemetics Inc., President Andrew Barr said.

"Arafura Rare Earths is very pleased to be working with Chemetics Inc as a global leader that is able provide the Nolans Project with highly efficient, robustly engineered and low emission sulphuric acid technology. This sulphuric acid plant represents a key component in achieving our sustainability goals," General Manager Projects, Stewart Watkins, said.

UNITED STATES

MECS wins two contracts for electronic grade acid production

MECS, a subsidiary of Elessent Clean Technologies, has been selected to supply propriety technology and equipment to clients in the US and Taiwan to enable production of high-purity electronic-grade acid for the global market. Governments from several countries around the world have implemented incentive programs for electronic-grade acid production. Tax credits, grants, and research and development investment are some of the ways in which acid manufacturers are being rewarded for contributing to the supply chain.

"The semiconductor industry is experiencing growth we have not seen in decades. Because of our robust history in the sulphuric acid industry, using MECS® tech-

nologies and equipment to produce high purity electronic-grade acid feedstocks provides assurances our competitors cannot replicate. We are at a critical point in high purity sulphuric acid production. With high demand around the globe, and the passage of the CHIPS Act in the United States, we are excited to help meet the needs of the expanding global marketplace and to assist the US in being more competitive within that space." said Eli Ben-Shoshan, CEO, Elessent.

Work begins at Thacker Pass lithium project

Lithium Americas Corp. has begun construction at its 100%-owned Thacker Pass lithium project in Humboldt County, Nevada, following the receipt of notice to proceed from the Bureau of Land Management. Thacker Pass is targeting 80,000 t/a of battery-quality lithium carbonate production capacity in two phases of 40,000 t/a respectively. Phase 1 production is expected to commence in the second half of 2026.

EXP Global Inc. has been awarded the contract for the engineering, procurement, construction support, commissioning and start-up services for the project's sulphuric acid plant. The plant will have a capacity of 3.000 t/d.

MECS, Inc. was awarded the contract for the technology license, engineering and equipment for their MECS® Heat Recovery System, to harness waste heat to generate steam which will subsequently be converted into carbon-free electricity for the processing plant.

"Starting construction is a momentous milestone for Thacker Pass and one we have been working towards for over a decade," said Jonathan Evans, President and CEO. "We are excited about the prospect of generating economic growth in Northern

Sulphur 405 | March-April 2023

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SULPHURIC ACID NEWS

Nevada and playing a major role in the domestic lithium supply chain for electric vehicles."

MECS says that, when combined with more traditional means of energy recovery within sulphuric acid plants, HRS™ enables a plant to utilise up to 95% of the process heat it generates internally as steam, which can be converted to electricity that is either employed to power the facility or sold to a neighbouring industrial complex or the local power grid. Through the production of both high-pressure and intermediate-pressure steam, HRS[™] technology can prevent up to the equivalent of 100 tonnes of carbon dioxide emissions over the course of a year for each t/d of acid that is produced by the plant.

The State of Nevada has become a critical supplier of lithium within the US as the nation's leaders make plans to reduce reliance on imported lithium. As the pivot away from fossil fuels becomes increasingly urgent, consumers are buying more electric vehicles (EV) to support the energy transition which requires lithium, and other raw materials like nickel and cobalt, for the production of EV batteries.

"We are thrilled to be working with Lithium Americas and EXP on this project. It is very exciting to be part of such a monumental project in the United States that has the potential to make a global impact on the battery metal supply chain. Throughout the planning process our team has been cognizant of environmental preservation, and we want Thacker Pass to be the prototype for environmental stewardship for other projects of this nature. We have worked closely with Lithium Americas to ensure maximum efficiency so they can meet industry growth needs while prioritizing carbon reduction initiatives." said Eli Ben-Shoshan, CEO, Elessent.

INDONESIA

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New smelter off-gas acid plant

Indonesian mining company PT Amman Mineral Industri (AMIN) says that it will partner with Elessent Clean Technologies for the provision of a new smelter off-gas MECS® sulphuric acid plant equipped with DynaWave wet gas scrubbing technology. The new plant will be constructed in Sumbawa, Nusa Tenggara Barat, Indonesia with anticipated start-up in 2024. Over the last few years, Indonesia has become a critical region for the battery metal marketplace. As the electric vehicle revolution sweeps the globe, consumers are procuring more vehicles to support energy transition. Battery metals are essential for the production of electric vehicles, as well as numerous other electronics, and producers are turning to Indonesian mining operations for access to materials.

"AMIN chose Elessent for their reputation in meeting environmental regulations and the high reliability of their technologies. Using MECS[®] acid plant design and its incorporated technologies, our new plant will expectedly meet site-specific environmental, cost and operational goals, as well as environmental requirements," said Mr. Anil Upadhyay, Copper Smelter Project Director, AMIN.

BRAZIL

Award for sulphur-burning acid plant

Brazilian chemical maker Unigel RI, one of Latin America's largest chemical companies and Brazil's top manufacturer of nitrogen fertilizers, has contracted with the MECS subsidiary of Elessent Clean Technologies for the construction of a new sulphur-burning acid plant to displace the import of sulphuric acid for their downstream





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46



chemical processes. The new plant will be constructed in the coastal state of Bahia. With sustainability as a core value, Unigel's new plant will also be used to generate utility steam that will provide reliable and carbon-free power throughout their industrial complex. Start-up of the plant at the Bahia, Brazil site is expected to take place in the first half of 2023.

The project also contributes to the challenges of decarbonising the production chain, since the steam produced in the plant will be carbon free, reducing greenhouse gas (GHG) emissions. This is in addition to other environmental initiatives promoted by Unigel, including Brazil's first green hydrogen plant which Unigel is pioneering.

The process design for Unigel incorporates state of the art products and technologies, such as GEAR® catalyst for ultra-low emissions and high conversion, Brink® AutoDrain[™] technology for operational efficiency, as well as UniFlo® distributors, acid coolers and acid piping.

"The design and construction of this new sulphuric acid plant, the first for Unigel and the first for Brazil in over 15 years, is an integral step to enabling more streamlined operations and positioning Unigel as a key player in the widespread distribution of sulphuric acid to consumers. Unigel operates on four major pillars: sustainability, quality, safety and reliability; and we knew we needed the market leader for this project. The MECS® technology, products and equipment used in the plant's design... will ensure our commitment to our customers while ESG practices are met." said Unigel CEO, Roberto Noronha Santos.

SAUDI ARABIA

Metso Outotec signs MoU with Ma'aden for sustainable phosphogypsum processing

Metso Outotec and thyssenkrupp Uhde have signed a memorandum of understanding with Ma'aden for developing a novel circular concept to improve the sustainability of Ma'aden's phosphate operations. The aim is to design a ground-breaking integrated complex for processing of phosphogypsum waste from phosphoric acid production, to reduce the amount of solid waste and allow the capture of CO2 emissions. The new circular process will be incorporated into Ma'aden's phosphate operations to support the company in achieving their ambitious sustainability goals aligned with the Kingdom's objectives.

"We are honoured to be part of this unique initiative. Decarbonisation and circularity are relevant for all industries, and the new concept to be developed for phosphogypsum processing will be a major step forward in the fertilizer industry, contributing to efforts limiting global warming," commented Hannes Storch, Vice President for Metals and Chemicals Processing at Metso Outotec.

Ma'aden names Phosphate 3 project partners

Ma'aden has selected Worley and JESA International S.A. (JESA) as engineering and construction contractors for the initial phase of its Phosphate 3 mega project. The company issued a preliminary agreement (notice of award) to both partners on 1st February, covering engineering, procurement, and construction management (EPCM) services for phase 1 of the project.

"The parties expect to work towards a definitive agreement for the ... EPCM contracts in the next few months," Worley said in statement.

These EPCM contracts cover the design and construction of new process plants in the industrial cities of Wa'ad Al Shamal (WAS) and Ras Al-Khair (RAK) in Saudi Arabia. Both cities will form part of an integrated production complex that is expected to produce up to 1.5 million t/a of phosphate fertilizers, once operational. Worley will provide in-Kingdom services for the project from its offices in Saudi Arabia and India. JESA, meanwhile, will provide out-of-Kingdom services, executed by its offices in Morocco.

"We are pleased that Worley has been selected for providing services to Ma'aden's Phosphate 3 development program that is expected to make Saudi Arabia one of the leading phosphate fertilizer exporters worldwide," said Chris Ashton, Worley's CEO.

FINLAND

Metso Outotec shareholders to vote on name change

The board of directors of Metso Outotec has proposed to the company's upcoming Annual General Meeting that the current name of the company is changed to Metso Corporation, on the grounds that the integration of Metso and Outotec, which became effective on July 1st, 2020, is completed, and the company's current strategy focuses on growing a strong unified company that builds on the long history and legacy of its businesses to create significant customer value.

CZECH REPUBLIC

Nuberg awarded sulphuric acid plant project

Nuberg EPC says that it has been awarded a 550 t/d sulphuric acid plant project on an EPC basis in Neratovice, Czech Republic. The project is owned by Spolana s.r.o, a leading chemical manufacturer located on the Elbe riverbank, and one of the largest chemical companies in the Czech Republic, the country's only manufacturer of PVC and caprolactam, as well as ammonium sulphate and sulphuric acid. Nuberg will be executing this project based on the latest double conversion double absorption (DCDA) technology. The plant is expected to be delivered in three years. Acid pro-

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duced by the plant will be used for petrochemical and fertilizer based applications. It will also be used in mining and processing of some ores and minerals, manufacturing batteries, and etching surfaces.

A. K. Tyagi, MD, Nuberg EPC said, "This undertaking illustrates Nuberg's competency of combining intelligence and knowledge in terms of Engineering aspects. It is a pleasure that Spolana has chosen our EPC services for this project."

Copper output falls on higher input prices

A new report by state copper commission Cochilco indicates that direct copper mining costs in Chile increased from \$0.134/lb in 3Q21 to US\$0.169/lb in 3Q22 at 19 of the 22 local operations that represent 93.9% of national production. The biggest increases related to smaller operations, with the main drivers being price rises for diesel fuel of 85%, of electricity by 10% and freight for concentrates and insurance by 36%. The sulphuric acid price increased 142% due to the Russia-Ukraine war and the consequent oil refining stoppage and operational difficulties at Chinese smelters, Cochilco said. The average price of this key material for hydrometallurgical operations was \$220-225/t last year. As a consequence, copper production fell 252,000 t/a to 3.6 million t/a. Collahuasi, controlled by Anglo American and Glencore accounted for the biggest drop, 11%, from 480,000 t/a to 428,000 t/a. Output at state copper miner Codelco's El Teniente and Chuquicamata assets fell by 7.5% and 5.1% from 342,000 t/a to 291,000 t/a and from 239,000 t/a to 200,000 t/a respectively. Antofagasta Minerals' Los Pelambres registered 4.9% lower output, down to 193,000 t/a from 259,000 t/a in 2021.

BULGARIA

Pirdop sees small fall in acid output

German copper producer Aurubis says that the cathode output of its smelter in Pirdop, 80km east of Sofia, Bulgaria, increased by 7% year on year to 58,000 tonnes in the first quarter of its fiscal year 2022/2023, which started on October 1st. Copper concentrate throughput at Pirdop decreased by 1% yearon-year to 369,000 tonnes in the October-December period of 2022, but in general the smelter recorded a strong performance similar to the previous year, Aurubis said in an interim financial statement. Sulphuric acid

output at the smelter amounted to 367,000 tonnes in the review period, also down 1% on the prior-year first quarter.

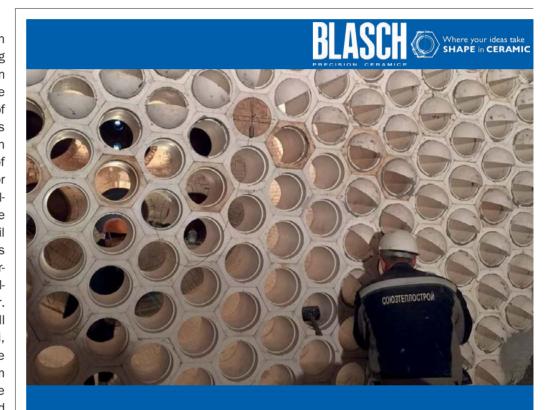
SERBIA

Restart for Zijin Bor Copper after smelter overhaul

Zijin Bor Copper, the Serbian unit of China's Zijin Mining Group, has restarted its flash smelting furnace following a \$340 million overhaul of its production facility in Bor, according to the Serbian energy ministry. The reconstructed smelter will use

clean natural gas instead of fuel oil, coal and other highly polluting fuels, and the concentration of powdery substances will not exceed five milligrams per cubic metre, bringing the smelter in line with EU environment protection standards.

"When the smelter starts working, we will produce 180-200,000 t/a of cathode copper of high purity, about three tonnes of gold and 700,000 t/a of sulphuric acid. The value of annual output will be more than \$2 billion," the ministry quoted CEO of Zijin Serbia, Djin Siming, as saying in a press release.



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Sulphur 405 | March-April 2023

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50

4

13

25

22

32

30

OBITUARY

Bo Levander, founder of ChemTrans, passed away on 5th February 2023. He worked in the sulphuric acid industry all his life, beginning in the late 1960s at Boliden in Stockholm. In 1971 he moved to Switzerland, where he was responsible for the Boliden office in Zug. Ten years later, in 1981, he left Boliden and struck out on his own, founding ChemTrans AG, also based in Zug. Two years later, the company sold its first parcel of sulphuric acid; 85,000 tonnes from Spain to Tunisia, and in 1987 it purchased its first ship, the 8,700 dwt MT CT Star. By 2005, the company had grown to be one of the largest shippers and traders of sulphuric acid, with 600,000 tonnes of acid shipped and a turnover of 73 million Swiss francs.

Bo is survived by his son Henrik, who has been CEO of ChemTrans since 1995. Henrik adds: "Bo was a very respected and esteemed person in the sulphuric acid world, and a light for all of us at ChemTrans. We will continue shining his light by carrying it within us in our own lives. Death means to say goodbye, but never to leave a loved one behind."



GERMANY

Trafigura buys Ecobat Stolberg lead smelter

Swiss-based commodity trader Trafigura says it has completed its purchase of Ecobat Resources Stolberg (ERS) multi-metals processing plant in Germany, and plans to bring it online in the coming weeks to supply European battery producers. The Stolberg plant will be operated and managed by Nyrstar, which Trafigura owns, and the Stolberg business will be renamed Nyrstar Stolberg GmbH, Trafigura said in a news release. The plant was among several industrial sites damaged by massive flooding in Germany's west and south last year and has suffered months of lost production. It has the capacity to produce 155,000 t/a of lead, and more than 100 different specifications of lead alloys as well as 130,000 t/a of sulphuric acid.

CANADA

First Phosphate looking at long term offtake agreement with Prayon

Canada-based First Phosphate Corp has entered into a collaboration agreement with Belgian producer and technology provider of purified phosphoric acid Prayon SA. First Phosphate and Prayon have committed via memorandum of understanding to explore the potential of a long-term offtake agreement for phosphate concentrate to be produced by First Phospahte in its Quebec mining operations. The agreement also allows First Phosphate to be able to toll process its phosphate concentrate to battery-grade purified phosphoric acid at Prayon's facilities. The partners also plan

to explore the development of a facility to produce lithium ferro-phosphate (LFP) -grade phosphoric acid and even active LFP cathode material in Quebec. Prayon's technology is used to produce phosphoric acid at 130 sites worldwide. In addition, Prayon operates five of its own plants.

Commenting on the signing of the MoU, Marc Collin, Prayon's Chief Technology Officer said: "We are excited to partner with First Phosphate and test our recognised technologies for the production and processing of high quality phosphoric acid to supply the LFP battery industry in North America. The opportunity to partner with First Phosphate is an important step in our global diversification initiatives."

MOROCCO

Phosphate exports down 12% in 2022

Morocco's phosphate and derivatives exports reached \$11.3 billion last year, according to data from the country's customs service. The number represents an increase of 43.9% compared to a year earlier, and the phosphate sector topped the list of Morocco's best-exporting sectors in 2022, ahead of the automotive sector. However, the rise was mainly due to an increase in price of 74.4% over the year, and the actual physical quantity of phosphate fertilizer exported actually fell by 11.8% compared to 2021. Morocco holds 75% of the world's phosphate rock reserves. OCP, which manages those reserves, announced a turnover of \$8.32 billion throughout the first nine months of last year, up 55% on the same period of 2021. The group announced last year its plan to increase fertilizer input by 10% to meet the rising global demand for fertilizers. The company's decision comes amid the Ukraine-Russia war, which created uncertainty in the international fertilizer supply chain.

INDIA

Reopening for Sterlite Copper smelter?

After almost five years of closure, the prospects of a reopening of the Vedanta group's Sterlite Copper smelting plant in Thoothukudi look a little brighter. There has been a groundswell of popular opinion in the local community on behalf of villagers and business owners in the city badly impacted by the closure of the smelter, and even a protest in New Delhi. According to the Pro-Sterlite Plant Federation, 600 truck owners, and 13,500 truck drivers have been left with no source of income, as well as 5,000 workers engaged in repair shops, hotels, and tea and coffee shops catering to the lorry industry. Sterlite has also gained some credit from producing medical oxygen to assist local hospitals during the covid pandemic, and points out that rather than a fall in SO₂ levels in the vicinity, there has actually been a rise since the closure, supporting Sterlite's claim that the SO₂ pollution it was blamed for is actually coming from local coal-fired power plants. The shutdown in 2018 followed violence that broke out among anti-Sterlite protests over alleged environmental degradation caused by the plant. Fourteen rioters were killed by police.

The plant's capacity of 400,000 t/a of copper represented almost 40% of India's output. The Indian Supreme Court is currently hearing Vedanta's petition to overturn the Tamil Nadu state government order to close the plant.

Sulphur 405 | March-April 2023

16

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46

People

Suncor has selected Rich Kruger to be the company's next president and CEO, effective from April 3rd, according to the company. Kruger will also join the Suncor board of directors. The announcement follows a search process conducted by a special committee of the board. Rich Kruger previously worked for ExxonMobil for 39 years, and was the chairman and CEO of Imperial Oil Ltd from 2013 through 2019 before retiring from the company, where he focused on safety, reliability and operational excellence. Kris Smith, who has been interim CEO since July 2022, will work with Kruger to ensure a smooth transition before assuming the role of Chief Financial Officer and Executive Vice President of Corporate Development, at the conclusion of Suncor's annual general meeting on May 9, 2023. Alister Cowan, the current CFO, plans to retire but has offered to remain with the company through the end of the year to support the transition to Mr. Smith and to provide advisory services. Smith replaced previous CEO Mark Little, who resigned in July 2022 following investor pressure after a series of safety incidents and fatalities.

"Rich is a highly capable and seasoned CEO with an impressive track record of leading a safety culture," said chairman Mike Wilson. "Known as a strong and engaging leader, Rich is well regarded for his strategic and commercial aptitude, and for his experience in the Canadian oil sands. The Board looks forward to working



with Rich, as he provides the leadership to deliver world-class performance that maximises shareholder returns."

"I am very excited and energized about the opportunity to lead Suncor into the next chapter," said Rich Kruger. "Suncor has great people and assets. Combined with strong leadership and the right culture, we can leverage the company's competitive advantages to excel."

Emerging African phosphate producer and developer Kropz has appointed Louis Loubser as CEO and executive director with immediate effect. Kropz chairperson Lord Robin Renwick said: "the board are delighted to welcome Louis Loubser to the board as the company's new CEO. Louis has significant operational experience, which is what the company most needs at this stage of its development. The

board would also like to take this opportunity to thank [former CEO] Mark [Summers] for his very significant contribution while he had been at Kropz and wish him well in all his future endeavour." comments.

The board of directors of Brazilian state oil firm Petrobras has approved the appointment of Jean Paul Prates as its new CEO. He was voted to be added to the board at a directors meeting, and designated as CEO on a temporary basis to April 13, after which his appointment is expected to be extended for the long term. Prates previously served as a senator and energy secretary for the state of Rio Grande del Sul before becoming an energy advisor to the administration of President Luiz Inacio "Lula" da Silva. He is known for championing renewable power projects in the state as well as his consulting work as the executive director of Expetro Consultoria em Recursos Naturais Ltda. Prates is expected to carry out the priorities of the Lula administration, which include keeping Petrobras more active in refinery projects and finding a way to cushion the sting of higher fuel prices, which are pegged to global markets under the company's current policy. He is also expected to develop a greater role for renewables within the company, which has hitherto largely stuck to its mandate to produce oil and gas during the term of former President Jair Bolsonaro despite pressure from investors to expand its low-carbon remit.

Calendar 2023

2023 Australasia Sulphuric Acid Workshop, BRISBANE, Australia Contact: Cathy Hawyard. Sulfuric Acid Today Tel: +1 985 807 3868 Email: kathy@h2so4today.com

TSI Sulphur World Symposium 2023, EDINBURGH, UK Contact: Sarah Amirie. The Sulphur Institute Tel: +1 202 296 2971 Email: SAmirie@sulphurinstitute.org

MAY

REFCOMM 2023, GALVESTON, Texas, USA Contact: CRU Events Tel: +44 (0)20 7903 2444 Email: conferences@crugroup.com

Middle East Sulphur Conference (MESCon), ABU DHABI, UAE Contact: CRU Events Tel: +44 (0)20 7903 2444 Email: conferences@crugroup.com Web: www.events.crugroup.com/ middleeastsulphur/

Ninth International Acid Gas Injection Symposium, CALGARY, Canada Contact: Alice Wu, Spheretech Connect Email: alicewu@spheretechconnect.com Web: www.spheretechconnect.com

JUNE

45th Annual International Phosphate Fertilizer & Sulfuric Acid Technology Conference, CLEARWATER, Florida, USA Contact: Michelle Navar, AIChE Central Florida Section Email: vicechair@aiche-cf.org Web: www.aiche-cf.org

ESA General Assembly, VIENNA, Austria Contact: Francesca Ortolan, **European Sulphuric Acid Association** Sector Group Manager Tel: +32 499 21 12 14 Email: for@cefic.be

SEPTEMBER

Web: www.sulphuric-acid.eu

30th Annual Brimstone Sulphur Symposium, VAIL, Colorado, USA Contact: Mike Anderson, Brimstone Tel: +1 909 597 3249

Email: mike.anderson@brimstone-sts.com.

NOVEMBER

CRU Sulphur & Sulphuric Acid Conference 2023, NEW ORLEANS, Louisiana, USA Contact: CRU Events

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Sulphur 405 | March-April 2023

www.sulphurmagazine.com

51

52

14

26

32

34

46

Advances in sulphur battery technology

Lithium sulphur batteries have many advantages over conventional lithium ion batteries in terms of energy density, and they also avoid the use of costly cobalt, but they deteriorate rapidly and cannot be recharged as frequently. However, recent advances in Li-S batteries could overcome this problem and lead to widespread adoption.

he electrification of our society, now beginning to extend into personal transportation as well as all of the other myriad ways we consume electricity these days, puts a premium on electricity storage, especially for mobile applications such as smartphones, laptops, tablets etc. More advanced mobile devices, with wi-fi connections streaming large files such as movies, place greater demands upon batteries, resulting in shorter battery lifetimes between charges. Electric vehicle performance is similarly limited in terms of vehicle range by their batteries' capacity, and providing power via conventional lead-acid cells imposes a significant weight penalty.

Battery technology has been increasing steadily over the past few decades, moving to progressively higher energy densities in terms of Watt-hours per kilogram. A conventional lead acid cell can produce around 25-45 Wh/kg. The nickelcadmium batteries that were developed in the 1940s expanded this to 40-60 Wh/kg, and in the 1990s nickel metal hydride batteries reached 75 Wh/kg. But undoubtedly the greatest breakthrough was the development of lithium-ion batteries, which can store up to 250 Wh/kg, and which have made the development of the present generation of personal electronics possible.

Lithium-based batteries now represent 40% of the global battery market, with the rapid increase in electric vehicles meaning that the use of Li-ion batteries is still growing at around 15% year on year. Even so, while it has allowed manufacturers to make your laptop, tablet or smartphone smaller and lighter, few of us are, I imagine, particularly impressed with the battery life we get between charges; usually only a few hours of continuous use. And while lithium



Theion sulphur crystals for Li-S batteries under the microscope.

itself is light, lithium-ion batteries typically require bulky cathodes, often made from ceramic oxides like cobalt oxide, to house the ions, which increases the weight and so limits the battery's energy density.

Using sulphur as a cathode, however, lowers the battery's weight considerably, as well as increasing the energy density. Lithium-sulphur batteries can already achieve energy densities of 500 Wh/kg; twice that of lithium-ion batteries. This is the equivalent of doubling the range of an electric vehicle or the continuous usage time of a laptop or smartphone. And the theoretical limit of the technology is as high as 2,500 Wh/kg.

Technical issues

In theory, then, we should be switching to lithium sulphur batteries. However, the battery chemistry also presents some problems which have prevented its large scale commercialisation. Lithium and sulphur can form a wide variety of lithium polysulphide compounds with differing oxidation states, from Li_2S through Li_2S_2 , Li_2S_3 , Li_2S_4 etc, all the way up to Li_2S_8 . These form at the cathode as lithium migrates from the anode. However, higher lithium polysulphides tend to be soluble in the electrolyte, and over time this can destroy the structure of the cathode, leading to the formation of dendrite structures of polysulphide and cracks in the sulphur cathode with repeated cycling, reducing the number of times that the battery can be recharged.

Overcoming this issue has been the key to the development of Li-S batteries, and there are signs that progress is being made. Initially efforts focused on inserting a redox-inactive layer between the cathode and anode. But this layer was heavy and dense, reducing energy storage capacity per kg for the battery. More recently, researchers at the US Argonne National Laboratory have developed and tested a porous sulphur-containing interlaver. Tests showed initial capacity about three times higher in batteries with this active, as opposed to inactive, layer. More impressively, the cells with the active layer

Sulphur 405 | March-April 2023

18 www.sulphurmagazine.com

47

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49

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charge-discharge cycles; a performance similar to lithium-ion batteries. Research also continues elsewhere. In

maintained this high capacity over 700

Europe, the EU has been part funding the LISA (LIthium sulphur for SAfe road applications) project with 13 project partners throughout the EU and UK. Running since 2020, LISA identified nine promising lines of research for achieving their goals of a stable 450Wh/kg automotive LiS battery with 1,000 recharge cycles, and in 2022 the project moved to pilot production for these, for testing and validation in vehicle trials. Likewise there is considerable excitement in the US over the new Inflation Reduction Act (IRA) which offers large government subsidies for battery development.

Commercialisation

But perhaps the most promising recent development has been the announcement by Korean giant LG, through its energy arm LG Energy Solution, which supplies batteries for Tesla, amongst others, that it plans to try to commercialise a lithium-sulfur battery in 2025, with mass production by 2027, LG is also looking at aviation applications for the technology, with electric or electric-hybrid light aircraft using the new lightweight battery technology. In 2020, LG supplied Li-S batteries to an experimental unmanned drone aircraft, the EAV-3, developed by the Korea Aerospace Research Institute. The plane charged the batteries using solar power during the day and ran off battery power at night during a 13 hour test flight at an altitude of 12-22 km. Reportedly, the LNG battery uses a sulphur-carbon composite for the anode and lithium metal for the cathode. LG has been working with the Korea Advanced Institute of Science and Technology (KAIST), and announced in January 2023 that its research team, led by professor Lee Jin-woo has developed an energy density- and duration-improved lithium-sulphur battery using an iron cathode composite that reduces lithium polysulphide dissolution, albeit at the expense of some weight (the battery has a claimed energy density of 320 Wh/kg - still more then 50% higher than Li-ion).

Germany company Theion also claims to have developed a lithium sulphur battery, using crystalline sulphur with carbon nanotubes and a proprietary solid electrolyte. Theion grows a pure sulphur wafer by a 'direct crystal imprinting' method directly from molten sulphur. Because of the flexibility of the process, the company says

Sulphur 405 | March-April 2023

that it can grow any geometrical shape of wafer adapted to a customer's product shape. The company says it will be shipping its first batteries later this year, as with LG first to aerospace customers, as part of the qualification stage, and then aircraft, air taxis, drones, mobile phones and laptops, before servicing the electric flight and automotive sectors in 2024.

However, there have also been a number of exits from Li-S battery development. British tech startup Oxis, originally one of the partners in the LISA programme, went bankrupt in May 2021. Sion Power, which also claimed to be developing a Li-S battery, has moved onto lithium oxides instead.

Sodium sulphur batteries

Lithium sulphur batteries are not the only game in town. There is also the sodium sulphur battery, originally developed by Ford in the 1960s and subsequently sold to the Japanese company NGK. NGK now manufactures the battery systems for stationary power applications; the batteries use molten sulphur as the cathode and molten sodium as the anode, separated by a solid ceramic, sodium alumina, which also serves as the electrolyte. The ceramic allows only positively charged sodium-ions to pass through. The electrons that are stripped off the sodium metal move through the circuit and then back into the battery at the positive electrode, where they are taken up by the molten sulphur to form sodium polysulphide. The positively charged sodium-ions moving into the positive electrode compartment balance the electron charge flow. However, as well as the additional weight (sodium is heavier than lithium, and the alumina also adds to the weight), because it works in the liquid phase the battery must also be kept hot (typically >300°C) to facilitate the process, making it unsuitable for non-stationary applications. Nevertheless, the batteries are very efficient (up to 90%), and Na-S battery technology has been used at over 190 sites in Japan, with more than 270 MW of stored energy suitable for 6 hours of daily peak shaving installed. In Abu Dhabi, fifteen Na-S systems acting in coordination provide 108 MW / 648 MWh to defer fossil generation investment and provide frequency response and voltage control services. The market for Ns-S batteries is estimated at \$480 million/ vear at present, and is forecast to grow at 15% year on year as projects powered by intermittent renewable energy look to battery storage to even out the flow of electricity.

Lithium constraints

The cost and availability of sulphur is not a factor for Li-S batteries, indeed, it is one of their major selling points - it is less than 1% of the cost of the cobalt used in some other modern batteries. Lithium is a different story, however, and may be the key constraint in the production of Li-S batteries. In fact, concerns about the availability of lithium have already been raised in the context of lithium-ion batteries. Demand for lithium is expected to rise to 300,000 t/a by 2025 and more than 1.0 million t/a by 2030 because of lithium's use in lithium ion and other batteries.

While this is a large increase in demand to meet, production of lithium is nevertheless increasing very rapidly. In 2021 total global output of lithium reached 106,000 t/a, four times its value a decade earlier, with batteries accounting for 75% of all lithium demand. Production is concentrated in just three countries; Australia, Chile and China represented 90% of production that year, but there are a number of new lithium projects across the world, particularly in the United States. Even so, lithium availability may put a cap on how fast lithium battery production is able to expand over the coming decade.

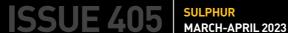
The impact on sulphur

With promising new developments in improving the battery technology, the commercialisation of lithium sulphur batteries is increasingly looking like a question more of 'when' rather than 'if'. If LG are to be believed, then large scale production could be just a couple of years away. Once Li-S batteries are commercially available, and assuming that the technology works as advertised, it is quite possible that their uptake may be as fast as that for Li-ion, which cornered 80% of the market for personal electronics and vehicles inside a decade.

The actual volumes of sulphur required for Li-S battery production are unlikely to be large within the current decade; it may be a matter of a few hundred thousand tonnes per year at most by 2030. However, it may be the impact on sulphuric acid demand for lithium mining that has the largest effect. In the US, new lithium projects are expected to add 2 million t/a of additional sulphuric acid demand in the next couple of years, and if the boom extends elsewhere, this could mean several million tonnes of acid and a concomitant increase in sulphur demand.

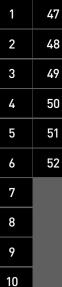
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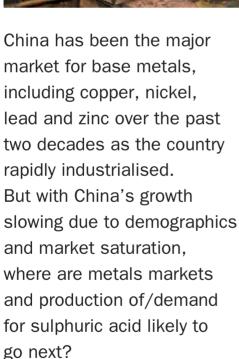
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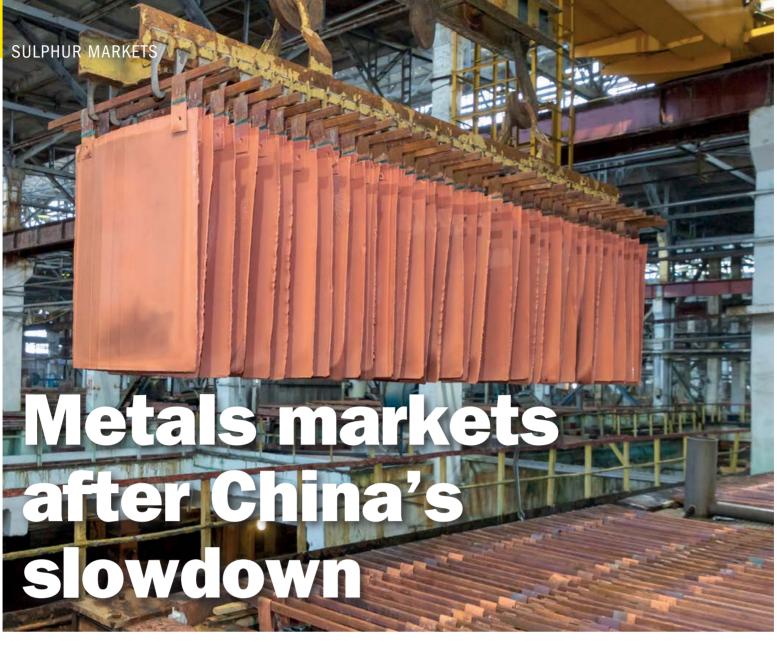
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Above: Copper production at the Balkash smelter, Kazakhstan.

20 www.sulphurmagazine.com



hina's growth, since Deng Xiaoping began his 'Four Modernisations' in 1979, has been spectacular. GDP growth averaged around 10% year on year from 1980-2010, in effect multiplying the size of the economy 15-fold over that period. The transformation has been a remarkable one, lifting many millions out of poverty and turning China into one of the powerhouses of the global economy. The rapid growth, especially in the industrial sector, also sucked in enormous volumes of raw materials to feed it, with the net result that China came to occupy around half of all global demand for key metals such as copper, nickel, zinc and lead. With much of production of these metals occurring via smelting of ores, this in turn meant a huge increase in sulphuric acid production. At the same time, China was able to harness this acid in phosphate production to improve its agricultural productivity.

Since 2010, however, the breakneck era of growth has slowed. While China had achieved the position of 'workshop of the world', these markets had become saturated and Chinese domestic capacity in most sectors had been over-built. The government has begun to try and steer the Chinese economy towards a more mature, service-driven model and boost consumer demand domestically,

but this has been dampened by a buildup in domestic debt, especially in the housing market, where over-construction has left the sector depressed. Moreover, China has also begun to face a major demographic shift, as the effect of its 'One Child Policy', which slowed its population growth dramatically over the 1980-2010 period, began to be felt. With Chinese citizens living longer, healthier lives, this has meant a boom in the number of retirees at the same time that fewer young people are entering the jobs market.

Because of the effects of all of these factors, even before the covid-19 pandemic, Chinese growth rates had slowed from 10.6% in 2020 to 6.0% in 2019, just 2.2% in 2020 as the pandemic struck, and while there was a bounce back in 2021 to 8.1%, last year saw China's strategy of trying to contain covid via lockdowns rather than a widespread campaign of immunisation result in the complete shutdown of several of its major cities for weeks and months on end, only ended in December following mass public protests.

As a result, GDP growth for 2022 is estimated at 3.0%, and while there has been a relaxation in covid restrictions, the most optimistic forecasts for this year and the coming few years are of growth of around 4.5% year on year, even assuming that



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you take Chinese government statistics at face value, and some economists argue for lower figures, from 3% down to 0.5%. Add to this China's crackdown on polluting industries and the switch towards a lower carbon economy, and the prospects are for much lower growth over the 2020s.

Metals markets

Base metal smelting makes up about 30% of the world's production of sulphuric acid, and because it is involuntary production to avoid emissions of harmful sulphur dioxide, production of smelter acid is driven primarily by the economics of metal markets rather than sulphuric acid prices. Needless to say, Chinese demand remains a key driver for all metals markets. In the short term, the relaxation of covid restrictions has seen economic activity pick up in China; a welcome respite for markets which had been subdued

Some analysts

in the copper

industry."

are calling this a

'generational shift'

in 2022, aside from nickel, which continues to soar due to rapidly rising demand for batteries. The invasion of Ukraine and subsequent economic sanctions of Russia did lead to spikes in most metal prices on fears of lack of supply, but from April onwards prices were falling as US interest rates were hiked in response to rising inflation. Copper and

zinc prices fell by around 15% over the year, though lead was unchanged and nickel up 46%. Slow global economic conditions have taken global GDP to 3.2% in 2022, and forecast to slow to 1.3% this year, while inflation remains a concern in many countries due to high energy prices.

Copper

Acid from metal smelting is predominantly (about 70%) generated by the copper industry. Copper is a leading barometer of global economic health due to its wide-ranging usage, particularly in electrical equipment and industrial machinery. Demand for copper has become concentrated in Asia (72%), with China alone representing more than 50% of all global demand. Copper prices had actually been on a high throughout 2021 and peaked in early 2022 on fears of supply disruption over the Russian invasion of Ukraine. However, as previously noted, the Chinese construction market, which uses copper for piping and wiring, has been subdued, and cop-

Sulphur 405 | March-April 2023

per prices declined throughout 2H 2022, in spite of some power restrictions affecting Chinese smelter output, rebounding at the start of 2023 due to protests in Peru, which produces 10% of the world's copper, low global stocks, and the loosening of lockdown restrictions in China. But the market remains very volatile over economic uncertainties, not least in China, where reports that the country had missed industrial production targets for two months in a row sent copper prices back down again.

On the supply side, the International Copper Study Group (ICSG) reports that mine output was at 21.6 million t/a in 2022. up 3.4% compared with 2021. For 2023, a 4.7% increase in copper mine production is forecast. Refined copper production in 2022 is forecast to be 24.8 million t/a, up 2.5% compared with 2021, and might be 25.4 million t/a in 2023. Global reported refined copper demand for 2022 was 24.7

> million t/a, up 1%, and might increase 2.6% this year to 25.3 million t/a, lower than previously forecast. Chinese demand for the refined copper in 2022 was put at 13.2 million t/a, up 1% compared to 2021, and is expected to increase by 2.6% in 2023 to 13.5 million t/a. Output from Chile, the world's largest copper producer, has not

moved as fast as expected and there are delays to new mine projects (and a recent cancellation for the proposed Dominga mining project for environmental reasons), although Teck Resources' Quebrada Blanca 2 project is now ramping up production, as is the Anglo-American Ouellaveco mine in Peru. There is also new production in the African copper belt.

Overall, as noted above, copper mine output is rising after several years of relatively modest increases. The compound annual growth rate (CAGR) for word copper mine production averaged 2.7% year on year in the 2010s, but fell to 0.8% from 2019-2022 due to a series of operational constraints that negatively affected output and the impact of covid-19 pandemic and global lockdown in 2020/2021. The bottleneck now appears to be smelter capacity, and treatment and refining charges, socalled T&Cs, which form the mainstay of smelter income, have risen dramatically over the past few months to the highest for several years, on average 35% higher this year than last. Chinese smelters face

challenges, including government efforts to reduce energy consumption and pollution. But this bottleneck is likely to only be short term, with major new smelters due to come onstream elsewhere in Asia in 2H 2024, including Adani Enterprises in India, Freeport McMoRan in Indonesia and Ivanhoe Mines at Kamoa-Kakula in the DRC.

Copper is seeing a swing back towards smelter-based production after a growth period for copper leaching. During the 2010s the SX-EW share of total mine production fell from 22% in 2012 to 18% in 2021. Although SX-EW annual output increased by around 200% in the DRC due to the start-up of new projects, production fell by about 30% in Chile mainly as a consequence of declining ore grades at operating mines or mines reaching end of life.

Perhaps the greatest prospect for copper, however, is represented by the increasing electrification of the world, particularly personal transport, as we move towards a lower carbon economy. Some analysts are calling this a "generational shift" in the copper industry, and BNY Mel-Ion has described it as "the new oil", as copper is used in renewable power and electricity transmission. Demand is likely to continue to be strong over the coming years; forecasts are of around 5 million t/a of extra copper demand out to 2030. While ore grades are falling and new copper projects are often in more remote (and hence expensive) regions, high demand may lead to high prices which will incentivise new production. Major copper miners say that the expect a significant supply shortfall starting around the middle of the decade, with a shortage of new projects in the pipeline, given how long it takes to develop a copper mine, compared to the forecast increase in demand due to the energy transition.

Lead and zinc

Zinc and lead production is responsible for around 20% of the world's smelter acid output. Both markets were in deficit in 2022, and are expected to continue to be this year, according to the International Lead and Zinc Study Group (ILZSG), though both markets are moving back towards balance. Refined lead output fell in a number of countries in 2022, especially Russia, Ukraine and Germany, with global supply dropping by 0.3% to 12.3 million t/a. Supply is expected to be 1.8% higher in 2023 at 12.6 million t/a, with new capacity in Australia, Germany, India and the UAE.

www.sulphurmagazine.com



50

52

6

10

15

33

42

46

■ Contents

22

Lead demand increased by 0.8% to 12.4 million tonnes in 2022 and is forecast to increase 1.4% to 12.6 million t/a in 2023, according to the ILZSG. Chinese demand grew by a modest 0.3% in 2022, due to reduced automotive output because of covid restrictions. China represents around 40% of lead and 35% of zinc demand, and the easing of lockdown restrictions has led

Global demand for zinc is forecast fell by 1.9% to 13.8 million t/a in 2022, but may rise by 1.5% to 14.0 million t/a in 2023. Production fell by 2.7% to 13.5 million t/a in 2022, with a substantial fall in Europe, but should rebound by 2.6% to 13.8 million t/a this year.

to a rebound in demand for base metals.

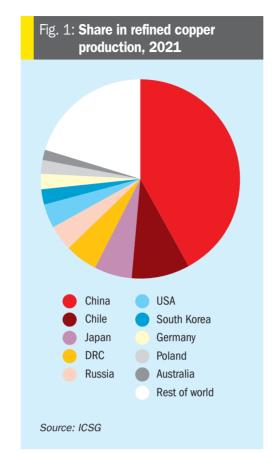
Batteries represent about 90% of all demand for lead, with electric scooters a particularly rapid growth area. Lead-acid batteries are gradually being replaced by lithium batteries in transport applications. but lead batteries remain a mainstay of the telecoms industry for back-up power in critical applications, and lead demand is expected to continue to rise over the coming decade. Zinc is mainly used in galvanising of steel (50%), and the manufacture of brass and bronze allovs and die casting, and as such tends to track industrial output. Overall, Wood Mackenzie expects demand for both metals to rise by about 2.5 million t/a each out to 2030.

Nickel

Nickel's primary use (ca 70%) is as an alloying component in stainless steel production, but its use in batteries and electric vehicle production, currently around 11% of demand, has risen rapidly in the past few years, and will be the fastest growing sector of demand for many years to come. World primary nickel production was 2.61 million t/a in 2021, but increased to 3.04 million t/a in 2022 and is expected to rise to 3.39 million t/a in 2023, according to the International Nickel Study Group. Demand was 2.78 million t/a in 2021, 2.89 million t/a in 2022, and is forecast to rise to 3.22 million t/a in 2023, in spite of the impact of the covid pandemic, the fallout from the Ukraine invasion, higher inflation, lower growth and energy constraints; stainless steel production decreased by 3.8% in 2022, and is expected to fall again this year.

Nickel smelting is often from legacy production based on sulphate ores, in places such as Norilsk, Russia, Harjavalta in Finland, and Jinchuan Non-ferrous Metals in Jinchang,

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China. Over the past decades, there was a major boost in pyrometallurgical production of nickel from lower grade oxide (laterite) ores, particularly as so-called nickel pig iron (NPI) in China for use in stainless steel production. China's NPI production often used Indonesia ore and concentrate, but a crackdown by the Indonesian government on exports of nickel ore has forced the development of NPI and ferronickel production in Indonesia. But the new demand for battery grade nickel requires mixed hydroxide precipitate (MHP) and this has led to a renewed focus on high pressure acid leaching (HPAL), again particularly in Indonesia, though there are also new projects in the Philippines and Australia.

Nickel demand is expanding at around 7% year on year, and will effectively double by 2030. However, nickel is likely to be a net consumer rather than generator of sulphuric acid.

A pivot from China?

While China's industrial growth has dominated metals markets over the past three decades, there are signs that this era is drawing to a close, in much the same way that it did for the Japanese 'bubble economy' in the 1980s. China now faces a similar demographic transition to that which Japan did then; last year the Chinese population actually fell for the first time on record. The overhang of debt, the move to a

service led, consumer driven economy, and the green transition will all place brakes on China's growth, which now looks set to fall to an average of 2-5% year on year. The focus of global growth is steadily shifting to south and southeast Asia.

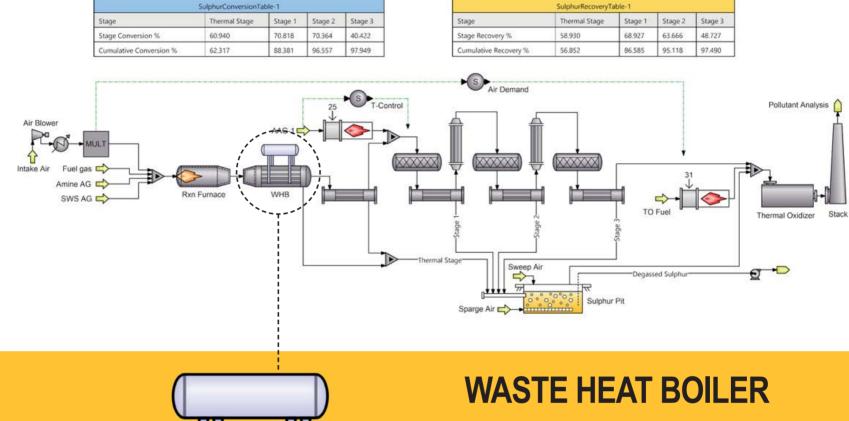
That is not to say that China will not continue to set the tone for metals markets. The country will remain the largest consumer of most base metals for the foreseeable future, as well as having the world's largest sulphuric acid industry. Smelter acid represents 35% of China's acid capacity, and a higher share of production, as smelter acid plants tend to have higher operating rates than sulphur burning or pyrite roasting plants, and a tranche of new copper smelter capacity is still coming onstream, increasing China's net acid exports at least in the short to medium term. However, Chinese authorities continue to crack down on energy-intensive industries as part of the country's aim to reduce its carbon emissions. The China Non-Ferrous Metals Industry Association (CNIA) has set a provisional goal of bringing non-ferrous metal carbon emissions to a peak by 2025 and cutting them by 40% by 2040. Chinese smelter acid capacity is expected to peak in 2025 and acid output from smelting fall thereafter.

The move away from China can be seen in the focus on new smelter capacity in Indonesia, where the government is trying to force the development of a downstream metal processing industry to capture more of the value chain. New projects include PT Smelting, a joint venture between Mitsubishi Materials Corp and Freeport Indonesia, which is expanding output from 300,000 t/a to 342,000 t/a of copper cathode by the end of December 2023, while a new Freeport/Chiyoda copper smelter at Gresik on East Java last year, with a projected capacity of 600,000 t/a of copper, is due for completion in 2025. Indonesia is also completing new lead and a zinc smelter capacity. Outside of Asia, as noted, the DRC is building a new 500,000 t/a copper smelter at Kamoa-Kakula, scheduled to open in 2025. Vedanta is also looking to build a new zinc smelter at Gamsberg in South Africa, and there are new projects in Chile and Peru.

Looking to the longer term, the increase in demand for metals such as copper and nickel, and to a lesser extent lead and zinc, for the green energy transition will keep demand and prices high and likely keep smelter construction activity going on the copper side, the acid output balanced somewhat by nickel HPAL consumption.



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Controlling SO₂ emissions

Most processes involving sulphur, from smelting to refining, produce sulphur dioxide as a by-product. Regulations continue to tighten on industrial SO_2 emissions worldwide, leading to greater recovery of sulphur and sulphuric acid at these sites.

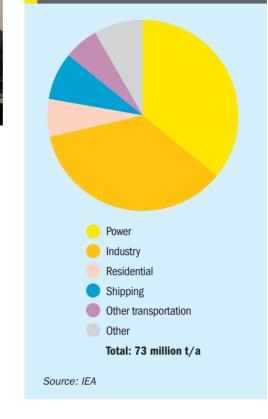


Fig. 1: Major man-made sources of

global SO₂ emissions, 2015

ulphur dioxide's deleterious effects on human health and the environment are well known. In the presence of water and oxygen, either in atmospheric water or moist mucous membranes in the human body, SO₂ can react to form sulphuric acid, leading to irritation of eyes and lungs in humans or in large scale deposition as 'acid rain'. While there are natural sources such as volcanoes and large scale forest fires, anthropogenic SO₂ mostly comes from three sources; burning of fossil fuels that contain sulphur in vehicles for transportation; burning of fossil fuels that contain sulphur in power plants (mainly coal), and industrial processes, particularly smelting of metal sulphides, cement and lime kilns, and production of fuels and gases in refineries and gas plants. Figure 1 shows the rough proportion of these for 2015.

Power

Power was one of the first segments to be tackled, in part by a switch away from burning coal to cleaner fuels like natural gas, and more recently renewables, and in part by the installation of abatement technology at power stations, particularly flue gas desulphurisation (FGD) scrubbers, which spray a mist of suspended calcium carbonate into the exhaust, converting sulphur dioxide

to calcium sulphate (gypsum). The impact of this has been a dramatic reduction in SO₂ emissions, by about 75% in Europe and North America from 1970 to the present. China, the largest producer of coalfired power in the world, only mandated FGD technology in 2006, but the impact since then has nevertheless been equally dramatic. Chinese SO₂ emissions fell by 62% from 2010-2017 in spite of a major increase in coal fired power use over that period, and the country's gradual switch from coal to cleaner fuels will lower that further. India is now the outlier, the largest SO₂ emitter in the world, and with 52% of those emissions coming from coal-fired power. India's Ministry of Environment, Forest and Climate Change introduced SO₂ emission limits for coal-fired power plants in December 2015, but the deadline for the installation of FGD was delayed to 2022, and more recently to 2024.

The natural gas industry also of course was once a major source of sulphur dioxide from the flaring of acid gas separated from methane, and moves to tackle this were the beginnings of the sulphur industry, in North America and Europe, dating back to the 1950s. While FGD scrubbing produces gypsum, which mainly goes to landfill deposits, hydrogen sulphide recovery from sour gas now produces half of the

world's elemental sulphur, particularly in the Middle East, central Asia and China.

Transport

Removal of sulphur from vehicle fuels has been another major source of sulphur dioxide reductions, and responsible for most of the remaining production of elemental sulphur. Tightening restrictions on sulphur content of fuels began in 1970, but were accelerated in 1992 by the European Union's adoption of the mandatory fitting of catalytic converters to road vehicles, necessitating the Euro-I fuel standard of a 2,000 ppm (0.2%) limit on sulphur, followed progressively by Euro-II (500 ppm), Euro-III (150/350ppm), Euro-IV (50ppm) and Euro-V (10ppm), the latter implemented in 2009. Most other regulatory regimes around the world have followed the same model, with all of North America, Europe, Russia, China and Australasia now having moved to the Euro-V standard, and most other countries outside of central Africa adhering to Euro-IV. Refineries have moved to supply fuels to the new standards, increasing their sulphur output accordingly. Reducing the sulphur dioxide output of road transport has reduced SO_2 emissions from this source by 99% in Euro-V countries and, set alongside the gains from desulphurisation of power noted above, has contributed to

24 www.sulphurmagazine.com

total SO₂ emissions in, e.g. the United States falling by 95% from 1970-2020.

Two transportation sectors still stood out until fairly recently; shipping and aviation, and particularly shipping was responsible for taking most of the sulphur from refinery bottoms as high sulphur fuel oil. But the International Maritime Organisation has now mandated a reduction in sulphur content of marine fuels to 5,000 ppm (0.5%) globally, and 1,000 ppm (0.1%) in heavily trafficked regions which have instituted Emissions Control Areas (ECAs). Ships can meet the standards using a variant on FGD (scrubbers), but so far only around 15% of the world's ships do so. This has led to a boost in production of vacuum gasoil and low sulphur fuel oil, and a corresponding increase in sulphur production at some refineries.

Industry

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Power-intensive industries are also a major source of SO₂ emissions. Cement and lime production have generally installed scrubbing systems similar to power stations, but metal smelters often generate large amounts of SO₂, and given the age of many smelters,

these have often operated without effective pollution control, becoming a major bone of contention with local communities. This has even enforced the shutdown of smelters on occasion, such as at Tuticorin in India and La Oroya in Peru. Some smelters, such as Norilsk in Russia, are among the top SO₂ emitters in the world, generating 1.9 million t/a of SO₂ alone in 2019. But SO₂ capture systems are progressively being added around the world to older smelters, and mandated for new ones. For example, Chile recently went through a programme of fitting SO₂ abatement to its smelters. This generates an increasing proportion of the world's sulphuric acid - around 35% at present. Norilsk also aims to reduce its SO₂ output by 90% by 2025, though, because of its remoteness, the company is taking a different tack, and will neutralise the acid to produce gypsum.

Emissions from the oil and gas industry as a by-product of recovering sulphur at refineries and gas plants also remain a major emitter of SO₂. Numbers 3 and 4 on the list of global SO₂ 'hotspots' are the Zagroz petrochemical complex in Iran and the Rabigh complex in Saudi Arabia, and installations in Mexico and the UAE are also in the top

ten. Saudi Arabia is actually another of the countries where SO₂ emissions are still rising, and there is growing pressure on these countries to reduce this.

More sulphur?

UN figures indicate that, while global population increased from 4.4 billion in 1980 to 7.4 billion in 2015, and global GDP rose from \$11.4 trillion to \$75 trillion (in 1980 dollars) over the same period, global manmade sulphur dioxide emissions fell from 151 million t/a to 73 million t/a over the same period - more than halving. This reduction in sulphur dioxide amounted to 78 million t/a, equivalent to 39 million t/a of elemental sulphur. And perhaps far from coincidentally, the total amount of recovered sulphur being produced rose during that period by 29 million t/a, from 33 million t/a in 1980 to 62 million t/a in 2015. While FGD in the power sector generates gypsum as a by-product, and hence is tangential to the sulphur industry, sulphur dioxide emissions control at refineries and gas plants will generate additional sulphur, and, from metal smelters, sulphuric acid.

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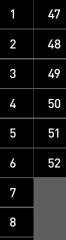








■ Contents



10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46



SulGas, South Asia's sulphur recovery and gas treating conference, returned to a live event in 2023, providing participants with a platform to interact with experts in the field, share best practices and troubleshooting tips with fellow refiners and discuss advanced technologies and operating procedures with technology providers, vendors and licensors.

hree Ten Initiative Technologies LLP organised the 5th edition of SulGas from 1-3 February 2023 at the Hotel Holiday Inn Mumbai International Airport, Mumbai, bringing together public sector oil companies, private refiners, petrochemical, chemical and fertilizer plants, licensors, engineering companies, solvent and column equipment manufacturers, and control and instrumentation companies.

SulGas Mumbai 2023 provided a threeday interactive technical programme and exhibition, attracting over 155 attendees from over 68 companies representing all major areas of sulphur handling and gas

The conference agenda was split over three days comprising expert forums, ten technical sessions and daily roundtables, as well as dedicated time to explore the exhibition.

The opening session on Wednesday 1 February started off with an expert forum on instrumentation basics for sulphur recovery units and tail gas units in which Jochen Geiger of Ametek Process Instruments reviewed and discussed the use of modern process analysers in SRUs and tail gas treating units, with detailed focus on how a feed gas analyser benefits the overall plant performance of an SRU and understanding process upset using installed analysers.

SRU instrumentation and control

The first technical session continued the theme of SRU instrumentation and control. David Inward of Sick discussed enhanced monitoring requirements from SRUs, providing detailed insights for a recent extended field trial at an oil refinery which applied a multi-component hot extractive infra-red analyser to meet reporting requirements both for conventional emission limit values as well as mass emissions.

Nirmalya Nandi of Bharat Petroleum Corporation shared experiences of how a problem of sticking tail gas treating unit (TGTU) feed valves was solved through inhouse modifications, resulting in improved reliability and availability of TGTU feed and incinerator control elements.

Jochen Geiger returned to the podium to discuss oxygen enrichment and its impact on the control of sulphur recovery units.

Changing SRU feeds

The next session focused on the design modifications required to SRUs when processing different feeds. Debopam Chaudhuri of Fluor discussed the design modifications required for Claus plants which co-process significant SO₂ (e.g. SO₂-rich refinery flue gases) along with the normal feed gas cocktail of H₂S and NH₃. While small amounts of SO₂ in the Claus feed gas have a favourable impact on the overall hydraulic design of the unit, at higher concentrations of SO₂ the positive impact of reduction of air demand tends to be overshadowed by the quenching effect on the Claus reaction, reducing the furnace temperatures below allowable operating limits for proper NH₃ destruction.

The production of renewable fuels by retrofitting existing refineries and their infrastructure is witnessing exponential growth and is changing the composition and flow rate of the feeds to the sulphur removal and recovery units, which will invariably require suitable modifications to meet overall sulphur recovery or emission specifications. Based on several case studies, Marco van Son of Worley Comprimo discussed the various options available to holistically review the sulphur block to determine the impact and mitigation of processing bio-feed.

Design and equipment advances in sour systems

Matt Thundiyil of Transcend Solutions presented a case study in which a refiner on the US Gulf Coast was forced to clean a heat exchanger in a sour water system every 3-6 months due to fouling. The problem was successfully solved by installing the $\mathsf{TORSEP}^\mathsf{TM}$ oil and solids removal system which removed the solid and hydrocarbon contamination from the sour water stripper units that were causing the problem.

Harnoor Kaur of Optimized Gas Treating demonstrated the importance of addressing the complex sour water chemistry using a true rate-based model such as ProTreat® to evaluate different SWS unit design configurations.

A novel approach for processing ammonia-rich sour gases and converting them to valuable products such as

Sulphur 405 | March-April 2023

26 www.sulphurmagazine.com



Contents

2

47

48

8 9

7

10 11

13

14

12

15 16

17

19

20

18

21 22

23 24

> 25 26

28 29

30

31

32

33 34

36

35

37 38

39

40 41

43

42

44

45

46

anhydrous NH3 or aqueous NH3 was the topic of Saptarshi Paul of EIL's presentation. Demand for ammonia in India has been rising year on year. EIL's patented technology (patent no. 350771) will not only help towards domestic ammonia demand but also reduce operational problems in the SRU as well as reducing NOx emissions.

Fibre and membrane-based contactors

In the next session the focus turned first to CO₂ membrane advancements to reduce emissions and enable CCS which was presented by Tanzim Choudhury of SLB, followed by a presentation by Saurabh Agarwala of EIL & Evergreen Technologies on innovative hardware solutions for sulphur reduction in light hydrocarbons like naphtha or LPG which are often contaminated with acidic components such as H₂S, COS, CS₂, mercaptans, SO₂ etc.

Energy transition

Rajiv Srinivasan of Shell India opened day two of the proceedings with an expert's forum on gas processing technologies in the energy transition. Many organisations have set a target to become a net-zero emissions energy business by 2050. Some of the technologies at the forefront of the energy transition were discussed along with their impact.

CO₂ capture

Chandrakant Joshi of Sulzer introduced the new Sulzer Mellapak[™]CC packings for outstanding performance in absorption systems encountered in CO2 capture in large power plants, natural gas processing plants and the fertilizer industry.

Vijaya Durga Kakara of HPLC described the latest developments to HP-HiGAS' compact carbon technology based on a rotating packed bed. A first of its kind commercial scale plant is operational at its Vsakh refinery for fuel gas treatment and a demonstration plant with a capacity of 24,000 t/a is being put up in HPCL Vizag refinery for capture of CO₂ from a PSA feed slip stream.

SRU hardware improvements

Sean Matthew of Ametek/Controls Southeast shared experiences of the first commercial installation of the ICON[™] sulphur degassing system, as well as considerations for future installations, and the benefits of ICON™.

Sulphur 405 | March-April 2023

Roelof ten Hooven of Duiker Combustion Engineers discussed several refinery applications of its SCO technology for utilising stoichiometry-controlled oxidation to handle ammonia waste streams. Dedicated ammonia incineration offers an attractive alternative to conventional processing of SWSAG in the SRU/TGTU and allows for complete combustion of ammonia without the need for flue gas after treatment, due to low NOx formation.

Brian Visioli or Porocel explained how operators of tail gas treating units can now use a catalyst which has improved sustainability without sacrificing performance or

Protecting the integrity of your SRU

The afternoon of day 2 was dedicated to the analysis, monitoring and protection of the front end of SRUs. Bob Poteet presented a revolutionary method of temperature monitoring for Claus units which provides an easy way to monitor the condition of the brick lining of the thermal reactor by using a special continuous thermocouple system that reads only the highest reading anywhere along the sheath.

Mason Lee of Aecometric Corporation reported on thermoacoustic modal analysis for a large sulphur reaction furnace. In a study, the acoustic natural mode of the reaction furnace under operating conditions was analysed through numerical simulation and then used to diagnose whether the vibration frequency of the furnace body in field operation is close to acoustic natural modes, which can then be used to analyse the causes of furnace vibration.

Domenica Misale shone a spotlight on tubesheet protection systems and the key design and operating considerations for the SRU waste heat boiler (WHB), raising the awareness of its importance for reliability and to prevent WHB failures.

Nasser Abukhdeir of Continuum Engineering presented the results of a study on simulation-based analysis of vapour distribution and liquid recirculation in kettle-type waste heat boilers. The findings could enable the enhancement of existing WHBs through retrofits and the design of new units with significantly improved performance and reliability.

Troubleshooting

Amine solution foaming problems have been studied and reported extensively, however, direct correlations about the root causes of foaming have not been established. Ben

Spooner of Amine Experts described six different foaming related cases and provided systematic approaches for foaming troubleshooting as well as a series of measures for foam minimisation to ensure foam does not take place in the future.

Anand Govindarajan of Three Ten Initiative Technologies discussed the use of the simulation tool ProTreat® and how it is meant to be used in the context of troubleshooting amine systems, and the technically right way to interpret the results.

The focus then moved on to troubleshooting heavy TEG losses from a gas dehydration unit which was presented by Sivaraj N of SLB.

Optimising hardware and retrofits of treating units

Mohd Firdaus Sabturani of Petronas shared the results of an investigation into the root case of repeated failures of column trays and Schoepentoeter inlet devices in amine regenerator columns in the AGRU and highlighted the critical link between the design of column internals and their vibration characteristics. Design improvements to consider in order to increase the natural frequency of the column internals include shortening the length of panels, increasing the panel thickness and utilising fixed valve trays.

Wai choon Liong of BASF reported on a successful amine swap case study in which OASE yellow technology was successfully used to optimise an existing amine scrubber unit based on MEA.

Lessons learned - SRU operations

The final session on day three of the conference focused on lessons learned in SRU operations.

Dharmeshkumar Patel of Sulphur Recovery Engineering used case studies to highlight common problems seen in the SRU and TGTU and stressed the importance of regular performance checks e.g. using a combination of GC analysis, simulation with specialised programs, combined with evaluation of DCS date to mitigate problems and optimise the performance of SRU and TGTU units.

Harpreet Singh & Radhe Syam of IOCL concluded the session by sharing lessons learned during the commissioning of a new 225 t/d sulphur recovery unit at IOCL, Panipat during the height of the Covid -19 pandemic.

The sixth edition of the SulGas conference will take place in early February 2024.

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48

52

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31

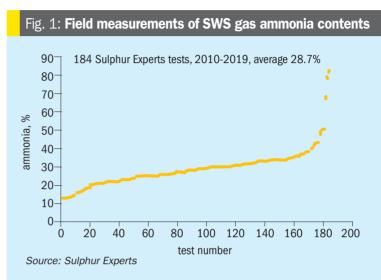
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46

A better understanding of SRU ammonia salt

formation

Gerald Bohme and **Joe Brindle** of Sulphur Experts Inc. combine new learnings, historical data, and recent onsite experience from operating companies to show what factors really impact ammonia plugging risk and what can be done to control them in order to allow for a wider operating range for SWS processing in the refinery SRU.



rocessing sour water stripper (SWS) gas in the refinery sulphur recovery unit (SRU) has always come with warnings about plugging downstream of the reaction furnace due to ammonia salt formation. These warnings usually result in self-imposed operating limits for SWS gas that may not be required and may limit production for the refinery.

Apart from some scientifically validated knowledge about minimum effective furnace temperatures for ammonia destruction, rules of thumb are generally used to establish the safe operating envelope for SWS gas processing in the refinery SRU.

The need to properly understand the science behind the processing of ammonia-bearing streams in the Modified-Claus sulphur recovery unit (SRU) continues to increase as evolving refinery operations, including processing of bio feeds, result in ever-increasing ammonia concentrations in SRU feed gas streams1. The potential risks associated with improper ammonia processing, primarily the concern regarding SRU plugging due to ammonia salt deposition, have resulted in several historical operating recommendations designed to minimise these risks.

As our understanding of ammonia processing continues to grow, however, and as more and more facilities have difficulty meeting these historical guidelines due to

evolving refinery operations, many of these past recommendations are being called into question. Although many papers have been written on the topic of ammonia processing in the SRU in the past2, this paper offers a number of important updates based on the following:

- A recent compilation of all of Sulphur Experts field data on ammonia processing from 2010 to 2019, which represents a very significant increase in actual field results on the subject.
- A number of recent case studies which provide results that deviate significantly from the historical and conventional expectations.
- New lab research (by Alberta Sulphur Research Ltd - ASRL) regarding the chemistry behind ammonia salt deposition3.

The primary purpose of this article is to reexamine these historical ammonia processing recommendations and to determine if they are supported by the updated laboratory and field data. Where appropriate, suggested changes to the historical processing recommendations are provided.

Typical ammonia sources

It is well documented that ammonia is a common product component from various oil refining processes and is usually collected in a plant sour water processing unit4. The facility operator can either recover the ammonia as a usable by-product or must dispose of the streams in an environmentally acceptable manner.

There are various processes available which recover the ammonia and H₂S as separate streams during sour water processing, potentially eliminating the need for processing of the ammonia bearing stream in the SRU process. In general, however, these processes have not been incorporated into most facilities due to capital cost issues and stream purity issues.

These sour water streams, therefore, are normally treated in a traditional single stage sour water stripper process in these single stage strippers, the ammonia is stripped from the water simultaneously with the H₂S, with both ending up together in a sour water stripper (SWS) gas stream. A typical SWS off gas will contain roughly equal parts (i.e. one-third each) hydrogen sulphide (H₂S), water, and ammonia (NH₃), along with small amounts of hydrocarbon and other contaminants. A compilation of Sulphur Experts' SWS gas analyses from 184 field tests (Fig. 1) shows reasonable agreement with this general expectation, although some SWS compositions can vary significantly from this expected one-third NH₃ value and field verification of the SWS composition is always recommended for design and operational purposes⁵.

48

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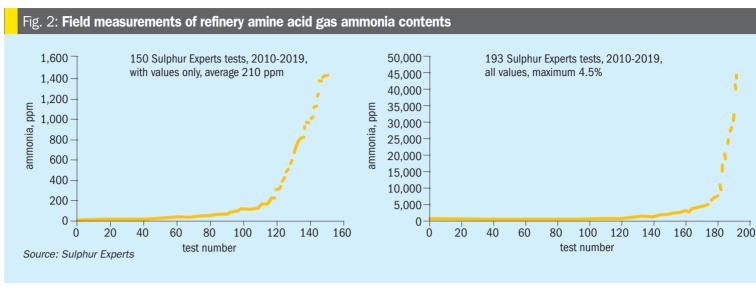
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To a lesser extent, ammonia may also be present in acid gas feed streams which come from the various amine treating systems. A compilation of Sulphur Experts' acid gas analyses from 193 field tests (Fig. 2) shows average ammonia concentrations of around 200 ppm for most streams, although with highly contaminated absorber feed streams and/or poorly controlled amine regenerator systems ammonia levels of 1 to 4+% have been observed. Problems associated with elevated ammonia levels in the amine acid gas stream can be mitigated by either pre-treating the sour gas streams to remove the ammonia or by rejecting the absorbed ammonia from the stripper's overhead reflux water stream4.

Concerns associated with ammonia processing

The primary concern associated with the processing of ammonia-bearing gases is that the chemically "basic" ammonia can react with the chemically "acidic" components present in the process gas streams to create salts.

In the feed gases, where no oxidised sulphur species have yet been created, the primary salt that can be created is from the reaction between ammonia and CO₂. There are a variety of salts that can be created in the SRU feed lines, with an associated variety of solidification temperatures, and a complete discussion of this topic is outside the scope of this paper. It is generally accepted, however, and it is well supported by actual plant operations, that keeping the ammonia bearing SWS gas stream above 85°C (185°F) will prevent formation of any salts in these feed lines. If salts are created at temperatures below these values (Fig. 3), experience has shown that they can be easily removed or reversed simply by increasing the temperature and allowing them to sublimate, or by washing them out of the system with hot water.

Downstream of the SRU thermal reactor. where oxidised sulphur species like SO2 are now present, additional salt species are now possible again with their own variety of solidification temperatures. Although a detailed review of all potential salt species and their formation temperatures is again outside the

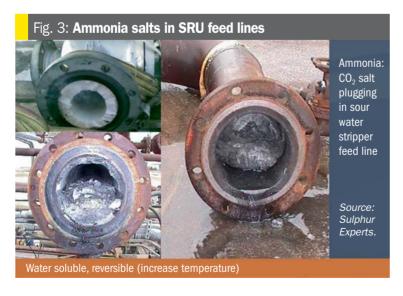
scope of this article, decades of SRU experience has shown that these salts can be created even at "normal" SRU condenser temperatures of 125 to 150+°C (260 to 300+°F). The industry belief is that the salts generated under these conditions are not easily reversed or removed, meaning that the potential for downstream SRU plugging (and associated loss of processing capacity) associated with these salts (Fig. 4) has always been of strong concern to SRU operators.

Ammonia destruction chemistry

To eliminate or minimise the risk of downstream SRU plugging from ammonia salts, a high degree of ammonia destruction in the SRU thermal reactor has always been desired. Previous research has shown the variety of chemical pathways that play a role in ammonia destruction⁶. Potential pathways are displayed in Fig. 5 and are not discussed further in this article.

Regardless of the actual destruction chemistry, both historical lab work and historical field work have proven that complete ammonia destruction is not possible under

Fig. 4: Ammonia salts downstream of the SRU thermal reactor





Ammonia: SO,

29





46

Contents

48

52

2

14

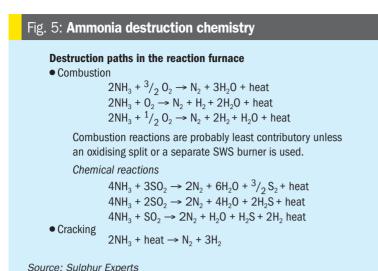
19

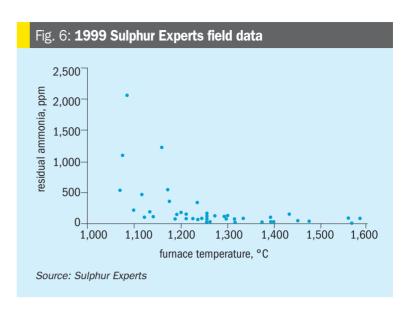
28

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any conditions in the SRU thermal reactor, meaning that the potential for ammonia salt formation in the downstream equipment is always present. Historical destruction recommendations, therefore, have primarily focussed on minimising ammonia breakthrough levels from the thermal reactor, with some additional focus on downstream SRU operating temperatures.

Historical rules for ammonia processing

Some of the earliest lab and field work that first attempted to specifically define the conditions required for optimising ammonia destruction and minimising ammonia salt risk was conducted in the early 1990s. and many of the historical "rules" for SWS gas processing come from this work^{7,8}. This early work was followed up later by detailed lab studies which more clearly defined the thermal reactor residence times and temperatures required to provide high ammonia destruction levels9, as well as by additional field work that confirmed these lab studies in real world settings (Fig. 6)2.

Based on this historical work, a set of "accepted" ammonia processing rules were gradually developed and that most SRUs follow to this day. These rules include:

- Optimal ammonia destruction requires thermal reactor temperatures of 1,250+°C (2,300+°F). Most SRUs use 1,200 to 1,300°C (2,200 to 2,350°F) as processing guidelines.
- Optimal ammonia destruction requires "long" thermal reactor residence times. Guidelines range from 0.8 to 2.0 seconds. There is no consensus, although times closer to the upper end of this range are becoming more common.
- Good mixing efficiencies in the thermal

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reactor are desired; mixing efficiency is primarily determined by the burner design.

- Residual ammonia levels downstream of the thermal reactor should ideally be less than 30 to 50 ppm. Values below 150 ppm have been considered to be "adequate" while residual concentrations over 300 ppm have been considered to significantly increase salt possibility.
- The amount of ammonia present in the feed (combined acid gas and SWS gas feed) should be minimised where possible. Different upper limits for ammonia in the combined feed have been suggested, with 25% being the highest accepted value. This is often expressed as a minimum acceptable acid gas:SWS gas ratio for a facility; 2:1 minimums are the most conservative used in the industry, with 1.5:1 and 1:1 ratios also commonly used. Processing of SWS gas alone (without acid gas) is considered extremely risky.
- The exact origins of many of these rules are unknown, and many are likely anecdotal and based on individual experiences rather than based on solid lab or field data.

Even though many of these "rules of thumb" were initially meant to be general guidelines, many sites have accepted them as hard limits. In some refineries these hard limits on the SRU are already acting as bottlenecks on upstream amine and SWS operation, which in turn limit refinery throughputs and directly affect operating profits. For these SRU-limited facilities, and even for other facilities that have previously had no problems following these rules, changes to refinery operations that affect thermal reactor temperature (i.e. elevated CO₂ levels in acid gas streams) or result in increased SWS gas production relative to acid gas production

(i.e. processing of bio feeds) are resulting in increased scrutiny of these historical guidelines and questions about their necessity.

The other reason that these historical rules are being called into question is the increasing anecdotal operating evidence that has been gathered over the years that contradicts these rules. In general, this anecdotal evidence includes cases where the guidelines have not been met and/or where elevated ammonia breakthrough levels have been measured, but where no ammonia issues have been noted. This anecdotal evidence also includes cases where the guidelines have been strictly followed and where very low ammonia levels are noted, yet ammonia salt plugging has been reported.

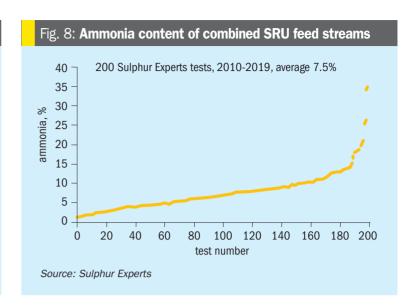
Updated field data on ammonia processing

Sulphur Experts has recently been able to compile a data base of most of its field test results from ammonia processing SRUs from the years 2010 to 2019, and this data has been reviewed with respect to the historical processing guidelines. Although this data set does not include residence time data and is also not able to take "mixing efficiency" into account due to the inability to determine the condition of the burner and thermal reactor internals, it can be used to examine the effect of thermal reactor temperature and feed gas ammonia concentrations on ammonia destruction.

Fig. 7 shows residual ammonia concentrations measured downstream of the thermal reactor relative to the adiabatic (calculated) front chamber thermal reactor temperature. Although this data set does confirm that some of the highest residual ammonia levels correspond to some of the lowest thermal reactor temperatures, it

Fig. 7: Thermal reactor temperature vs ammonia breakthrough

3,000
2,500
2,500
1,500
1,500
1,000
1,000
1,000
1,100
1,200
1,300
1,400
1,500
1,600
1,700
1,800
1,900
2,000
adiabatic temperature, °C



shows many cases where the residual levels exceed the historical guidelines regardless of the temperature. It should be noted that none of these cases of elevated breakthrough, regardless of whether they were associated with high temperatures or low temperatures, resulted in known ammonia deposition issues in any of these cases.

47

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The cause(s) of the elevated breakthrough levels for many of the cases at higher thermal reactor temperatures was not immediately evident from the operating data or design reviews. The elevated values did not appear to be related to issues with low residence time but may have been due to such issues as high heat losses (low actual thermal reactor temperatures), burner damage or other mixing issues, or ammonia present in the acid gas being bypassed to the colder rear zones. In any case, the lack of relationship between breakthrough levels and ammonia salt deposition likely makes further review of the cause(s) of the elevated residual levels less important.

Fig. 8 shows the range of feed gas ammonia concentrations taken from the same

data set. It confirms that, as expected, the large majority of SRUs process feeds well below the maximum recommended guidelines (average feed gas ammonia content was 7.5%); this guideline has been easy to meet for most facilities since most refineries create acid gas stream flows much higher than SWS gas stream flows.

Many facilities, however, process over 10% ammonia in the feed gas, with some exceeding even the most generous historical maximum guideline of 25%.

In order to see if there is any trend between feed gas ammonia and ammonia breakthrough, the data set was graphed in two different ways. Fig. 9 shows ammonia breakthrough directly relative to feed ammonia, while Fig. 10 shows the same ammonia breakthrough results relative to the feed SWS:acid gas feed flow ratio (reversed from acid gas:SWS ratio in order for a better display of the results).

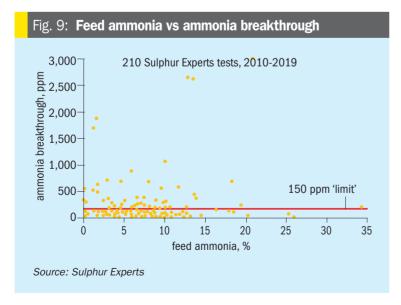
These two graphs again both show a large number of cases where the residual ammonia levels exceed the historical guidelines regardless of the feed gas ratio

or combined ammonia concentration. In addition, they don't show any distinct trend towards increasing breakthrough of ammonia at elevated feed ammonia levels or SWS:acid gas ratios.

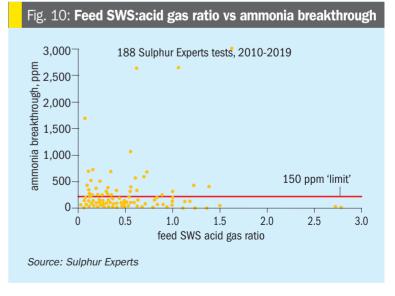
As with the previous graphs, it should be noted that none of these cases of elevated breakthrough, regardless of whether they were associated with meeting or exceeding the historical guidelines for feed, resulted in known ammonia deposition issues in any of these cases.

Overall, even though the data set generally confirms what was already known about improved ammonia destruction at elevated thermal reactor temperatures, it does not support the historical rules regarding feed concentrations and ratios and does also not show any link between residual ammonia and ammonia salt plugging risk (at least within the range of breakthrough ammonia values measured by the data set).

This clearly points to the fact that factors other than what were covered by the historical rules are likely related to ammonia salt risk.







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52

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12

9

18

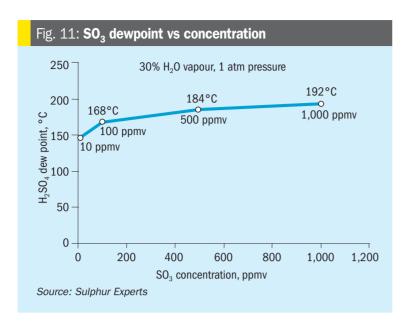
27

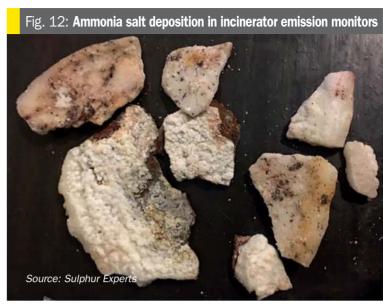
41

45

46

32





Updated lab data on ammonia processing

The most significant new research that provides an updated understanding of ammonia salt deposition was released by ASRL in 20213. The full results of this study are available in their paper, however the key findings related to ammonia residuals reacting with SO₂ are summarised below, along with Sulphur Experts' interpretations of these results:

- With typical ammonia residuals and no SO₃, ammonia salts will not form at temperatures above 98°C (208°F) for any range of NH₃ or SO₂ that might normally be expected in SRU process gases, even in a significant SO2 or NH3 upset case.
- The exact temperature of the salt formation depends on the partial pressures of SO₂ and NH₃ in the gas, however, again these salts will only be created at temperatures below the freezing point of sulphur under any normally expected conditions.
- To form salts at the 125+°C / 265+°F process temperatures seen even in the coldest areas of the SRU (condensers) required percent levels of NH₃ in the lab version of Claus tail gas with normal SO₂ content and no SO₃.
- In short, ammonia + SO₂ salts will likely only form at temperatures well below the sulphur freezing point. In this case, the frozen sulphur is the root plugging problem despite the fact that the salt may also be present in samples of the solid plugging material.
- Massive upsets (extremely high SO₂/ extremely high ammonia slip) might cause salt formation at normal SRU

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temperatures; however, any level of "normal" ammonia slip will NOT create salts at typical SRU temperatures without SO₃ present.

Instead of ammonia:SO2 reactions causing SRU salts, the same ASRL research showed the role of SO₃ in salt formation. Again, the full results of this study are available in their paper, however the key findings related to ammonia residuals reacting with SO₃ are summarised below, along with Sulphur Experts' interpretations of these results:

- The presence of SO₃ means that sulphuric acid can form by acid condensa-
- SO₃ dewpoints overlap Claus operating temperatures; even single digit ppm levels of SO₃ will condense at normal Claus condenser temperatures (Fig. 11)10.
- The sulphuric acid created during condensation readily reacts with ammonia to form salts; these salts are the same types are usually identified in ammonia salt plugging cases

 $NH_3 + H_2SO_4 \rightarrow NH_4HSO_4$ $NH_3 + NH_4HSO_4 \rightarrow (NH_4)_2SO_4$

In short, any ppm levels of SO₃ will react with any ppm levels of NH3 to create ammonia salts.

SO₃ formation

The chemistry required for optimal sulphur plant operations dictates that only one third of the H₂S entering the sulphur plant be combusted to SO_2 in the thermal reactor, with H₂S and SO₂ then reacting in a 2:1 ratio throughout the rest of the SRU11. This initial one-third combustion of H₂S means

that the thermal reactor is a very reducing atmosphere, and even large upset conditions will almost never end in an oxidising atmosphere. Because of this extremely reducing condition, and because of the high thermal reactor temperatures, any SO₃ that might be created in the combustion zone of the thermal reactor would not be stable and would reduce back to SO2 before exiting the thermal stage. This typical lack of any SO₃ formation from the thermal reactor is confirmed by the low prevalence of ammonia salt problems in the industry; if the presence of SO₃ exiting the thermal reactor was common, then ammonia salt issues would be equally common.

Laboratory research has shown that SO₃ can be released by sulphated alumina catalyst12. Once again, however, the generally low level of ammonia salt problems in the industry suggests that any SO₃ present in the sulphur plant process gas due to this chemical pathway must be extremely low.

The one place in an SRU where SO₃ is almost always created is in the sulphur plant incinerator/thermal oxidiser. The same oxidising conditions, however, that create the SO₃ would also destroy any ammonia present at this point, meaning that ammonia salt deposits in the incinerator are not a common issue. Sulphur Experts has, however, worked with plants where incinerator SO₃ and incinerator NH₃ are both present, and rapid and constant ammonia salt deposition in the relatively cold incinerator emission monitoring systems at these locations (Fig. 12) have confirmed that salting and plugging are an issue.

The most likely location where SO₃ could be created and sustained upstream of an SRU incinerator is in an acid gas fired reheater (also commonly called an acid

Fig. 13: Case study 1 flow and pressure trends 130,000 Total SRU 2 throughput and front end pressure -12 18 SRU Train 2 normalised pressure, 27 July - 3 September 2021 switch to rising dP 16 11 120,000 14 normalised pressure, psig 110,000 12 100,000 90.000 plugging resolved and capacity 80,000 restored 70,000 total train throughput front end pressure (right axis) $23.07.24 \times 07.02.08.21.08.21.08.21.08.21.08.21.08.21.08.21.09.21.09.21$ 27.07.21.07.21.08.28.08.21.08.21.08.21.08.21.08.21.08.21.08.21.08.21.08.21.08.21 Source: Sulphur Experts

gas-fired auxiliary burner). These reheaters burn a slipstream of the feed acid gas in a fired heater, which then mixes with the cool upstream process gas from an SRU condenser before entering the downstream catalyst bed and then the next condenser. Although these reheaters are designed to operate under substoichiometric (reducing) conditions, usually 60 to 75% of stoichiometry¹³, they could operate either partially or fully under oxidising conditions in cases such as inaccurate metering, use of air for burner purges, or damaged burners where multiple stoichiometry zones are present. Since this reheater stream is immediately cooled/quenched by mixing with the relatively cold condenser outlet stream, the further reaction of SO₃ back to SO₂ downstream of the reheater may not be possible. This SO₃ would then condense when it drops below its dewpoint, most likely in the next condenser, and be available to react with whatever NH₃ is present at that point.

Other sources of SO₃ could also be present in a sulphur plant, including SO₃ created by fires within the SRU during poorly controlled shutdowns or hot standby operations, 100+% combustion of acid gas in the thermal reactor, or any other type of SRU operation that results in an oxidising atmosphere in any part of the plant.

Case studies supporting new lab data – example 1

In 2021, Sulphur Experts was involved with an SRU plugging study for a USA refinery where this knowledge of the role

of SO₃ could be put to a real-world test. The background behind the request for assistance was:

- Two identical SRUs both processing similar acid gas and SWS gas volumes and having similar thermal reactor operating conditions.
- Both SRUs use three fired reheaters which normally operate on acid gas, although they were also capable of operating on natural gas.
- Only previous plugging history had been due to carbon soot deposition, with the plugging materials analysed and confirmed to be ammonia free (carbon and sulphur only).
- Sudden onset of rapid and persistent plugging in the final condenser of one SRU only. Resulting pressure drop issues were reducing the capacity of the SRU and, correspondingly, of the entire refinery.

The first round of Sulphur Experts' analytical testing of the affected SRU determined the following conditions:

- Normal SWS composition; approximately one-third NH₃
- Clean acid gas; 16 ppm NH₃.
- Measured thermal reactor temperature 1,298 to 1,358°C (2,370 to 2,477°F), consistent with historical operation.
- Measured ammonia residuals 65 ppm.
- Near identical conditions for the second (unaffected) SRU.
- Third reheater showed variable oxygen exiting the reheater of 650 to 4,200 ppm which could not be eliminated by ratio changes.

Although direct measurement of SO₃ from the reheater was not undertaken due to the lack of reliable field test methods for this type of analysis, the measured excess oxygen confirmed an oxidising atmosphere in the reheater. Although the metered air and acid gas flows to the reheater were consistent with significantly substoichiometric operation, a visual examination of the burner through the site glass showed obvious burner damage meaning that poor mixing efficiency and simultaneous high/ low stoichiometry zones within the same burner were likely. This poor mixing efficiency was also evident from other analytical results, which showed that a portion of the hydrocarbons present in the acid gas feeding the burner were not combusted.

Since oxygen (SO₃) could not be eliminated by ratio changes to the acid gas burner, the reheater was switched to a substoichiometric natural gas burning mode, which used a separate undamaged burner assembly within the same reheater chamber. This change resulted in the immediate elimination of measured oxygen (and hydrocarbon) from the reheater effluent.

As soon as the switch to natural gas was conducted, the rapid increases in pressure drop that had been noted through the sulphur plant for the previous week of operation immediately stopped (Fig. 13). In an even better, and unexpected, outcome for the plant, the pressure drop actually started to gradually decline and within two weeks the pressure drop and plant throughput were both back to, or even slightly better than, normal.

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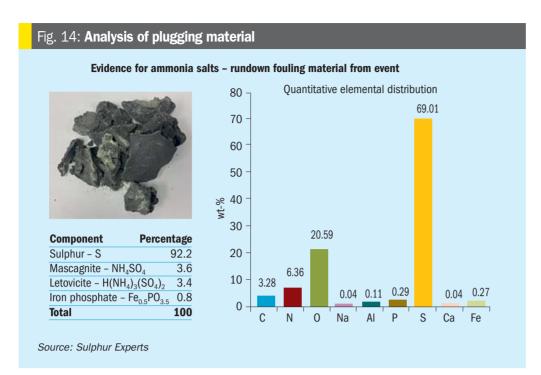
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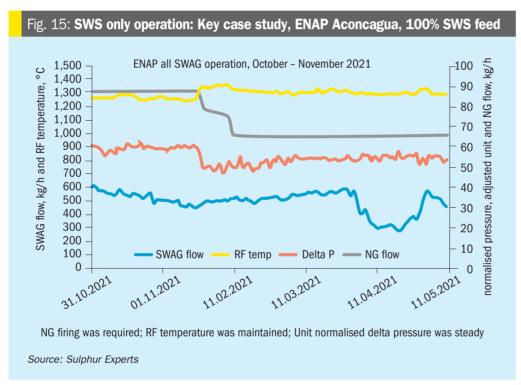
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Prior to the reheater changes, plugging material was also collected from the final condenser, since some of these materials were present as solids in the rundown system. Analysis of these materials confirmed the presence of ammonia salts (Fig. 14) confirming that the plugging was indeed ammonia related.

It should be noted that no other changes to the SRU operation were conducted other than switching the reheater fuel source: both the thermal reactor temperature and the final condenser temperature remained unchanged.

The only difference was the elimination of the reheater oxidising atmosphere, meaning the minimisation or elimination

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of the possibility of forming SO₃ in the reheater. The reduction of the pressure drop after the SO₃ formation was eliminated suggests that the ammonia salts that had been formed were disappearing, either being physically washed from the system by the liquid sulphur flow or by some type of chemical decomposition.

It is notable that this case study was consistent with other Sulphur Experts' past troubleshooting experiences where ammonia salt plugging issues occurred almost exclusively in sulphur plants with fired reheaters, and where modifications to these reheaters were the ultimate solution (as opposed to trying to change the ammonia breakthrough levels). This case study,

as well as these other field experiences, are completely in keeping with the ASRL work showing that the presence of any SO₃ even with low ammonia residuals leads to salt formation, and the elimination of the SO₃ is the key to stopping the salt formation. The reversal / removal of the salts in this field result case provides optimism that ammonia salt issues in other facilities can not only be stopped through SO₃ elimination, but that lost capacity can actually be recovered once the ongoing salting issue has been corrected.

Case studies supporting new lab data - example 2

The data presented above, including Sulphur Experts' historical data, the ASRL findings, and supportive case studies, have resulted in an increased willingness by Sulphur Experts and some of its clients to question and even abandon (at least temporarily) some of the historical rules regarding ammonia processing. In a second case study, a client with a strong operational incentive to process only SWS gas when acid gas was not available was encouraged enough by the changed understanding of ammonia processing to attempt a five-day run on SWS only. The plant data collected from the SWS-only run is shown in Fig. 15.

Although on-site analyses were not collected for this test run, Sulphur Experts provided advice on operating conditions (primarily regarding maintaining acceptable reaction furnace temperatures through the cofiring of natural gas) and advice on process monitoring (constant pressure monitoring as an indication of any ammonia salt deposition). The refinery design included high pressure steam reheaters only, so the possibility of SO₃ formation downstream of the thermal reactor was considered to be zero. Using the updated understanding of ammonia salt deposition, this meant that the risk of ammonia salt deposition, despite running SWS gas only (33% NH_3) was also near zero.

The Fig. 15 data shows that no increase in normalised pressure through the SRU was noted during the five day run, and no operational issues overall were encountered. This has provided the client with the confirmation needed to conduct further SWS-only operational periods when no other economic alternative to this mode is available in the future (i.e. when acid gas is unavailable and when sour water storage is also not available).

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Case studies supporting new lab data – example 3

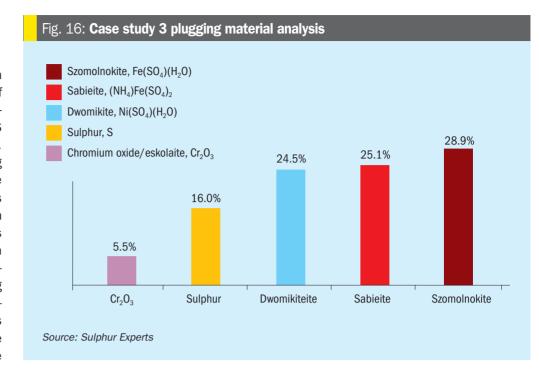
A final recent case study that once again supports the new understanding of ammonia processing comes from a nontraditional sulphur plant that treats H₂S on a batch (instead of continuous) basis. Despite having no SWS gas and having only small ppm levels of ammonia in the acid gas feed, and despite test results showing less than 20 ppm of ammonia exiting the thermal reactor, the plant has experienced ongoing plugging issues with both ammonia salts and corrosion products appearing in analyses of the plugging materials (Fig. 16). Preliminary troubleshooting for the site confirmed periods of overall oxidising operation within the sulphur plant related to the batch nature of the operation, which likely lead to periods of SO₃ formation and subsequently to both the corrosion and the ammonia salt formation. Using the new understanding of ammonia processing, the site is currently focussing on eliminating the SO₃ formation rather than on any attempts to control ammonia feed or residual values.

Conclusions/summary

The data presented in this article has given Sulphur Experts a high degree of confidence that cases of ammonia salt deposition are primarily related to rare instances of SO₃ formation within sulphur plants and that ammonia salt formation has a much lower connection with ammonia feed or breakthrough values than historically believed. Although Sulphur Experts is not ready to fully abandon the old rules, and believes that further research and further field studies and cases will be required before an industry-wide modification of the rules can be recommended, the modified conclusions and recommendations that Sulphur Experts currently provides to industry clients can be summarised as follows:

- High destruction of ammonia is still generally desirable in order to limit the quantity of ammonia available for salt formation. Exact ammonia breakthrough concentrations, however, are not a primary determinant of plugging risk at any reasonable levels - don't fixate on exact levels or limits.
- Reasonable reaction furnace temperatures are still desirable, but again are not a primary determinant of plugging

Sulphur 405 | March-April 2023



- Minimum acid gas to SWS ratios and/ or maximum total feed NH3 levels are likely not required; focus on temperature regardless of ratio.
- When deviating from the historical rules for the first time, keep a close eye on SRU pressure profiles. As long as pressures don't change, ammonia salts are likely not occurring to any extent that vou care about.
- For any pressure issues believed to be associated with ammonia salts, focus first on possible sources of SO₃ formation. Acid gas fired reheaters are the most likely source, although SO₃ could also be created under other oxidising conditions.
- Be aware that ammonia salts may also be present due to SO₂ + NH₃ reactions at temperatures below the freezing point of sulphur. In these cases, however, the low temperature (frozen sulphur) is the root cause of plugging problem and the fact that ammonia salt is also present does not mean that poor ammonia processing is at fault.

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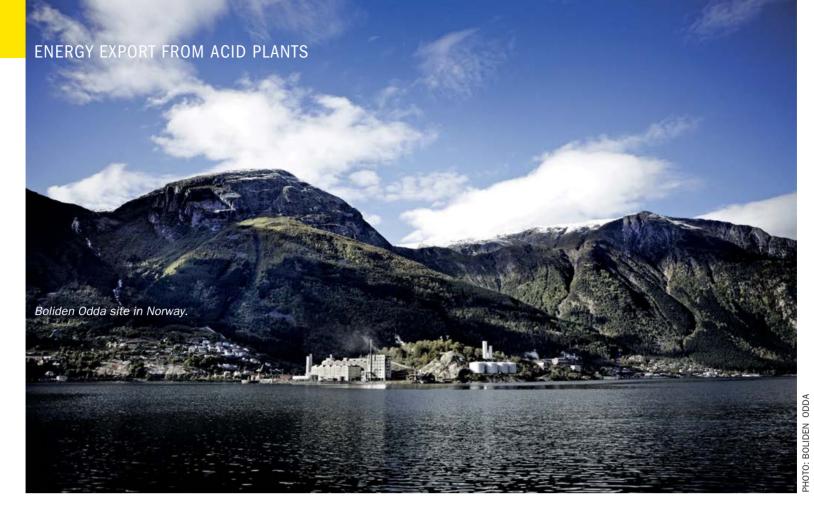
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Sulphuric acid plants as a source of carbon free energy export

The sulphuric acid process is virtually carbon free and, as such, it is important to consider the energy requirements of the associated industrial complex before deciding upon what form the energy should be exported from the acid plant. In this article, Stefan Braeuner, Stefan Mohsler and Anne Mohsler of Metso Outotec use case studies to exemplify the need to fully analyse the local conditions at site before a decision is taken on a specific flowsheet.

irst, some home truths regarding sulphuric acid plants as a source of carbon free energy. In general, sulphur burning sulphuric acid plants can be considered virtually carbon free in their entirety. This is also the case for the complete metallurgical value chain - in other words, the pyrometallurgical process (smelter/roaster), gas cleaning and associated sulphuric acid plant. In all that we strive for in the industry, it has little to do with carbon!

It is therefore important to consider what form of 'carbon free' energy best suits the specific needs of the upstream/ downstream operation and not just consider that maximising steam generation to produce electrical power as the one and only solution for an acid plant complex. For example, payback for an optimised, high efficiency turbogenerator set and associated infrastructure in a country where abundant hydropower is available at low cost must be investigated for its economic sense. The aim might not be to maximise the export of electrical energy, but rather produce just enough for the plant's own needs and thus remove the reliance on external power sources.

Surplus energy can then often be used as, for example, heating steam in processes for drying of ores or other sections requiring heat input. The same consideration needs to be given to low level heat available in acid plants, as such heat can on one hand be transformed to low pressure steam with significant additional equipment or recovered as hot water for applications such as phosphoric acid preconcentration or district heating with a much lower level of investment intensity and added complexity within the acid plant.

Beside these fundamental considerations there is a need to consider details in plant design to improve operational KPIs such as specific energy or water consumption. Here a critical review of initial investment versus operational cost needs

36

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to be carried out. Furthermore, the impact of digitalisation in supporting operational KPIs is not yet fully visible today and first initiatives show promising results.

In the following pages, a number of existing metallurgical acid plant references are presented as case studies that have, for a number of site-specific reasons, chosen 'carbon free' energy export related solutions to suit their specific operational requirements.

The common denominator of all the projects is that specific technologies for the particular needs of the overall plant complex have been introduced, supporting the overall operational KPIs.

Case 1: MP steam export

Metso Outotec is currently delivering a copper smelter complex, with scope including flash smelting, flash converting, gas cleaning and Lurec® technology. This smelter complex will process 1.7Mt/a copper concentrate.

The sulphuric acid plant, based on the proprietary Lurec® technology, has a number of distinct features that have been proven in operating reference plants and can be considered particularly sustainable and indirectly mitigate significant CO₂ emissions:

Thanks to the off-gas composition originating from the flash smelting furnace (FSF)/flash smelting converter (FSC) combination, the acid plant processes approximately 300,000 Nm³/h of gas at 17% SO₂ in a single process train and ultimately produces some 5,500 t/d of sulphuric acid - the largest single train acid plant in the world.

- The Lurec® technology enables the gas to be processed in a single acid plant, leading to a significant reduction in plant footprint, equipment size and scope of supply, civil works and plant erection. Although no calculation has taken place to estimate the inherent CO2 savings, this may well be significant.
- Due to processing a reduced but higher SO₂ strength gas stream, significant savings in specific energy consumption and cooling water can be achieved.
- SO₂ emissions are reduced by approximately 40% based on utilising the Lurec® concept versus two conventional acid plants.
- Furthermore, the plant is expected to export around 75 t/h medium pressure steam at 24 barg, which was considered the most valuable energy export format for the copper complex as a whole. This steam is used for copper concentrate and matte drying, thus allowing the high pressure smelter steam to be utilised for power generation.

Case 2: Excess heat utilisation

A further example of utilising the excess heat of the sulphuric acid plant is exemplified at Boliden's Harjavalta plant.

Boliden's Harjavalta sulphuric acid plant.

Sulphur 405 | March-April 2023

As already presented at the Sulphur + Sulphuric Acid Conference in 2018, the acid plant processes an offgas volume of approximately 149,000 Nm³/h @ 14% SO₂ from various sources including a Ni FSF, weak acid thermal decomposition and partially from two Peirce Smith converters and one Cu FSF. The 2,400 t/d plant includes a five-bed converter enabling compliance with SO₂ emissions of 100 ppm, as well as a modular NOx removal system.

Boliden's carbon free energy export requirements were for steam and hot water to export into their existing infrastructure, namely:

- 25t/h steam at 38 barg is produced from the exothermic reactions around the five-bed converter HX configuration. The boilers are arranged directly after bed 3 and 5 to keep their outlet temperatures higher than in conventional layouts; this is to gain an extended lifetime especially under fluctuating operating conditions.
- The reactions in the IAT and FAT as well as the DT are also exothermic, leading to a temperature rise of the acid. The heat from intermediate absorption is removed via a shell-and-tube type acid cooler which is operated in a closed loop water circuit. With such a system, power plant water is safely heated up from 55°C to 92°C which yields 37 MW under design flow conditions. The heat from the other sources is not utilised. A trim cooling is installed for operating conditions when there is no demand for hot water.

Case 3: Additional heat recovery from the sulphuric acid circuit

Whilst the first two examples focussed on efficient use of heat from the gas phase, Eti Bakir's integrated fertilizer and metals recovery complex in Mazidagi/Turkey additionally recovered the heat from the sulphuric acid circuit.

Back in 2013, Eti Bakir was considering how to balance the following issues into a viable business case:

- to build a combined fertilizer and metals processing facility at one location;
- energy production from the various unit processes would also provide a degree of self-sufficiency for the integrated plant complex;
- intent to produce 20% of Turkey's fertilizer needs indigenously;

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48

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■ Contents 46

38



Eti Bakir's sulphuric acid plant in Mazidagi, Turkey.

a fertilizer complex capable of producing the fertilizer requirements for the whole of the Harran Plain.

The project was presented in detail at the Sulphur + Sulphuric Acid Conference in 2019 and involves steam raising capability of the complete pyrite roasting value chain (roaster-gas cleaning-acid plant) which enables 33.5 MW of electrical power to be produced, enough to cover the needs of the entire metals complex (some 16.5 MW), as well as exporting a further 17 MW to the external electrical grid.

The sulphuric acid production of 2,080 t/d is quite conventional with an acid quality requirement of As <0.1 mg/kg acid, Hg <1 mg/kg acid and plant emission of <2 kg SO₂/t acid. The sulphuric acid plant has one distinct feature, namely the recuperation of low-pressure steam (via the HEROS[™] process). In a metallurgical acid plant with interdependencies of upstream and downstream demands, it is critical that interruption of production is minimised.

Case 4: Sustainable operation

The relevance of sustainable operation operation is depicted in this case study, namely Boliden Odda's Green Zinc Project in Norway.

In December 2021, Metso Outotec secured a contract with Boliden for the expansion of the current Odda site where they plan to increase their annual production capacity of zinc metal from 200,000

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to 350,000 tonnes. The project is called Green Zinc Odda, and its energy consumption is based on fossil-free energy. Metso Outotec scope of delivery includes roasting and off-gas cleaning solutions and a sulphuric acid plant. Metso Outotec will also supply hydrometallurgical equipment and technology for calcine leaching, solid liquid separation, solution purification, as well as process and plant engineering and site services. Plant commissioning is anticipated to take place in summer 2024.

The roaster/gas cleaning/acid value chain will produce approximately 50 t/h superheated steam in total. Extracted low pressure steam is used for internal processes and also routed to further consumers within the Odda facility. With the installed turbine generator unit, which can be operated in island mode, 10 MW of power is generated. Depending on the roaster feed, the acid plant processes some 74,800 Nm³/h of offgas, produces 817 t/d of sulphuric acid monohydrate and reaches best in class SO₂ emissions of less than 20 mg/Nm³.

The Boliden website quotes as follows, "The expansion enables Odda to almost double the zinc production [whilst] reducing the carbon dioxide intensity by 15% from already a world record leading position. Most of the facilities will be expanded alongside we will modernise our processes, increasing digitalization and automation." and Metso Outotec is deservedly proud to be part of this leading-edge initiative in the industry.

Case 5: Brownfield acid plant retrofit

Beside such greenfield cases, where the design can be optimised from the get-go, there are many instances of brownfield acid plant requiring significant retrofits to maximise operational KPIs.

A copper smelting complex, commissioned in the 1970s with a capacity of 40,000 t/a of copper from concentrate, has undergone several expansions and technical modifications in the interim period and the production level is currently around 300,000 t/a of copper. Nowadays, the smelter uses an Outotec flash furnace, Peirce Smith converters, anode furnace, an electrolytic copper refinery and three sulphuric acid plants, and produces 1,000,000 t/a of sulphuric acid.

The addition of the heat recovery system in one of the acid plants drastically increased the efficiency of operation. Highgrade heat, which used to be dissipated to the atmosphere, is now recovered as superheated steam and turned into carbon neutral, additional electricity in copper complex's power plant. The superheated steam now produced at the heat recovery system at a pressure of approximately 40barg is sent to the power plant turbine for electricity generation. The average steam generation amounts to around 9 t/h, depending on the SO₂ gas strength fed to the plant.

Further reductions in energy consumption were achieved by the no longer required cooling fan, reduction of heat transferred to the acid and the reduced pressure drop of the plant. Although the plant flowsheet complexity has increased, the operation of the plant has not.

Safe operation of the heat recovery system was considered from design to execution and operation of the project. Rather than ignoring the possibility of a leak, the rapid detection by online moisture measurement as well as strict monitoring of critical process parameters were considered a first priority. Together with the well-trained staff of the copper complex, this has resulted in a trouble free and efficient operation.

Summary

When considering what form of energy is exported from a sulphuric acid plant, the above case studies exemplify the need to fully analyse the local conditions at site before a decision is taken on a specific flowsheet. One size does not fit all.

Sulphur 405 | March-April 2023

Improving the performance of the SRU thermal incinerator

Following the success of VectorWalls™ in the reaction furnace of sulphur recovery units over many years, VectorWalls™ are now delivering similar benefits in SRU thermal incinerators. Uday N. Parekh of Blasch Precision Ceramics reports on the deployment of VectorWalls™ to improve the performance of the SRU thermal incinerator and provide benefits such as lower fuel gas consumption and lower CO₂ emissions.

hermal incinerators treat the tail gas effluent from SRUs prior to emitting the waste gas to the atmosphere. Their key function is to facilitate the combustion / oxidation of H2S, COS, CS2, sulphur vapour, H₂ and CO to the mandated stack gas outlet specs for CO, TRS, etc. Achieving this objective requires the careful optimisation of various input parameters: Higher incinerator temperatures and excess oxygen in the stack improve the ability to meet performance specs but

with an economic penalty of higher fuel gas consumption and an environmental penalty of higher CO₂ emissions. Also, higher residence times in the incinerator achieved via larger incinerator size can help but this comes with higher capital cost. So, these parameters must be optimised to minimise capital costs and more importantly the operating costs and CO₂ (GHG) emissions.

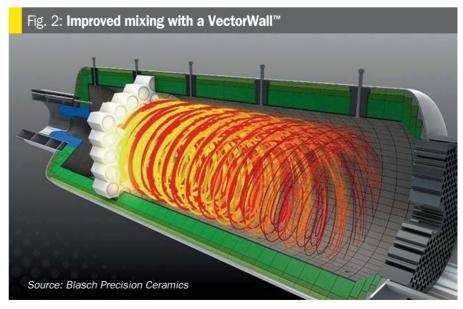
This article describes the deployment of customised checkerwalls (VectorWalls,

Fig. 1) to improve the performance of the incinerator. For background, these walls were developed for use in the SRU reaction furnace (RF), first to offer improved structural integrity, but were subsequently refined to provide better RF performance via tighter residence time distribution, higher front-end temperatures and enhanced turbulence for better mixing (Fig. 2), the three Ts of combustion1. These have been successfully deployed at hundreds of SRUs worldwide over the past 20+ years, significantly improving RF conversion and contaminant destruction. Based on this success there has been a strong interest in these VectorWalls[™] delivering similar benefits in the thermal incinerator. These walls have been recently deployed in a few incinerators in the Middle East and have yielded the desired performance benefits via providing better mixing, and higher temperatures and residence times. Specifically, they have resulted in lower fuel gas consumption contributing to operating cost savings and also lower CO₂ emissions that are becoming increasingly desirable.

Incinerator theory

Sophisticated models based on rigorous theory and empirical correlations are used for the design and optimisation of the thermal incinerator. These models honed through the years using field measurements to develop kinetic correlations help predict the extent of the various oxidation reactions and breakthrough of H₂S, COS, CS₂, H₂ and CO². The correlations predict exit species concentration as a function of inlet compositions, excess O2 at the stack outlet, incinerator temperature, residence time and a kinetic design factor "K". K is an empirical factor





Sulphur 405 | March-April 2023

www.sulphurmagazine.com

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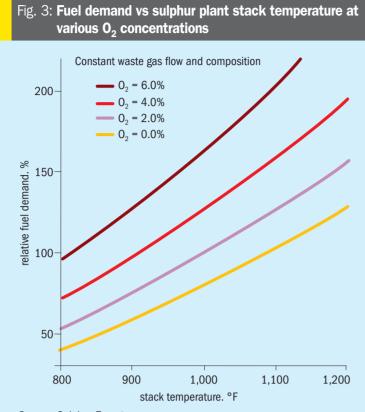
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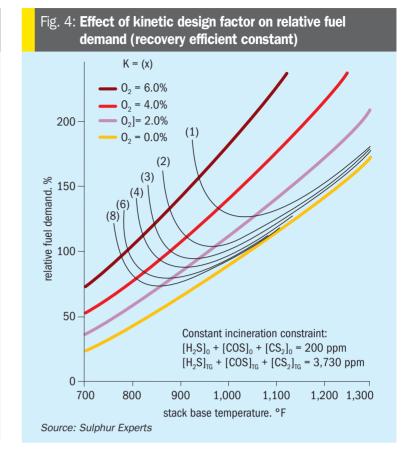
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Source: Aspen Technology

H,S concentration, ppm





which describes the extent of mixing between the various process streams entering the system and is equipment and design specific. A higher K value results in lower component breakthrough; alternatively same exit compositions can be achieved at lower temperatures and fuel gas consumption resulting in substantially lower CO₂ emissions.

Fig. 3 depicts how higher temperature and excess oxygen result in better thermal incinerator performance but at the cost of higher fuel gas consumption and hence CO_2 emissions. Figs 4 and 5 demonstrate the dramatic decrease in fuel gas consumption

Fig. 5: Effect of kinetic design factor on H₂S emissions

and H_2S emissions respectively from higher K factors. So, besides the design parameters of operating temperature and excess oxygen it can be seen that higher K factors can also significantly improve the performance of the incinerator and importantly this is achieved without the direct penalty of higher CO_2 emissions. Blasch VectorWalls through their ability to provide extremely enhanced mixing, have been discovered to be ideally suited to provide higher K factors and improved incinerator performance. Additionally, the shielding of the heat loss by the Vector tiles provides higher front-

K = 1

K = 2

K = 3

K = 4

K = 6

K = 8

end incinerator temperatures and improved kinetics resulting in improved incinerator performance. Further, Blasch has developed different tile geometries that can provide even better capture of the heat in the incinerator (Fig. 6) resulting in even greater fuel savings and these will be tested in collaboration with one of the operating companies.

The benefits of better mixing (higher K factor) and higher temperatures in the incinerator offers the following options to an operating company based on where they stand with current operations:

- same performance at lower temperature and fuel gas consumption;
- better performance at same temperature and fuel gas consumption.

Fig. 7 depicts the relationship between CO concentration and incinerator temperature for an operating unit in the UAE. It shows that a slightly higher temperature than 700°C is required to achieve the CO limit of 400 ppmv. This is an ideal case where deployment of a VectorWall would aid in achieving the higher incinerator temperature needed without the need for firing additional fuel gas with its attendant higher CO_2 emissions.

Operating results

The preliminary results from the deployment of the Blasch VectorWalls $^{\text{TM}}$ in the thermal incinerator have been very encouraging. Fuel savings of close to 10% have



40 www.sulphurmagazine.com

temperature, K

Sulphur 405 | March-April 2023

Fig. 7: Relationship between CO concentration and incinerator temperature U 52/53/54/57 incinerator temperature and CO concentration at 3 mol-%, O_2 (dry) 3,200 2,950 2,800 (dry) ppmv 2.400 CO concentration at 3 mol-% 02, 2,000 1,600 1,552 1.325 1.060 1,200 880 800 665 517 ADNOC limit: 400 ppmv 400 0 640 700 720 620 660 680 incinerator temperature, °C Source: GASCO, MESPON 2017, Mr. Dheeraj Nagwani

been realised and it is anticipated that this can be further enhanced with the Gen 3 Vector Tile designs that can offer even higher front-end incinerator temperatures and resultant greater fuel gas savings. Applying these fuel savings to say a 1,500 t/d gas plant SRU will result in operating cost savings of about USD one million per year plus the associated carbon credits.

Conclusion

The various avenues to improve the performance of the SRU thermal incinerator include:

- reduce COS and CS₂ load to the incinerator via specialised catalysts in the first converter;
- higher residence times in the incinerator;
- higher fuel gas firing to provide higher temperature to meet CO and other emission regulations;
- high efficiency burners:
- oxygen enrichment

A VectorWall[™] through its unique ability to improve mixing and front-end temperatures can supplement or even be a substitute for some of the above options, offering operational savings, lower CO2 emissions and an improved margin for operating within the specified emission regime.

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Sulphur 405 | March-April 2023

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Sneaky SO, breakthroughs

SO₂ breakthroughs remain an ever present threat to the successful operation of reductive, quenchamine-based tail gas clean-up units (TGUs). Effects can range from mild and annoying to quite severe, including failure to comply with environmental permit regulations and refinery shutdown.

G. Simon A. Weiland, Nathan A. Hatcher, Prashanth Chandran, Daryl Jensen, Ralph H. Weiland, Jeff Weinfeld of Optimized Gas Treating, Inc. and Michael Huffmaster, Consultant.

t has been shown that SO2 breakthroughs are one of the most damaging and devastating process upset events that can occur within a sulphur processing unit. The damage, if not caught and mitigated in time, can include both the quench water loop and TGU amine section. Of the extensive list of problems that can occur, corrosion and plugging are the most common for the quench water loop while solvent degradation and loss of selectivity leading to high CO₂ recycle rates are most common if the problem is severe enough to make it into the TGU amine section. In a refinement to work conducted by OGT in 2016 and focused on the effects of these breakthroughs on the downstream equipment, this article assesses the way aged and poisoned Co/Mo catalyst can increase the risk of SO₂ breakthroughs. A plausible explanation for chronic, low-level SO2 ingress into a quench column that happened off and on at one facility for many years is demonstrated through a newly available kinetic hydrogenation reactor block in the SulphurPro® simulator. With this work, OGT hopes to raise awareness in the industry for other facilities with SCOT-type TGUs by looking more specifically at how these upsets occur in the first place. The hydrogenation reactor is the main equipment item responsible for converting SO₂ back into H₂S which the downstream amine unit can then absorb and recycle to the front of the sulphur recovery unit (SRU).

Process background

Understanding how an SO₂ breakthrough can occur in an SRU requires a basic understanding of the overall process and the path that sulphur takes. The sulphur recovery complex in a refinery or gas plant is visualised as part of the overall system for extracting H₂S as well as other acid gases and organic sulphur compounds

from the product stream. The acid gases (which include H2S) are extracted and produce a generally concentrated H₂S stream. This H₂S-rich stream is then fed to an SRU which consists of Claus-type sulphur conversion, a tail gas unit (TGU), and a thermal oxidiser (TO) before the gas is then vented to the atmosphere. The sulphur compounds are recovered as elemental sulphur and, because these systems are not 100% efficient, the small remainder that is not recovered is emitted to the atmosphere.

The fundamental Claus chemistry converts H₂S into elemental sulphur through a thermal stage and two or three catalytic stages with around 95-97% efficiency:

$$H_2S + \frac{3}{2}O_2 \rightleftharpoons SO_2 + H_2O$$
 (thermal stage)

$$2H_2S + SO_2 \rightleftharpoons \frac{3}{\chi} S_{\chi} + 2H_2O$$
 (thermal and catalytic)

The TGU processes the off-gas from the SRU which helps to meet the tight sulphur recovery requirements of today's environmental standards. The TGU consists of a multi-step process where the off-gas from the SRU is first passed through a catalyst bed, where the hydrogenous conversion of non-H₂S sulphur species to H₂S occurs. This catalytic stage is also responsible for continuing the Claus process and it watergas shifts carbon monoxide into hydrogen which helps the hydrogenation reactions along with reducing CO emissions. In the hydrogenation reactor the main sets of reactants in the reactor are:

- COS, CS₂ hydrolysis on alumina cata-
- SO_2 , S_x , COS, CS_2 hydrogenation on Co/Mo catalyst
- CO water gas shift on Co/Mo catalyst

The actual process chemistry is complex consisting of several parallel reactions and reactions between SO₂ and other reduced sulphur species to be discussed later.

The next step in the TGU is quenching the hot gas produced from the hydrogenation reactor. This step not only cools the hot gas but removes much of the water that is produced as a by-product from the Claus reactions. This is the first line of defence when facing an SO₂ breakthrough. The pH of the quench water is monitored, and caustic (or sometimes ammonia) is injected when the pH drops below a certain threshold in order to neutralise and absorb the acidic SO₂ before it makes its way to the next section of the TGU, the

The amine circuit of a TGU aims to absorb H₂S selectively while letting CO₂ continue out of the absorber with the remainder of the gas. The H₂S absorbed is then sent to the amine regenerator where the H₂S is stripped out of the solvent and returned back to the front of the SRU. The addition of a TGU to an SRU can give an overall recovery performance of >99.9% efficiency (depending on the amine and the general operation of the amine circuit).

A critical performance requirement for the catalyst used in the hydrogenation reactor is that SO₂ should be fully converted to prevent residual SO2 from entering the quench circuit where fouling, corrosion, and (if severe enough to make it to the amine circuit) deactivation and degradation of the amine selectivity occur. High conversion of COS, CS2, and mercaptans are also required as the hydrogenation reactor is the last line of defence for these compounds before these sulphurous species are vented to the atmosphere. Amines generally have very little affinity towards these non-H₂S compounds and, as such, will not remove much (if any) from

Sulphur 405 | March-April 2023

42 www.sulphurmagazine.com



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Fig. 1: Temperature profile: Operating data of a typical refinery over 1,360 days (3.75 years) 80 75 70 65 60 55 50 45 DT/reaction zone, 40 35 30 25 20 15 10 5 0 days on stream Source: Optimized Gas Treating, Inc. bottom zone ◆ middle zone
 ◆ top zone

A temperature profile across the TGU reactor is commonly used to provide insight into catalyst performance and health. Fig. 1 presents operating data for a typical refinery TGU reactor showing the temperature profile across a four-year operating window4. The adiabatic reactor experiences a total temperature rise. DT. from the exothermic reactions associated with conversion of various sulphur species to H₂S and shift of carbon monoxide to hydrogen. Three approximately equal segments of the bed are shown with their respective percentages of overall temperature rise across the bed: top zone (green) shows 70% of DT, middle zone (blue) shows 30% DT, and bottom zone (red) shows negligible DT. Fresh catalyst achieves almost complete conversion in the first two zones.

The overall temperature rise across the bed is virtually constant across time (not shown), reflecting that even with sulphur slip as outlet concentrations of non-H₂S species increase, there is still high percentage conversion. The size of the temperature rise is related primarily to the concentration of sulphur dioxide, carbon

Sulphur 405 | March-April 2023

Contents

monoxide, and elemental sulphur in the feed. The relative temperature rise in each zone reflects its degree of conversion.

OGT | SulphurPro® hydrogenation reactor model

The model implemented into SulphurPro is a kinetic-rate model and takes into account several key factors. The reaction set includes not only major reactions but also the parallel side reactions. The kinetic rate model has been fitted to experimental data, and a key part of the model is the inclusion of catalyst aging and poisoning because catalyst activity determines reactor performance, and deactivation occurs through aging and poisoning. The gradual loss of catalytic rate is inevitable and must be fully accounted for and addressed in the initial design of the TGU.

Activity decline as a function of time and exposure to normal process conditions is related to loss of surface area and active sites and is treated as aging. The fractional active surface area can be represented as an aging factor. Aging tends

to occur uniformly throughout the catalyst bed, with catalytic activity or conversion of reactive species declining rapidly at first and then slowly over catalyst lifetime.

Poisoning is treated as activity loss related to any of several contaminants in the feed. The causes include:

- chemisorption of strongly interactive species;
- reactive contaminants modifying active metal sites, alumina support;
- oxygen slip from burner mal-operation; fouling, soot, or sulphur formation;
- coking;
- sintering, base structure transformation, or even mechanical damage.

Certain streams which wind up at the TGU are known to contribute to poisoning. Although not ideal for an SRU, using the SRU for waste disposal is sometimes taken to be of least consequence. Wastes

- reformer hydrogen as supplemental hydrogen - source of BTEX or chlorides;
- refinery gas as reducing gas generator (RGG) fuel - source of BTEX, olefins,

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heavier hydrocarbon plus variable heating value which aggravates RGG sooting or oxygen slip;

acid gas enrichment (AGE) off-gas usually contains heavier hydrocarbons and BTEX.

The model developed and implemented into SulphurPro accounts for both aging and poisoning as decline functions that necessitate providing the service run time of the catalyst and the poisoning stresses present in the individual configuration of the particular SRU. The different configurable poisoning factors include options to specify the use of a RGG burner, refinery gas as the fuel source for the burner, reformer hydrogen, whether the unit process off gas from an acid gas enrichment unit, specifying how much (if any) BTEX is in the feed, and how much excess air is present. Each of these options contributes to a poisoning factor that is built into the mathematical framework of the catalyst bed. A much more detailed analysis and explanation for the model can be found in Huffmaster, et al1.

Figs 2 and 3 show the interface for the reaction set and for catalyst aging and poisoning.

Case study introduction

The case study is based on an operating refinery in North America. The SRU processed both high-quality, amine, acid-gas (AAG), as well as sour-water, acid gas (SWAG), as shown in Fig. 4. The main complaint of the operating personnel was that SO₂ breakthrough-like symptoms were observed for years through cloudy quench water, frequently plugged and bypassed quench water filter elements, and thiosulphates in the downstream TGU amine section. However, despite their best efforts, the plant was never able to detect any SO₂ in the feed gas entering the quench column even with the help of expert, specialised, analytical testers brought in to help troubleshoot. The general conclusion was that either there were intermittent. low-level amounts of SO₂ being slipped or there was some amount of gas bypassing the reactor. To get a deeper understanding of how SO₂ breakthroughs occur and try to pinpoint what might be going on in this particular plant, a set of case studies was performed to gauge how small changes in the operating condition of the SRU affect the performance of the TGU hydrogenation reactor.

Since the focus was on how the

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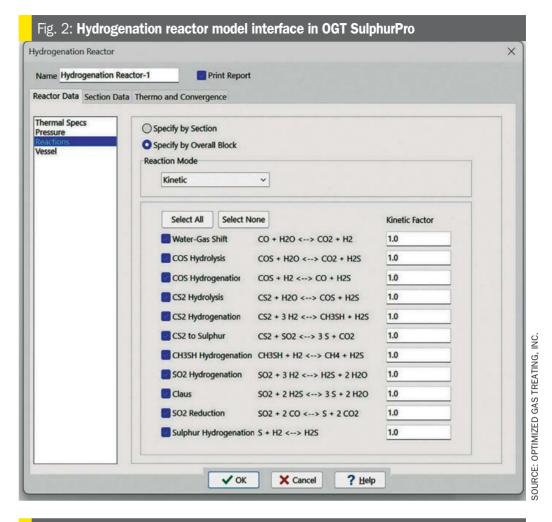
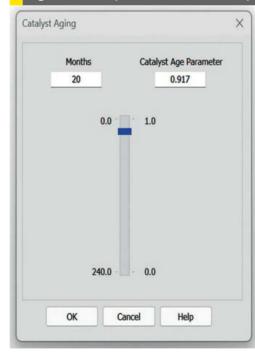
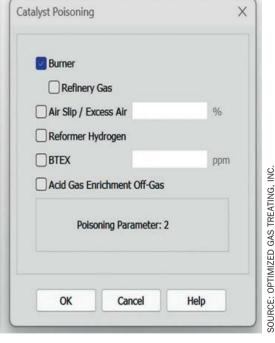


Fig. 3: OGT SulphurPro interface for specifying catalyst age and poisoning level

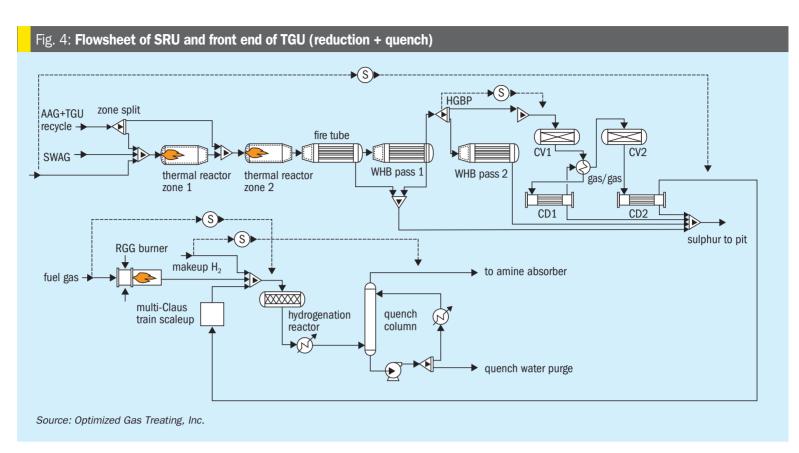




operation of the upstream SRU affects the performance of the TGU hydrogenation reactor, the downstream amine section of the TGU (amine contactor and regenerator) was omitted from the simulation to shorten convergence time and reduce unnecessary interference. The base case was established using test run data provided by the operating plant (Table 1) with

the catalyst age set to the specific number of months the catalyst bed had been in operation (this controls the hydrothermal aging of the catalyst) and the specific poisoning agents that the catalyst bed had seen. Careful comparison was made between the test run CO/COS data and the bed temperature profiles to ensure the model was an accurate representation of

Sulphur 405 | March-April 2023



Data point	Data value	Data obtained by †
Natural gas flowrate feeding RGG	10.6 MSCFH	Material balance and meter
Hydrogen flowrate feeding RGG	5.7 MSCFH	Material balance
	<0.1 MSCFH	Meter
Air flowrate feeding RGG	89.6 MSCFH	Material balance
	89.7 MSCFH	Meter
Quench column overhead gas composition (feeding TGU absorber)	1.5-1.8% H ₂ 2.4-2.6% H ₂ S 4.7% CO ₂ 190-230 ppmv CO ~60 ppmv COS	Dry gas chromatograph measurement
	1.8-2.1% H ₂ 840-1,000 ppmv CO	Plant analyser readings

the plant performance at the time of the snapshot. Once the model was validated, upset conditions were simulated by placing the Claus air on manual and stepwise increasing its flowrate. During this simulated upset, it was assumed that the hydrogen analysers were either malfunctioning, blocked in, or were ignored by operations. It was also assumed that the rapid caustic or ammonia injection for quench pH control was delayed or not done properly. For this set of case studies, process variables were monitored for signs of damage and indications of an SO_2 breakthrough.

Sulphur 405 | March-April 2023

Case study findings

The initial simulation of the base case used several iterations to reconcile the model and plant data. Fig. 5 shows how the data (solid points) experience a fairly sharp drop before the exotherm approximately halfway through the reactor bed. As shown by the dashed line, simply modelling this using a hydrothermal-aging-only model does not really capture the nature of this temperature profile and is clearly missing something. Adding the poisoning model to the overall bed calculations (solid

line) shows results more closely aligned with the top-down deactivation shown by the actual operating data.

Having established a representative case, the model showed that with the given test run data, there were 2-11 ppmv of SO₂ slipping from the hydrogenation reactor through to the quench column. This varied depending on the poisoning agents from the poor-quality reducing hydrogen assumed in the plant and the model. The amount of hydrogen in the quench overhead was right at the desired 2.0% level and certainly did not indicate anything was going wrong with the hydrogenation reactor. Even as the excess air was increased by 1% over the base case, excess hydrogen in the quench overhead did not drop very much even though the amount of SO₂ slipping more than doubled. Because of the aging and poisoning of the catalyst, even with excess hydrogen, non-zero levels of SO₂ were exiting the hydrogenation reactor and entering the quench loop.

Because this is a refinery, the SRU is processing ammonia, which inevitably slips through the Claus unit in small quantities and ends up in the quench water loop downstream. This ammonia in the quench water loop acts as a buffer to counteract trace quantities of ${\rm SO}_2$ that escape from the hydrogenation reactor, but only to an extent. The small amount being slipped in the base case, and even at 1% excess air, was well within the range of buffering

www.sulphurmagazine.com

51

5

15

19

30

32

34

36

42

Contents

capacity of the ammonia in this instance. However, even a small upset of 5% or more excess air exceeds the ammonia's buffering capacity in the quench water loop and begins to send 100+ ppmv SO₂ through to the amine system. If left untreated for any appreciable length of time, this has devastating effects on the health of the amine solvent and the equipment.

The baseline pH of quench water varies depending on the source of the sulphur being processed. Refinery SRUs generally process ammonia and have fairly low levels of CO₂ in the feed gas so the pH generally is 7-9 because ammonia builds in the guench loop. Gas plants, on the other hand, generally have lower quality feed gas containing higher levels of CO₂ and do not generally process ammonia. CO₂ does not participate in the Claus reaction so it will have some (acidic) accumulation in the quench water which also lacks buffering ammonia. The result is pH in the range 5-7. In this particular case, the baseline pH of the quench water was around 7.5 which is right in line with the expected 7-9 range. As the amount of SO₂ slip from the hydrogenation reactor increases, the buffering ammonia prevents pH from dropping very sharply, so pH was not a good indicator of an SO₂ breakthrough.

As Table 2 shows, the amount of SO₂ slipping through the reactor exponentially increases with small step changes in the amount of excess air feeding the unit. In the base case (and even the 1% excess-air case). this small amount of SO2 would be undetectable even with the sophisticated equipment of the some of the analytical companies.

Conclusions

In the case study presented, the OGT $\mbox{\scriptsize I}$ SulphurPro® model suggests that the plant is experiencing a chronic SO₂ leak due to the aged and poisoned hydrogenation catalyst. This was undoubtably the result of heavy hydrocarbons in the makeup reformer hydrogen. Over the years, plant personnel learned to keep the hydrogen valve cracked to keep a small flow through the pipes in order to keep them purged and flowing. This was put into practice to avoid the potential disaster of heavy hydrocarbon liquid carry over. The fear was that if the valve was closed and there was any liquid hydrocarbon carry over into the hydrogen line, liquid entering the hot hydrogenation catalyst bed would be utterly disastrous and potentially deadly. This particular plant operated at a slightly elevated H₂S:SO₂ ratio (above the

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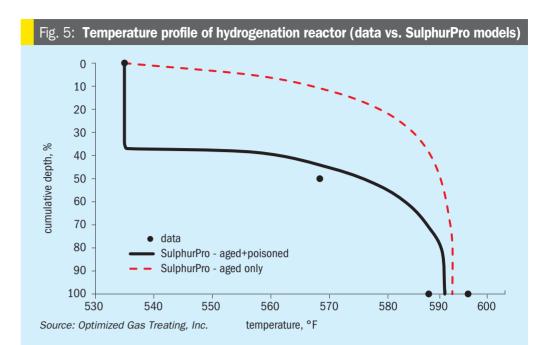


Table 2: Case study results: Effect of excess air on TGU reactor performance SO_2 in Dry hydrogen in pH of quench SO₂ in quench hydrogenation quench column column overhead water loop reactor outlet overhead gas (ppmv) (mole %) (ppmv) 5.6 7.53 0.013 Base case 2.1 7.47 1% excess 12.9 1.8 0.031 3% excess 74.7 1.0 7.09 0.232 5% excess 414.2 0.4 4.63 367 1,473.1 3.83 7% excess 0.1 1.910 4,014.1 0.02 5,516 10% excess 3.19

typical 2:1) stoichiometry which may have allowed it to operate for a long period of time without noticing SO₂ breakthrough.

Using this exceptionally rigorous and highly detailed rate-based kinetics model with its catalyst aging and poisoning features took a long-term reliability and operability problem and systematically identified and resolved it. SulphurPro's detailed reaction-kinetics and mass-transfer-rate model is matchless for analysing intervention techniques and mitigation methods, too. OGT | SulphurPro's hydrogenation reactor model provides the ultimate in simulation power for hydrogenation and could save a sulphur constrained refinery from a multi-million-dollar per day shutdown to correct an otherwise undiagnosable problem. Here, the economics of switching the hydrogen make-up source for the refinery could be more readily quantified by better understanding the run lengths given the specific conditions of the plant. In the interim, stop-gap measures for this plant could include a more conservative practice around caustic or ammonia injection into the quench water loop.

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Sulphur 405 | March-April 2023

49

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Life cycle of a sulphur melting plant

Mathijs Sijpkes, Nuria Pascual Vasco and Jan Hermans of Sulphurnet discuss the importance of a whole life cycle cost analysis at the conceptual design phase when making investment decisions about new sulphur processing facilities.

ulphuric acid is one of the most widely used chemicals in the world, its main applications are the extraction of minerals in the mining industry as well as the production of fertilizers. Due to the increase in demand in these applications, the sulphuric a cid industry is set to continue to grow over the next decades.

An important part of the sulphuric acid plant is the sulphur melting and filtration facility. This is where the solid sulphur is treated and prepared as a raw material for the production of sulphuric acid. To keep the sulphuric acid plant running continuously and to keep costs under control, it is essential to feed high-quality liquid sulphur and have a reliable sulphur melting and filtration plant. Achieving this goal requires the expertise of a sulphur plant designer and a significant investment.

Sulphur in itself is a neutral non-corrosive product, but due to the presence of humidity, air, and the bacteria thiobacillus, elemental sulphur is oxidised into sulphates that react further with the moisture from the environment producing sulphuric acid derivatives. The solid sulphur then turns into a very corrosive product that will cause serious damage to the plant if it is not handled properly.

Besides corrosion, the exceptional properties of sulphur also require attention. Sulphur is liquid only between 125°C and 158°C, a temperature range that should be maintained at all times; its weight cannot be neglected; and its impurities need to be removed. Thus, it is fundamental to consider experienced designers that select appropriate materials of construction and instrumentation, and to consider the reasons for the required investment.

In general, the sulphur section has an exceptionally low priority in the financial budget when designing a new facility. However, there has been a shift in mindset with plant owners increasingly looking for sulphur processing facilities that demonstrate value for money over the long term, rather than simply opting for the design which leads to the least expensive solution. Returns on invested capital costs are essential in making decisions and a combination of knowledge of the potential investment, analytical skills, and the capability to draw conclusions from available data and experience are all important. For example, a major maintenance cost in the sulphuric acid plant is catalyst screening due to high pressure



Sulphur 405 | March-April 2023

www.sulphurmagazine.com

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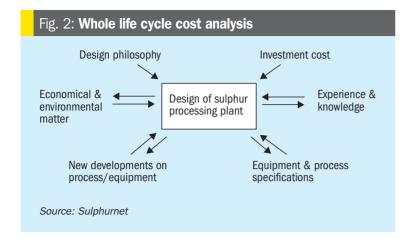
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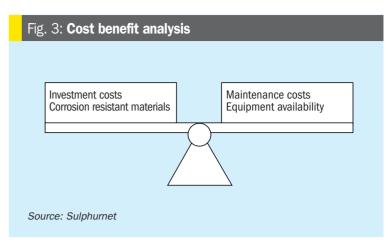
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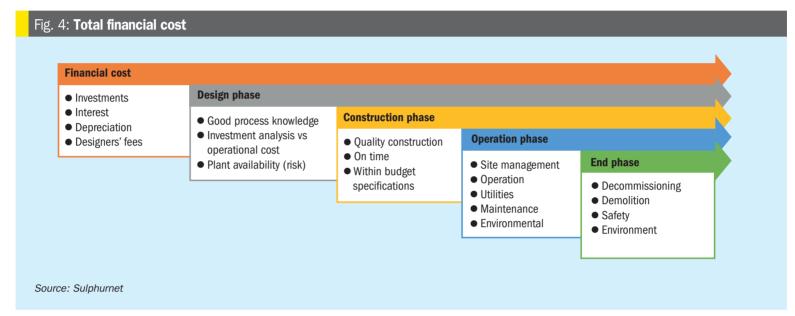
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losses in the converter. These costs can easily add up to \$2.5-3 million over a period of ten days. However, by investing much less than that in the sulphur section an acid plant can be in operation for more than 32 months before catalyst screening is required.

This change of mindset increases the importance of finding the maximum benefit of the investment. Thus, it is highly recommended to carry out a whole life cycle cost (WLCC) analysis as early as possible in the decision-making process, preferably in the conceptual design phase, where 70% of the WLCC can be examined and the design versus costing decisions can be justified.

The WLCC evaluates all costs in all stages involved in the operation of the sulphur melting plant, from design to decommissioning and disposal, together with the effects on the sulphuric acid plant. The ultimate goal is to construct the plant in a "build right first time" methodology while taking into account the long-term costs and economic performance of constructed assets. In addition, operator health, environmental legislation must be considered,

as well as maintenance and operation

The WLLC should be performed together with a risk analysis when evaluating a new sulphur melting project. During the risk analysis, internal and external risks and potential impacts are identified, the cause of those possible risks are analysed and evaluated in order to make decisions.

Design phase

The design stage, which starts with planning and engineering the sulphur plant, is the major phase of the project. Here the specific needs, requirements and specifications of the operation need to be defined. This may include determining the appropriate future needs and selecting the melting technology and filtration systems as well as implementing safety measures.

During the design phase, estimates must be made for the overall whole life cycle costing of the plant. This goes well beyond the technology of the process. Shortcuts in the design causes problems in operation and always results in high expenses.

During the design phase the following topics can be studied/evaluated:

Equipment selection

All viable options must be thoroughly analysed while evaluating the expected overall costs and benefits, i.e., investment cost versus operational benefits considering equipment lifetime and process availability. Risk management is an important task in this process. As projects continue to increase in cost, greater risk must be accepted.

In this context, various considerations should be evaluated, for example:

- Back-up equipment to assure plant availability will increase the investment but ensure almost 100% operation.
- Using corrosion resistant materials of construction to increase the plant lifetime implies higher investment costs but reduces maintenance cost.
- Melting sulphur requires a lot of energy in the form of steam to evaporate the water from the solid sulphur. This is generated in the acid plant but could also be converted to electricity.

Sulphur 405 | March-April 2023

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- Should the solid sulphur warehouse be covered to protect it from rain or not? Under roof storage requires higher investment but ensures better raw material quality.
- Savings in the design of a sulphur melting tank reduces investment but increases risks and maintenance costs.

Construction phase

The construction phase includes the installation of equipment, such as solid handling equipment, various tanks, filters, and the construction of buildings and other structures. The quality of construction is important. A well-constructed plant using high-quality materials and equipment is likely to have a longer lifetime than one that is poorly built.

During this stage the plant should be built according to the design and within the time schedule and budget. Considering the tasks, material and personal resources, contingencies and costs involved in all the stages of construction during the design phase will always raise unforeseen topics and costs, help in the decision making and make the team better prepared.

Cost estimates during the operation phase

The operation phase includes various key factors:

Operating conditions

Analyses of the operational cost in various forms must be assessed. Some considerations for operating a sulphur melting plant include:

- number of operators required versus the level of automation;
- reliable recovery of steam/condensate and the requirements of other utilities must be controlled to minimise costs without endangering plants operation;
- effect of the quality of raw materials like solid sulphur on the operation (water content, acidity and organics will all affect the operation). Poor quality sulphur leads to difficulties in processing and is a potential risk for production losses, and creates extra waste.

Maintenance

Maintenance can be defined as regular programmed maintenance, or response maintenance e.g. in case of emergencies.

Sulphur 405 | March-April 2023

Scheduled maintenance will help to extend the lifetime of a plant by preventing equipment failures, wear and tear. Once the plant is operational, it will go through a period of production, during which it will melt and filter sulphur according to the needs of the operation. This stage may last for many years, depending on the lifetime of the equipment and the quality of sulphur used in the plant.

Emergency maintenance is needed when an asset or piece of equipment suffers an unexpected breakdown or situations occur that result in an immediate threat to health and safety or could cause serious property damage. Lack of commitment to a scheduled maintenance program, increases the probability of emergency maintenance. The cost of emergency maintenance is many times higher than the costing of scheduled maintenance. Only considering time as a factor, shutting down while waiting for spare parts to arrive on site leads to production losses.

Utility costs

Melting sulphur requires a considerable amount of heat in the form of steam, which is produced in the acid plant, were it could also be converted to electricity. Decreasing steam consumption and recycling of condensate is an objective. Minimising power consumption, plant air, and instrument air are further objectives.

Most of those topics can be studied to a good extent during the design phase of a project. For example, correct measures in the process design or in the selection phase of equipment can reduce the power consumption of rotating equipment.

Environmental load

Gaseous emissions occur during the sulphur melting process both in the form of H2S, which is present in sulphur, and in the form of sulphur flour. Sulphur flour consists of fine sulphur particles and droplets that escape mainly through the stack of the melting tank and solidify on cold spots. These fines can cause serious corrosion and can result in reduced plant lifetime or increased maintenance costs. Design of the gas cleaning system requires an excellent knowledge of the chemistry and physical properties involved in the process and the technology required.

Site management

The responsibility of the site management team is broad. This cost centre is responsible for keeping the physical plant and its

assets running. It includes the physical workplace of the people, the day-to-day plant operation, keeping plant changes updated, complying with the latest legislations, the organisation and planning of all the side works, maintenance, inventory of spare-parts and the study of potential future projects.

All things considered, site management is an essential aspect of any operational plant. When overall safety is a priority and regular maintenance is well executed and according to a defined schedule, the life cycle of assets, systems, and equipment is extended and personnel injuries are minimised. This reduces the company costs for emergency repairs or replacements for expensive assets, adding revenue to the bottom line.

Decommissioning phase

When the plant eventually reaches the end of its operational lifetime, the decommissioning phase starts. This may involve the removal of equipment, the demolition of buildings, and the clean-up of any contaminated soil or water according to environmental regulations. Site restoration is carried out to return the site to its original

Total financial cost

The total financial cost is built up through the whole life cycle of the plant in all phases of the project, which should include the decisions made as a result of the risk assessment. Other costs not specifically mentioned should also be considered. It all comes down to the predicted overall investment, operational and other costs versus benefits

Conclusion

The construction of a reliable sulphur melting and filtration plant may require a higher investment cost, but making the wrong choices in the initial phase of the plant design will lead to high unexpected maintenance costs, production losses and poor safety, that at the end of the day will translate into higher operational expenses in the sulphuric acid plant. By performing a WLCC with a qualified partner at an early stage of the project, it is possible to anticipate these costs, and instead, get the right design and construction for the sulphur melting plant from the outset.

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52

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