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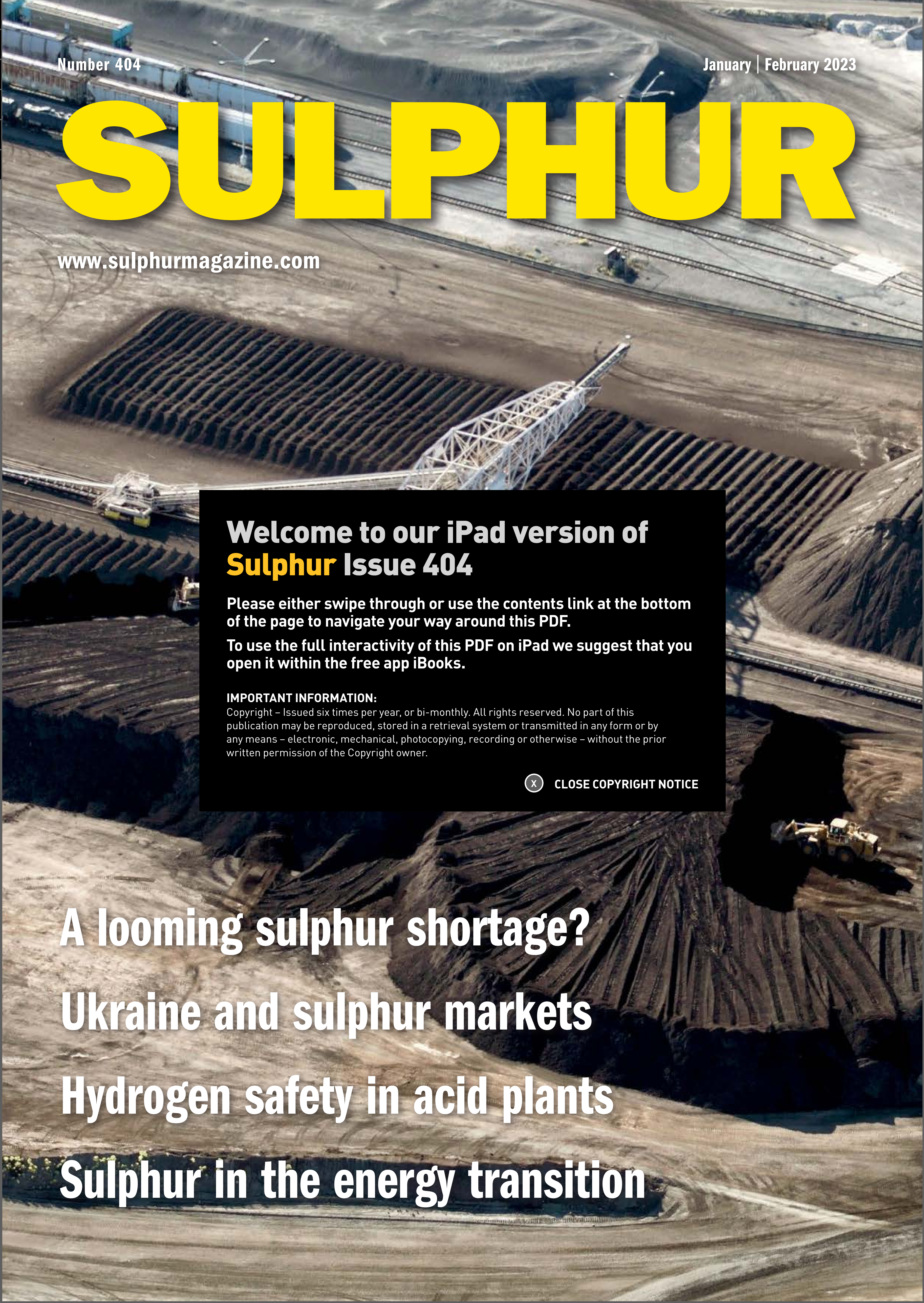

Number 404

January | February 2023

SULPHUR

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A looming sulphur shortage?

Ukraine and sulphur markets

Hydrogen safety in acid plants

Sulphur in the energy transition

Cover: *The Monsanto phosphate mine processing facility near Soda Springs Idaho, USA. The phosphate market is the key driver for sulphur demand. Brian Brown/Alamy Stock Photo*

Sulphur shortage

Will the world run out of sulphur?

Hydrogen safety

Preventing hydrogen incidents in sulphuric acid plants

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Burning sulphur to lower temperatures

It has long been known that sulphur dioxide aerosols can reflect sunlight back into space. On a large scale, this has tended to come from volcanic eruptions. The explosion of the island of Krakatoa in 1815 led to the following year, 1816, becoming known in Europe as 'the year without a summer'. More recently, it is estimated that the eruption of Mount Pinatubo in the Philippines in 1991, the second largest eruption of the 20th century, sent around 18 million tonnes of SO_2 into the stratosphere. Temperatures in the troposphere – the atmospheric layer closest to the earth – dropped by about 0.5°C as a result for about two years afterwards.

As concerns about the effects of man-made climate change increase, it has been suggested that this could be a way of temporarily reducing global temperatures to buy more time for a switchover to a lower carbon economy – so-called geoengineering. The most recent edition of the UN's Montreal Protocol report includes a chapter on stratospheric aerosol injection, and in the US, the Biden White House Office of Science and Technology Policy began a five-year research plan last October to study ways of modifying the amount of sunlight that reaches the Earth in order to temporarily temper the effects of global warming.

> **"But it is also to combat the effects of atmospheric sulphur dioxide on the environment... that sulphur is currently removed from fossil fuel."**

But while the topic has gained scientific respectability as the effects of climate change become more pronounced, it also has plenty of detractors. The most common aerosol suggested is the one known to work via volcanic eruptions – sulphur dioxide. But it is also to combat the effects of atmospheric sulphur dioxide on the environment (via acid rain), and on human health, that sulphur is currently removed from fossil fuels. While the idea is to release the SO_2 at high levels, where it can have maximum cooling effect, and it is hoped that little makes its way back down to sea level to cause the kind of problems we saw in the 1970s and 80s, how much of it will do so is still poorly understood. Likewise the impact of SO_2 on warming the stratosphere is still uncertain. While it cooled climate at sea level, the Pinatubo eruption is believed to have warmed the upper atmosphere by 3.5°C, and potentially caused disruption to high level atmospheric air currents like the Jet Stream.

That being the case, a small US start-up company called Make Sunsets has also made waves in the past few weeks by saying that it has already begun releasing SO_2 into the stratosphere via weather balloon flights, and it is selling what it describes as $10 'cooling credits' to fund larger scale releases. It claims that every gramme of sulphur released as high level SO_2 counteracts the effect of one tonne of CO_2 – a somewhat contentious claim, as CO_2 emitted today can stay in the atmosphere for 100 years, while the effects of the SO_2 only last for 1 or 2 years. Still, Make Sunsets – the name comes from the increased redness of dusks and dawns that would be caused by upper atmosphere particulates – argues that sulphur geoengineering is not a panacea, but a 'less worse' option than enduring a global temperature rise of 1°C or more over the next few decades.

For the moment, the releases are very small scale, and more for publicity and research purposes than any serious attempt to change the climate. A cynic might suggest that Make Sunsets is more of a green-tinged cash grab than a true attempt to save the planet, and there is widespread opposition to the idea of geoengineering on a for-profit basis, and calls for a global framework to prevent such tinkering without global agreement.

But here at *Sulphur* I couldn't help wondering what the impact might be were scientific consensus move to decide that releasing high level SO_2 was indeed the way forward. An annual release on the scale of the Pinatubo eruption – 18 million t/a of SO_2 – equates to 9 million t/a of sulphur. That is a lot, but not outside the bounds of possibility were we to have to start supplying it. And Make Sunsets claims that to achieve 0.5°C of cooling only a targeted 1 million t/a of SO_2 would be required, or 500,000 t/a of sulphur – less than a large scale gas project or a couple of major refineries and well within the reach of the industry. The science is very much up for grabs at the moment, but if it were true, it might be a very cheap way of reducing global temperatures.

Richard Hands, Editor

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 have been on a softer trend since the end of the fourth quarter of 2022 and going into the new year. All key indicators point towards a softer sulphur market in the short term. Spot demand out of southeast Asia was a key driver for prices firming during the tail end of firming towards the end of last year but other major markets appear to be on the sidelines, at least for now, particularly during the period when quarterly contracts are beginning to conclude, while some discussions are ongoing. Chinese demand for the short term is subdued and fundamentals appear weak. Markets have been somewhat sluggish coming into 2023 with some contracts for the first quarter of the year settle at increases on the fourth quarter but below the peak of spot pricing achieved in the period.

Average Middle East prices decreased by around $18/t between the end of 2022 and mid-January 2023, down to $155/t f.o.b. and are around $160/t lower than prices at the start of 2022. Kuwait's KPC set its January sulphur lifting price at $154/t f.o.b., down by $29/t from the December price. Qatar's state-controlled Muntajat set its January Qatar sulphur price at $155/t f.o.b. Ras Laffan/Mesaieed, down by $30/t from the December QSP of $185/t f.o.b. The January QSP implies delivered pricing to China of $177-184/t c.fr at current freight rates, which were estimated at $22-25/t to south China and at $27-29/t to Chinese river ports for a shipment of 30,000-35,000t. Meanwhile Abu Dhabi's state owned ADNOC set its January official sulphur price (OSP) for liftings to India at $160/t f.o.b. Ruwais, down by $20/t from the December price of $180/t f.o.b. On quarterly contracts, Middle East prices were reported at around $140-155/t f.o.b. for supply to be delivered in the first quarter of 2023, though the low end was not confirmed.

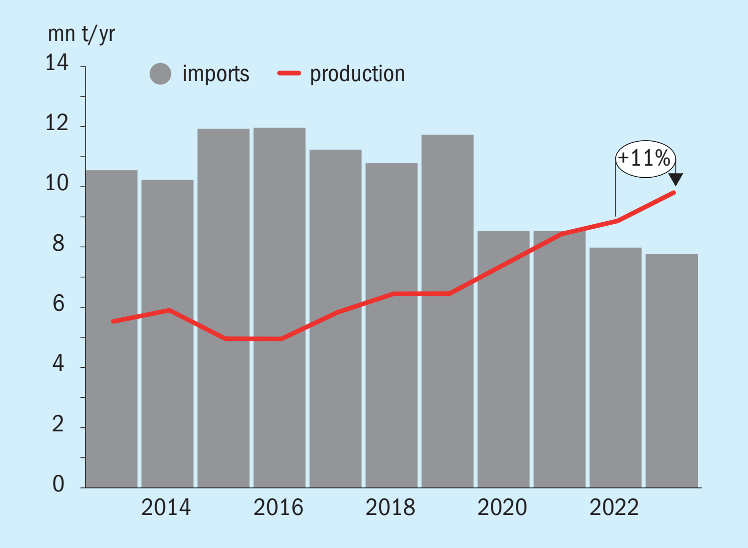
Sulphur capacity from Kuwait is on the rise following the start of commercial operations of Kuwait's state owned KPC's Al Zour refinery at the end of 2022. Operations are expected to ramp up at the 615,000 bbl/d project with the start-up of a second crude distillation unit (CDU) in the second quarter of 2023. Al-Zour has so far sold low-sulphur diesel, low-sulphur fuel oil and jet fuel cargoes. The refinery project faced repeated setbacks, first because of technical and logistical issues with contractors and more recently because of issues related to the Covid-19 pandemic. Kuwait had aimed to begin commissioning al-Zour in mid-2019 and have it fully operational by 2020.

China's post-Covid reopening is fuelling a rally in the country's gasoline demand, even as infections surge. The national health commission announced 10 policy changes on 7 December 2022, including relaxing some quarantine and testing requirements, better targeting of lockdown measures and encouraging vaccination among the elderly. The relaxation of the zero-Covid policy is going to have important ramifications for Chinese and global GDP growth, as trade bottlenecks potentially ease. The IMF projects that China will account for 30pc of aggregate global growth in 2023. GDP growth and oil demand are closely linked and we are already seeing an uptick in oil demand, supporting the view for robust sulphur production in the coming months.

On the demand side, the future of Chinese export restrictions on processed phosphates will impact fundamentals this year. We expect to see exports returning to normal from the second quarter, which will help push the global sulphur balance into a potential net deficit in the second half of the year. Sulphur pricing in China has been easing in line with the shift in sentiment, assessed by Argus at the start of January at $90-173/t c.fr. for the 'all forms' spot range, with the low end representing molten shipments. Further decreases were expected in the second half of January in the run up to the Lunar new year.

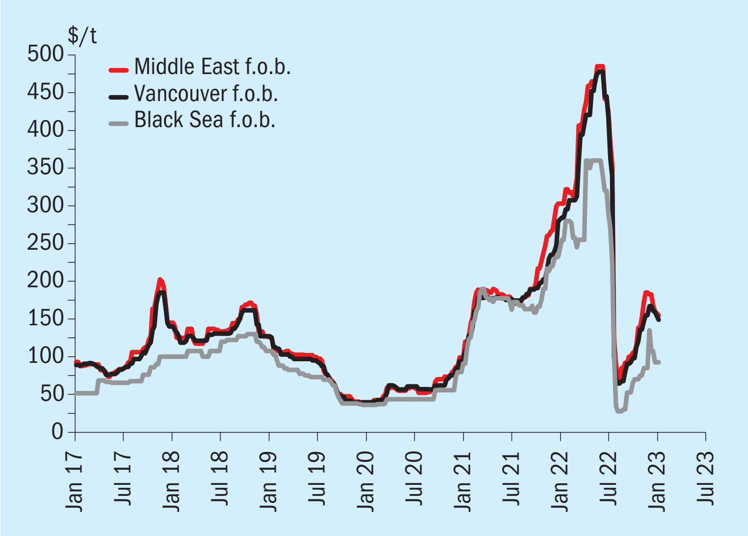
New supply is expected to come onstream in China and add additional sulphur capacity to the balance this year, adding downward pressure to import demand in the country. In project news, Shenghong Petrochemical started trial runs at its 320,000 bbl/d Lianyungang refinery in east China's Jiangsu province from around 6 November and was running at around 60% for the month. Shenghong may raise Lianyungang's

Fig. 1: **Chinese sulphur exports, October 2020-October 2022**



Source: Argus Sulphur Analytics

Fig. 2: **Global sulphur capacity changes by region**



Source: Argus Sulphur

operating rates to nameplate capacity after the lunar new year holiday ends in February 2023. PetroChina is preparing to start up its new 400,000 bbl/d Jieyang refinery in Guangdong province. PetroChina started injecting crude into the refinery's crude units at the end of October 2022. Combined, these two projects will add around 1.4 million t/a of sulphur capacity.

Elsewhere in Asia, there is much focus on Indonesia with the continued ramp up of sulphuric acid capacity at nickel HPAL projects. PT Ningbo Lygend was in the market for early February arrival, covered by traders from the Middle East. The first phase of Lygend's project reached 42,000 t/a of nickel metal equivalent in 2022. The company is planning to build more than 400,000 t/a of nickel metal equivalent capacity by 2024. Sulphur trade to the country is expected to rise to over 2 million t/a in 2023 because of developments in the nickel sector.

SULPHURIC ACID

Global sulphuric acid price movements have been more limited compared to sulphur in the new year and have increased or decreased, pointing to a continued mixed picture in the market. Average prices out of Northwest Europe increased on the December average by just $2.5/t, assessed by Argus $37.5/t f.o.b. at the midpoint in mid-January. High freight rates to key export markets have exerted downward pressure on the benchmark in recent months. On the contract front, most first quarter 2023 negotiations were complete at a rollover to euro 30/t for both smelter and sulphur burner acid. Uncertainty remains in the region because of high energy prices impacting downstream consumers and smelter operating rates.

Phosphoric acid production is expected to see a boost in 2023 following demand destruction last year, supporting the view for sulphur and sulphuric acid in this sector. Total sulphuric acid consumption in the sector is forecast to rise by around 4.5 million t/a in 2023, representing 44% of global growth. Key markets to see a boost include Morocco and India. Both markets are importers of sulphuric acid. We expect Moroccan sulphuric acid imports to rise slightly on 2022 levels to just under 2 million t/a. This will be dependent on the ramp up of sulphuric acid capacity at OCP's processed phosphates facilities.

Global acid consumption is forecast to rise by over 10 million t/a in 2023 on 2022. Outside of fertilizers the metals and industrial sectors are also expected to rise. Around 4 million t/a of demand is forecast for industrial uses, while metals processing will grow by over 1 million t/a on the previous year. On the supply side we now expect this to rise by 11.1 million t/a in the 2022-23 period. Smelter-based capacity is expected to see a boost of 1.8 million t/a, representing 15% of growth over the period. Northeast Asia is the main driver for this sector as new smelters continue to ramp up in China.

China's copper concentrate imports in 2023 are likely to increase from a year earlier, despite Beijing's push to boost copper scrap consumption at smelters to achieve its target of peak carbon emissions by 2030 and carbon neutrality by 2060. There is expected to be a limited increase in production for domestically produced copper concentrate in China. The new 400,000 t/a copper smelting facility at China's Daye Non-ferrous started feed supplies on 23rd October 2022 and is expecting to ramp up production this year. This is the biggest demand driver for copper concentrate imports in the coming year and a major sulphuric acid supply addition. We expect a gradual ramp up at the project, located in Huangshi city in Hubei province with 1 million t/a of sulphuric acid capacity to be brought online in 2023.

Copper prices on the London Metal Exchange (LME) hit a seven-month high in official morning trading on 11th January, supported by continued expectation of slower target interest rate rises by the US Federal Reserve and increased demand from China driven by the reopening of its economy. This is supporting the forward view for sulphuric acid consumption and pricing. Three-month LME prices of copper settled at $8,995/t, up by 2.3% on the day to their highest official session close since June 2022. The contract breached the $9,000/t mark in intra-day trading. China reopened its borders on 8th January after three years of travel restrictions as part of its zero-Covid policy. Incoming travellers will now no longer need to quarantine upon arrival. Markets reacted positively, though concerns persist over further spikes in Chinese Covid cases as a result of the relaxation of lockdown restrictions.

Price Indications

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

Cash equivalent	August	September	October	November	December
Sulphur, bulk ($/t)					
Adnoc monthly contract	85	92	103	139	180
China c.fr spot	120	150	165	179	195
Liquid sulphur ($/t)					
Tampa f.o.b. contract	352	352	90	90	90
NW Europe c.fr	380	380	123	123	123
Sulphuric acid ($/t)					
US Gulf spot	188	150	150	150	150

Source: various

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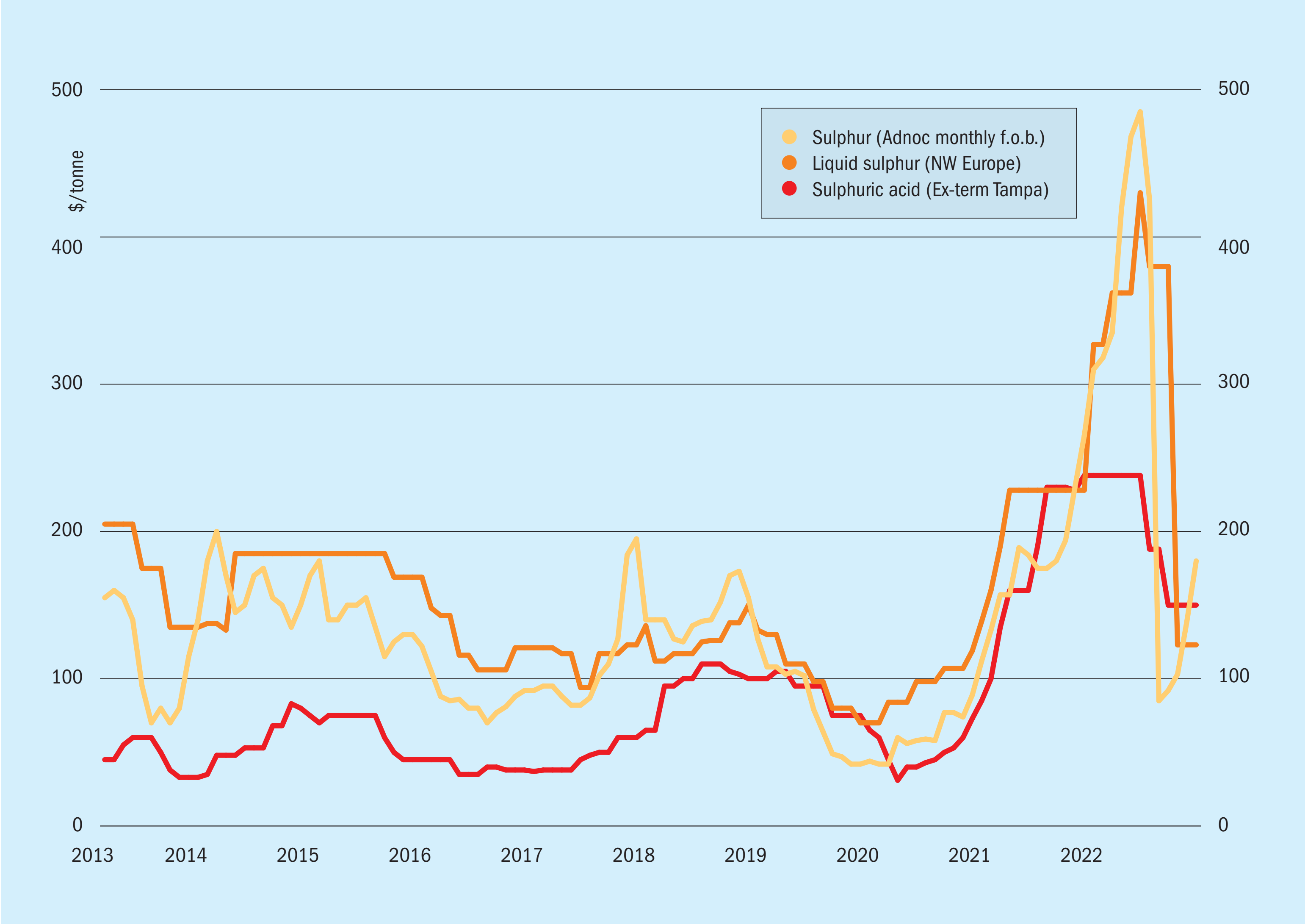
Market Outlook

Historical price trends $/tonne



Source: BCInsight

SULPHUR

- Processed phosphates pricing will be a major influence in the coming months. A gap remains between historical levels of sulphur and DAP pricing that points to the potential for sulphur prices to recover to higher levels during 2023.
- Whether China returns to the processed phosphate market and at what pace will be key to sulphur consumption levels for sulphur from the second quarter onwards. Sulphur imports in China are forecast to drop to 7.8 million t/a in 2023, but this could drop lower if phosphoric acid-based demand does not reach expected levels.
- Developments in the Russia/Ukraine conflict still pose many questions for the sulphur market. Exports of Russian sulphur are estimated to have totalled around 1 million t/a in 2022, with a similar level forecast for 2023. This will be subject to revision as policy and sanctions continue to restrict the movement of supply from the country.
- **Outlook:** Prices are expected to continue to soften in the short term on the back of weak sentiment before potentially stabilizing and rebounding. Following the demand decline in 2022, a return to growth is expected this year, but the macro-economic picture remains a risk to this. New capacity additions will add to the balance but this is expected to be exceeded by an increase in demand, leading the market to an overall deficit in 2023.

SULPHURIC ACID

- Chile contract negotiations have concluded for 2023 supply. The majority of contracts settled in a range of \$143-148/t c.fr. Meanwhile spot prices were below this level at the start of January, at \$135-140/t c.fr. Little spot demand is expected to emerge in the short term. The deficit for Chile this year is forecast to drop on 2022 levels, adding to the expectation for lower prices.
- Copper projects in Western US continue to progress and demand in the country for the sector is forecast to rise by around 200,000 t/a in 2023 on a year earlier.
- Japanese and South Korea acid export availability is expected to drop this year because of scheduled turnarounds. Combined supply is forecast at 5.3 million t/a in 2023.
- **Outlook:** The price correction in the global acid market is expected to persist in 2023 following the upward trend in the past year. Stability is expected in the short term with the potential for prices to increase later in the year as demand improves, supporting acid trade. The expected rise in sulphur prices in the second half of 2023 will also support acid markets.

Sulphur Industry News

UNITED STATES

Ioneer signs sulphur supply contract with Shell

Lithium miner Ioneer Ltd has signed a non-binding Memorandum of Understanding with Shell Canada Energy for the supply of sulphur to Ioneer for its Rhyolite Ridge lithium-boron project in Esmeralda County, Nevada. Ionner said in a statement that "securing the supply of key reagents for ore processing is an important step along the critical pathway to developing the Rhyolite Ridge project". Under the memorandum, Ioneer will purchase up to 500,000 t/a of high-quality sulphur from Shell, which would fulfil the estimated annual sulphur requirement for the Project.

The signing of the MoU builds upon the letter of intent signed in December 2019 and, with a binding commitment to negotiate exclusively with one another, it is the intention of both parties to advance the MoU into a definitive agreement at the appropriate time. Ioneer and Shell say that they also intend to collaborate through strategic initiatives focused on accelerating the energy transition.

Ioneer's Managing Director, Bernard Rowe, said: "Sulphur is a primary input for our process as it will be converted into the sulphuric acid required for leaching the ore as well as releasing heat which is recovered to produce carbon free power and steam for the facility. Shell is an ideal partner for this effort, and we look forward to furthering our partnership together on additional decarbonisation solutions while providing materials for a sustainable future."

Peter Zissos, GM Global Sulphur & Thiogro from Shell, added: "We are excited to expand our partnership with Ioneer to include the sale of sulphur while collaborating on various decarbonisation solutions. Sulphur's second largest use is for mining, including for the extraction of EV metals like lithium. With safe and reliable delivery of sulphur to customers like Ioneer, Shell Sulphur Solutions is delivering inputs critical for renewable energy production and management."

Increase in sulphur fertilizer use

A recent paper in *Communications Earth & Environment* (Hinckley, EL.S., Driscoll, C.T., *Sulphur fertiliser use in the Midwestern US increases as atmospheric sulphur deposition declines with improved air quality*. Commun Earth Environ 3, 324, 2022) compares the rate of sulphur fertilizer use across 12 Midwestern states with falling rates of atmospheric deposition of sulphur. Using data from the US National Atmospheric Deposition Program, it found that the rate of sulphur deposition on cropland fell from 4.7 kg/ha to 1.1 kg/ha from 1987 to 2017 as sulphur was progressively removed from vehicle fuels and sulphur dioxide scrubbed from power plant emissions in order to tackle acid rain and improve public health. At the same time, compiled fertiliser sales data from the Association of American Plant Food Control Officials showed that use of sulphur containing fertilizers increased from 0.1 kgS/ha in 1985 to 4.9 kgS/ha in 2015, replacing almost completely all of the 'free' sulphur lost.

The paper concludes that, with air quality regulation and high agricultural productivity continuing as priorities not only in the US, but also in many parts of the world, the pressure to add S fertilisers will continue to increase.

SAUDI ARABIA

Contract tenders expected soon for Jafurah Phase 2

Saudi Aramco is reportedly in talks with potential equity investors for the $110 billion Jafurah shale gas project in Saudi Arabia's eastern province. Jafurah sprawls across 17,000 km², and is estimated to hold up to 200 tcf (5,660 bcm) of gas. The company has already awarded subsurface and engineering, procurement and construction (EPC) contracts for the Jafurah Gas Plant and gas compression facilities, as well as infrastructure and related surface facilities worth $10 billion. Invitations to bid for phase 2 of the project, including packages worth up to $6 billion each, have already gone out, and tenders are expected soon. Overall, capital expenditure at Jafurah is expected to reach $68 billion over the first 10 years of development. Gas production is expected to begin in 2025 at around 200 million cfd, rising to ten times that (2 bcf/d) by 2030, alongside 4.3 bcm per year of ethane and 630,000 bbl/d of gas liquids and condensates.

UNITED ARAB EMIRATES

More sulphur from ADNOC this year

Samsung Engineering is carrying out ADNOC's Refining Crude Flexibility Project at Ruwais, and expects to complete work this year. The $3.5 billion project will add new facilities and renovate existing ones, including the addition of an Upper Zakum crude refining facility to the Ruwais Refinery West plant in the complex. The refinery was designed to refine 420,000 bbl/d of Murban onshore crude. Taking crude additionally from the offshore heavier and sourer Upper Zakum field will necessitate additional sulphur recovery capacity. Samsung says that the new SRU and tail gas treating unit will have the capacity to process 800 t/d of sulphur (264,000 t/a).

ADNOC forms new gas processing and marketing company

ADNOC has announced the formation of ADNOC Gas, effective from 1st January 2023, its new world-scale gas processing, operations and marketing company. The company combines the operations, maintenance and marketing of the ADNOC Gas Processing and ADNOC LNG businesses into one global and market-leading consolidated business, according to the company. It argues that as ADNOC grows its gas production and processing capacity, the combined scale and capabilities of ADNOC Gas will maximise value and create new opportunities for ADNOC, its partners and the UAE. As a leading global player with capacity of around 10 billion scf/d, ADNOC Gas will serve a wider range of domestic and international customers with an expanding portfolio of gas products.

His Excellency Dr. Sultan Ahmed Al Jaber, UAE Minister of Industry and Advanced Technology and ADNOC Managing Director and Group CEO, said: "The formation of ADNOC Gas represents another major milestone in unlocking the full value of the UAE's vast natural gas resources and builds on ADNOC's more than 40 years' experience as a leading gas producer. Natural gas will be a critical fuel in the energy transition and ADNOC Gas, through its world-scale operations and significant growth and expansion plans, will be well-positioned to meet both local and international gas demand. In addition to enabling the growth of local industry and manufacturing, ADNOC Gas will play a critical role in delivering ADNOC's broader LNG expansion plans, including in international markets.

"For our customers, ADNOC Gas will continue to be a reliable provider of LNG, LPG and associated products. Led by a seasoned and highly-qualified senior management team, with unrivalled experience in the sector, this new flagship and world-scale company will strengthen our position as a responsible and sustainable energy leader in an evolving global energy landscape," H.E. Dr Al Jaber added.

Ahmed Mohamed Alebri has been appointed as Chief Executive Officer (Acting) of ADNOC Gas, Peter Van Driel as Chief Financial Officer, and Mohamed Al Hashemi as Chief Operating Officer. Ahmed Mohamed Alebri is the former CEO (Acting) of ADNOC Gas Processing and General Manager (Acting) of ADNOC Industrial Gases. With an ADNOC career spanning more than 18 years, he has held various senior management positions and has led the delivery of multi-billion dollar gas expansion programs. Peter Van Driel is a 28-year veteran of Shell, where he served in various key roles in Accounting, Investor Relations, M&A and Finance and Mohamed Al Hashemi is the former SVP of Production Planning & Transmission at ADNOC Gas Processing, where he previously held several leadership posts covering the full spectrum of Site Operations, Maintenance and Supply with an emphasis on HSE & Asset Integrity.

As one the world's leading gas companies, ADNOC Gas will operate eight processing sites both onshore and offshore with a pipeline network of over 3,250 km. As announced in November 2022, ADNOC also intends to proceed with an initial public offering (IPO) of a minority stake in ADNOC Gas on the Abu Dhabi Securities Exchange (ADX) during the course of 2023, subject to applicable regulatory approvals. The company will make further announcement in relation to the intended IPO in due course. Existing joint venture partners to ADNOC LNG (Mitsui & Co, bp and TotalEnergies) and ADNOC Gas Processing (Shell, TotalEnergies and PTTEP) will continue in their respective JV partnerships with ADNOC Gas, ADNOC said.

Tecnimont JV awarded preliminary Hail/Ghasha contract

Tecnimont SpA says it has been awarded a contract from ADNOC for the early engineering and procurement works related to the onshore facilities of the Hail & Ghasha Development Project, as part of a joint venture composed of Tecnimont, Technip Energies and Samsung Engineering. The overall contract value is approximately $80 million. The scope of work also includes the preparation of an open book estimate for the full project delivery scope, which will be considered as part of the final investment decision.

Alessandro Bernini, Maire Tecnimont Group CEO, commented: "We are honoured to keep on supporting ADNOC in accelerating its gas growth plans."

BAHRAIN

BAPCO modernisation program to start up this year

The Bahrain Petroleum Company (BAPCO) is aiming to complete its $6 billion refin-

OBITUARY

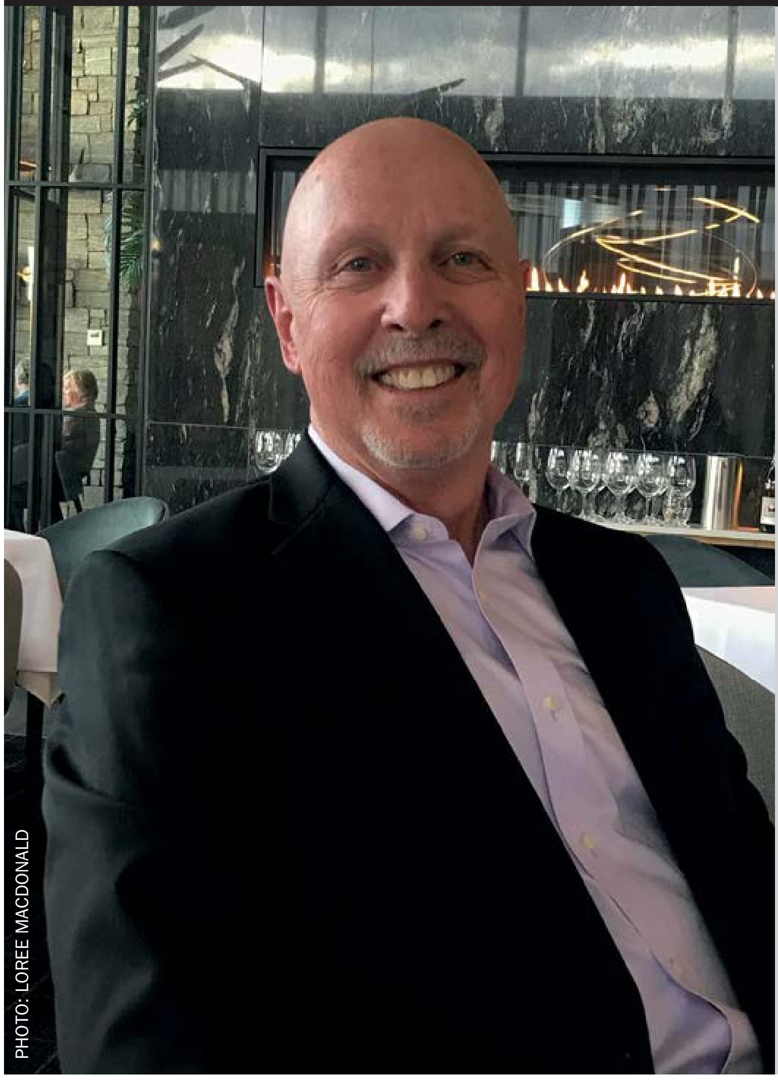


PHOTO: LOREE MACDONALD

John A. MacDonald, Director, Sulphuric Group Inc.

Les Lang writes: John Alexander Colin Grant MacDonald, 74, passed away on July 19th, 2022, at home, following a year-long battle with cancer. John came to the sulphur industry in 2000 after a lengthy career in senior roles in the Canadian trucking and railroad industry. As the Sales Manager for Enersul he led the negotiations that realised new long-term plant operating agreements for four of Enersul's Alberta facilities and replacing old forming processes with the new GXm2 granulators.

Assuming overall management of Enersul's international technology marketing group in 2003, John led the technical and marketing team in a succession of major sulphur forming and handling contract wins in Russia and Qatar. As one of the founding shareholders of The Brimrock Group Inc., John worked with fellow director Les Lang to bring a number of new sulphur processing technologies to the marketplace. Those new technologies will be an on-going legacy in the sulphur industry for many years to come.

In 2014, IPCO purchased the patented technologies developed by Brimrock, which led to the founding of the Sulphuric Group Inc., where John remained a director and founding shareholder until the time of his passing. John's wife Loree has assumed his director's responsibilities going forward. John will be dearly missed by those whose lives and careers were touched by his knowledge, excitement and love of the deal. ■

ery modernisation programme this year. It will boost the processing capacity of the country's only oil refinery to 360,000 bbl/d from its current 267,000 bbl/d by updating aging facilities. The upgrade includes a third sulphur plant; a sulphur recovery, amine and sour water treating facility being built as part of the modernisation programme, and will comprise 11 separate integrated process units. The plant's main purpose is to recover hydrogen sulphide from the new units' process streams and convert it into liquid sulphur. The liquid sulphur is then converted into solid pastilles in a separate unit, with the final product exported to other countries. Parsons is the technology licensor for the three sulphur recovery units (SRUs), two tail gas treating units (TGTUs), two bulk acid gas removal units, two amine regeneration units (ARUs) and two sour water stripping units (SWSs). The new SRUs will add 750 t/d of sulphur capacity, leading to post-modernisation refinery total sulphur production installed capacity of 1,535 t/d (500,000 t/a). The new block is located adjacent to the existing Low Sulphur Diesel Production Complex SRUs. Technology and unit configuration is similar to the existing SRUs, including a two-stage Claus process followed by tail gas treatment, giving 99.9% recovery of H_2S. However, the new SRUs will use an air sweep for degassing of the sulphur rather than a chemical dosing system, and will have a more energy-efficient incinerator which uses heat recovery with steam generation.

INDIA

New SRU for Numaligarh refinery

Thermax has secured an engineering, procurement and construction contract worth $150 million from an Indian public sector refinery to build a new sulphur recovery block on a lump sum turnkey basis. The Numaligarh refinery is 80% owned by Oil India Ltd, 15.5% by the government of Assam state, and 4.5% Engineers India Ltd (EIL). The sulphur recovery block will includes two 240 t/d sulphur recovery units along with a tail gas treatment unit, a 690 t/h amine regeneration unit, a 200 t/h phenolic sour water stripper and a 95 t/h non-phenlic sour water stripper, and forms part of Numaligarh's ongoing refinery expansion project. The project forms part of the government of India's North East Hydrocarbon Vision 2030.

Thermax's scope of supply includes project management, engineering, procurement, manufacturing, construction, and commissioning of the sulphur recovery block. The project is slated to be completed in 28 months. The company had previously supplied waste heat recovery boilers for the old SRU block at Numaligarh.

In a separate development, Engineers India has also signed a memorandum of understanding with the Numaligarh refinery to jointly develop technology for production of ammonia from ammonia-rich sour gases. The MoU paves the way for the demonstration of technologies jointly developed by EIL and the refinery.

UNITED KINGDOM

Lithium sulphur battery market could see 30% annual growth

A recent report by The Business Research Company: "Lithium Sulphur Batteries Global Market Report 2022", predicts that the market will reach a value of $0.43 billion in 2022 and grow to $1.18 billion in 2026 at a compound annual growth rate of 29.0%. Rising government investment in electric vehicles is significantly driving the growth of the lithium-sulphur batteries market. Major companies operating in the sector are focused on developing new technological solutions to accelerate growth in the market. For instance, in September 2021, Lyten, a US-based advanced materials company, launched lithium-sulphur battery LytCell EV for electric vehicles. Lyten Sulphur Caging is a technology employed in LytCell batteries to unlock the performance ability of sulphur by preventing the 'polysulphide shuttle', a cycle-life limiting issue that has prohibited practical Li-S application in battery electric vehicles up to now. This recent innovation is intended to produce three times the gravimetric energy density of traditional lithium-ion batteries and is being developed exclusively for the electric vehicle (EV) sector.

OMAN

Duqm Refinery nearing completion

Construction work was assessed as 96% complete at Oman's new $6 billion Duqm refinery at the end of November 2022. The refinery project, a joint venture between the OQ Group and Kuwait Petroleum International, is being implemented in the Special Economic Zone at Duqm as part of a wider plan to turn the port into one of the largest industrial and economic centres in the region. It includes 10 main processing units capable of producing diesel, aviation fuel, naphtha, liquefied petroleum gas, sulphur and petroleum coke. Crude refining capacity will be 230,000 bbl/d, almost doubling Oman's refining capacity. Around 65% of the crude feedstock for the refinery will be imported from Kuwait, while the remaining 35% will be supplied by Oman.

PANAMA

Topsoe technology selected for renewable fuels production

SGP BioEnergy is aiming to build South America's largest renewable fuels plant, with two units in Colon and Balboa, Panama to produce sustainable aviation fuel (SAF) and renewable diesel (RD), respectively. The company has chosen Topsoe HydroFlex™ technology to produce SAF and RD, while also deploying its H2bridge™ technology to ensure the plant has a net-zero greenhouse gas footprint, recycling green hydrogen generated by waste carbon and production by-product back into the plant's operations. Once fully operational, the biorefinery will produce 180,000 bbl/d of SAF and RD, and 405,000 t/a of green hydrogen. Construction is on schedule for first production by 2025.

Henrik Rasmussen, Managing Director, The Americas, Topsoe, said: "This is truly an amazing project, and we are proud to work with SGP BioEnergy to bring it to life. We are excited to support the production of low-carbon fuels with our proven technologies for what will be the largest renewable fuels plant in South America, while also facilitating the net-zero operations of the biorefinery. It is a true model for a low-carbon energy future."

Renewable diesel is made from waste or recycled animal fats, e.g. from restaurants, as well as inedible corn and soybean oil. These materials, that would otherwise be thrown away, are converted into diesel, producing a much cleaner alternative to regular diesel. HydroFlex™ can convert low value feedstocks into drop-in renewable jet and diesel that meets globally accepted specifications for these fuels, while H2bridge™ technology captures waste propane and carbon off-gas from the refining process, and converts it into green hydrogen to be included in powering facility operations.

Sulphuric Acid News

UZBEKISTAN

Metso Outotec to deliver two sulphuric acid plants to Uzbekistan

Almalyk Mining and Metallurgical Company (AMMC) has awarded Metso Outotec a euro 70 million order for the delivery of two sulphuric acid plants to be built for AMMC's zinc roasting facility in Almalyk, Uzbekistan. Metso Outotec's scope of delivery includes the design and delivery of Planet Positive equipment for two gas cleaning and sulphuric acid plants, which will process all off-gases from the zinc roasters into industrial-grade sulphuric acid. In addition, Metso Outotec will deliver utility facilities, such as a common cooling tower system and a common air compressor system.

The two plants, which will be identical, form part of work that Metso Outotec is conducting Almalyk's entire new copper smelter complex, including flash smelting, slag concentration and electrolytic refinery technologies, as well as sulphuric acid production. The two plants will replace AMMC's existing facilities for gas cleaning and sulphuric acid production. The plants will improve operational efficiency and reliability and significantly reduce the facilities' environmental impact. The sulphuric acid plants are expected to be operational by the end of the second half of 2025.

Almalyk MMC is the main copper producer in Uzbekistan. The company produces refined copper, gold, silver, zinc, molybdenum, lead concentrate and other products.

"We are extremely pleased that Almalyk has again selected us as the partner for providing gas cleaning and sulphuric acid technology. Metso Outotec's advanced Planet Positive gas cleaning and sulphuric acid plant solution will improve the environmental performance of AMMC's metallurgical operations," says Hannes Storch, Vice President, Metal and Chemical Processing at Metso Outotec. ■

AUSTRALIA

Port Pirie smelter restarts

Nyrstar is restarting its Port Pirie lead smelter in South Australia following a planned 55-day outage, according to its parent company, Belgian trading and logistics company Trafigura. The smelter was shut down in October 2022 for a major works and maintenance programme aimed at improving the site's operational performance and lowering emissions. Completed at a cost of A$45 million ($28 million), the works included replacing refractory brickwork at the top submerged lance furnace, as well as major capital works for the blast furnace and sulphuric acid plant. According to Trafigura, Port Pirie, one of the world's largest multi-metal smelters, with a history of operation going back 130 years, produced 160,000 tonnes of lead in 2018. In June 2020, Port Pirie signed a new licence agreement with Australia's Environment Protection Authority to cap emissions by 20% as well as submit a comprehensive lead monitoring plan.

Concentrator plant for West Musgrave copper-nickel project

Metso Outotec has been awarded an order for the supply of key minerals processing technologies to the OZ Minerals copper-nickel West Musgrave Project in Western Australia, for an undisclosed sum. The order includes a cone crusher and Planet Positive classified flotation units and high-rate thickeners. The TankCell® e630 flotation units are the most proven large-scale cells in the 600m³+ category and are the largest installed base of operating cells in the world.

Ardmore mine supplying NZ phosphate producers

Fertilizer producers in New Zealand have been taking phosphate rock from the new Ardmore Phosphate Rock Mine near Mount Isa, Queensland, operated by Centrex subsidiary Agriflex Ltd, to assess it for quality. Ballance Agri-Nutrients says it has completed a successful production trial and that it expects to take further shipments in 2023. "For some time we've been looking to diversify our source of phosphate rock, a critical mineral required to maintain healthy soils, and find a source closer to New Zealand to help mitigate supply chain disruptions," said Shane Dufaur, Ballance general manager operations and supply chain.

Agricultural cooperative Ravensdown in New Zealand has also imported 5,000 tonnes of rock from the mine for trial production of superphosphate. The phosphate rock will be tested and processed at Ravensdown's Christchurch and Dunedin manufacturing sites.

Centrex chief executive Robert Mencel commented that Ardmore's phosphate rock has a natural ultra-low cadmium level which eliminates the risk of heavy metal soil contamination and helps to maintain soil health. Agriflex's solar drying process utilises the sun's energy to naturally dry the product, also eliminating the most significant carbon emission stage of phosphate rock production. "It's very high grade, and Australia's proximity to New Zealand directly lowers carbon transport emissions on a percentage P basis," he said.

INDONESIA

Elessent Clean Technologies opens office in Indonesia

Elessent Clean Technologies is opening a new office in Jakarta. The company says that the new office will be a core maintenance and reliability solutions provider for sulphuric acid plants in the region, as well as providing the full scope of technical services to customers. The global drive toward net zero carbon emissions has created an increasingly rapid demand for access to electric vehicles, wind energy technologies, batteries, fuel cells and other innovations to support this effort by consumers around the globe. The production of such technologies requires the use of energy metals, like nickel and copper, and an increasingly preferred method to extract battery grade nickel is high pressure acid leaching (HPAL) which requires sulphuric acid.

"The Jakarta office is Elessent's sixth location serving the Asia Pacific market. The opening of the office demonstrates our commitment to serving this critical region. We're pleased to bring first-class M&R solutions to sulphuric acid production facilities during a time of significant expansion in metal extraction," said Kanson Xue, Director of Asia Pacific, Elessent.

"Elessent's foundation was built, in large part, on the desire to change our world through sustainability and carbon neutrality efforts, and we couldn't be more excited about the opportunities that our office in Indonesia will bring. We always strive to ensure our clients have the ability to meet their industry's growth needs through the most environmentally conscious methods, and as a global leader in sulphuric acid technology licensing and expertise, our close proximity to clients will be a massive asset with the ongoing demand for battery metals." said Eli Ben-Shoshan, CEO, Elessent.

Thickeners for HPAL plant

Chinese-owned Ningbo Lygend Resources Technology Ltd. has awarded Metso Outotec a contract to provide 25 state-of-the-art thickener units for its nickel laterite HPAL project on Obi island in Indonesia. Metso Outotec's scope of delivery includes High Rate, High Compression, and Paste Thickening technologies equipped with *Reactorwell*™ feed system where applicable.

"Ningbo Lygend produces high quality MHP (mixed hydroxide precipitate) raw material for battery production in Indonesia. They chose Metso Outotec thickeners for their project, thanks to our sustainable, state-of-the-art technology combined with our good understanding and references of similar process plants. The Metso Outotec thickeners enable optimized production and high recovery rates," explained Paul Sohlberg, Senior Vice President, Minerals Separation, Metso Outotec.

Work begins on new HPAL plant

Nickel miner PT Vale Indonesia has broken ground on its new joint venture high pressure acid leach (HPAL) plant, which is expected to have a production capacity of 120,000 t/a of nickel as a mixed hydroxide precipitate (MHP) for electric vehicle batteries, making it the largest MHP plant in the world. Speaking at the ground-breaking ceremony, director Bernardus Irmanto said that the company expected to complete construction in 2025. Vale is working with Zhejiang Huayou Cobalt to build the plant in the nickel-rich Pomalaa region of Sulawesi island, at a total investment cost of $4.29 billion. Under the joint venture agreement, Huayou will develop the Pomalaa project in Southeast Sulawesi and Vale will have rights to acquire up to a 30% stake in the project, and will supply nickel ore for the plant.

PAKISTAN

Shutdown for Fauji DAP plant

Fauji Fertilizer Bin Qasim Ltd (FFBL) has shut down its diammonium phosphate (DAP) plant at Port Qasim, near Karachi. The company says that the stoppage is in order "to more efficiently manage its DAP inventory owing to demand and supply situation in the market". During the shutdown period, planned annual maintenance activity will be carried out in January 2023 to ensure reliability and sustainable safe operations at the plant, but Fauji says a restart will be "based on the DAP market situation".

FFBL is the only DAP producer in Pakistan, using phosphoric acid supplied under a long-term joint venture arrangement with OCP. Pakistan consumes around 2 million t/a of DAP, around two thirds of which is imported. But DAP demand has declined significantly in 2022, due to heavy rains/flooding across the country and the high price of DAP on the domestic market. In spite of an increase in government subsidy to soften the price increases, demand in October 2022 was down 80% on the same month in 2021 according to the National Fertilizer Development Centre (NFDC).

FINLAND

Metso Outotec launches digital optimiser for wet electrostatic precipitation

Metso Outotec is launching a digital optimiser for its wet gas cleaning solution, the *Editube*™ wet electrostatic precipitator (WESP). WESPs are a necessity prior to sulphuric acid plants processing metallurgical off-gas to ensure high-quality acid. The *Editube* WESP has a very high removal efficiency potential, where dust levels in the outlet are commonly measured at below 0.5 mg/Nm^3.

The new WESP optimiser improves the operation of the WESP section by better adjusting it to changes in the overall process. Metso Outotec says that this means there is reduced risk of damage to plastic tubes during low acid load conditions, start-up, and commissioning; higher removal efficiency and lower flashover frequency during high acid load conditions; and that it also offers energy savings whenever there is spare capacity. It also monitors the WESPs for abnormal behaviour, providing operators with otherwise unavailable information and enabling faster detection of damages and facilitating troubleshooting, as well as faster and more accurate online support from Metso Outotec experts.

CANADA

Chemtrade wins lawsuit over Canexus acquisition

Chemtrade Logistics Income Fund says that the Court of King's Bench of Alberta has ruled in favour of the company in its lawsuit against Superior Plus Corporation. The lawsuit involved the failed attempt by Superior to acquire Canexus, prior to Chemtrade's 2017 acquisition of that company. The Arrangement Agreement between Superior and Canexus contained a clause requiring Superior to pay $25 million if the acquisition did not close due to a failure to obtain Canadian and US competition and anti-trust regulatory approvals.

Chemtrade operates a diversified business providing industrial chemicals and services to customers in North America and around the world. Itis one of North America's largest suppliers of sulphuric acid, and spent acid processing services, and is also the largest producer of high purity sulphuric acid for the semiconductor industry in North America. Chemtrade is a leading regional supplier of sulphur, and provides industrial services such as processing by-products and waste streams.

KAZAKHSTAN

Metso Outotec to supply SX/EW plant

Metso Outotec has signed a €35 million agreement with Kyzyl Aray Copper, a subsidiary of Caravan Resources, for the supply of copper solvent extraction and electrowinning (SX/EW) technology for a plant to be built in the Karagandy region of the Republic of Kazakhstan. Metso Outotec's technology package includes a modular *VSF*®*X* solvent extraction plant and the main process equipment for the electrowinning plant.

"We are looking forward to working with Kyzyl Aray Copper on this project. The energy-efficient solvent extraction plant, which is part of our Planet Positive product range, reduces emissions and is safe to operate. The Kyzyl Aray Copper project will become an important new reference for Metso Outotec in the growing Kazakhstan copper market as a supplier of a complete production plant that uses solvent extraction and electrowinning technology for copper recovery," said Mikko Rantaharju, Vice President, Hydrometallurgy, at Metso Outotec.

INDIA

Hindustan Zinc to convert to green energy

Hindustan Zinc Ltd (HZL), majority owned by the Vedanta Group as well as a 29% stake held by the Indian government, says that it will spend $1 billion on converting its diesel-powered mining vehicles into battery-operated ones and converting to green energy use. The company has been running four of its 900 mining vehicles on battery power on a pilot basis. HZL, which produces 0.75 million t/a of zinc and 0.25 million t/a of lead, has set itself the goal of becoming carbon neutral by 2050. To that end, it has signed a power purchase agreement for sourcing up to 200 MW of renewable energy, which will avoid 1.2 million t/a of carbon emission. Currently, it has a 475 MW captive thermal plant at the main smelter unit at Chanderiya and has over 275 MW of wind and 40 MW of solar power. As part of decarbonising operations, the company has signed a 25 year power purchase agreement with Serentica for 200 MW, which will reduce thermal power intake proportionately.

The company is also planning to set up a 500,000 t/a diammonium phosphate (DAP) plant at Chanderiya in Rajasthan in order to make use of its large sulphuric acid output. Work has already begun on the DAP unit and commissioning is expected in the second half of 2024 according to HZL. The plant will source 60-70% of its acid requirement from HZL's smelters and will use domestic Indian phosphate rock. HZL is cash rich at the moment with a 44% increase in profits for the first half of the 2022-23 financial year due to rising zinc prices globally. It operates eight mines and two zinc smelters, at Chanderiya and Patnagar.

Deal for phosphate rock import

India's government is reportedly planning to finalise supply agreements with Morocco and Egypt to obtain a secure supply of phosphate rock. The Indian government is concerned about sourcing phosphate rock and phosphoric acid to supply the country's major DAP fertilizer sector and has asked fertilizer companies to strengthen their supply chain resilience. The country has faced shortages as China halted supplies of DAP because of rising prices and falling demand. In the 2021-22 financial year, Indian fertiliser companies sold 9.2 million t/a of DAP and 12.1 million t/a of NPKs, but these figures have dropped to just 2.7 million t/a and 6.7 million t/a respectively for the 2022-23 year to date, with 4.7 million t/a of DAP and 1.9 million t/a of NPK imported. Rising fertilizer prices are also leading to a sharp rise in government subsidies paid to farmers.

Indian companies are understood to be looking at joint ventures with potential phosphate suppliers such as Morocco and Egypt. In August 2022, Coromandel International also bought a 45% stake in Baobab Mining and Chemicals Corporation, a phosphate mining company in Senega to supply phosphate for 1 million t/a of DAP/NPK production in India.

DEMOCRATIC REPUBLIC OF CONGO

New smelter for Kamoa

Kamoa Copper has selected Metso Outotec to supply a high-capacity direct blister furnace to the company's copper mining complex expansion in the DRC. Metso Outotec's scope of delivery consists of key equipment and automation for the production of blister copper in a single flash furnace without the need for separate converting stages. The 500,000 t/a copper throughput furnace will have the largest licensed flash smelting capacity in the world. The scope also includes intelligent safety and monitoring automation systems for the furnace.

"Non-ferrous metals play a key role in the green transition, and a major increase in global copper production is required to support this transition. We are pleased to support Kamoa Copper in their ambitious expansion project, in which high capacity and reliable, sustainable processes play a vital role. Our collaboration has been excellent throughout the initial stages of the process, including the initial study work, basic engineering as well as pilot testing," Jyrki Makkonen, Vice President, Smelting at Metso Outotec.

MOROCCO

OCP announces green investment strategy

OCP Group has launched a new strategic programme for 2023-2027 devoted to raising fertiliser production, investing in new green fertilisers and renewable energy. OCP's "green growth programme" provides for a global investment of about $13 billion over the period. It is based on increasing mining and fertilizer production capacities while achieving full carbon neutrality by 2040. This investment program aims to increase production capacity from the current 12 million t/a of fertilizer to 20 million t/a by 2027. In particular, it provides for an extension of mining capacities via the opening of a new mine in Meskala in the Essaouira region and the installation of a new fertilizer production complex in Mzinda. The latter will process rock from the mines at Benguerir and Youssoufia as well as from the new mine of Meskala.

OCP Group will supply all its industrial facilities with green energy by 2027 using wind, solar, hydroelectric and co-generation sources. The company says that this will not only strengthen OCP's competitive advantages but will also power new seawater desalination plants to meet the Group's needs as well as supplying drinking water and irrigation to areas bordering OCP sites. The investment in renewable energy will enable the Group, the world's largest importer of ammonia, to free itself from imports over the long term. Planned substantial investments in producing green hydrogen and green ammonia will enable OCP to produce wholly sustainable fertilizers and fertilization solutions adapted to the specific needs of different soils and crops. OCP aims to produce 1 million t/a of green ammonia by 2027 and 3 million t/a by 2032. A green ammonia production complex is planned in the south of Tarfaya, with a capacity of 1 million t/a which will be powered by a solar and wind farm with a total capacity of 3.8 GW. An electrolyser production plant will support this project, ensuring local industrial integration within the new value chain. A desalination plant with a capacity of 60 million m^3 will supply these industrial facilities and contribute to meeting regional water needs.

UNITED STATES

Copper project to receive SX/EW package

Metso Outotec says that it has signed an agreement for the supply of copper solvent extraction and electrowinning technology to an undisclosed client in North America. The order value was put at approximately €50 million. Metso Outotec's scope of delivery includes basic engineering, a technology package for the *VSF*® solvent extraction and electrowinning plants, as well as advisory services for mechanical installation and commissioning, start-up, and spare parts.

"We are looking forward to working on this project, which will be an important reference for Metso Outotec in North America's growing copper market," said Mikko Rantaharju, Vice President, Hydrometallurgy, at Metso Outotec.

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

People

Wael Sawan.

Ben van Beurden ended his tenure as Chief Executive Officer (CEO) of Shell and was replaced by **Wael Sawan** on January 1st, 2023. Van Beurden will continue working as adviser to the Board until June 30, 2023, after which he will leave the group.

Shell's Chair, Sir Andrew Mackenzie said: "Wael Sawan is an exceptional leader, with all the qualities needed to drive Shell safely and profitably through its next phase of transition and growth. His track record of commercial, operational and transformational success reflects not only his broad, deep experience and understanding of Shell and the energy sector, but also his strategic clarity. He combines these qualities with a passion for people, which enables him to get the best from those around him. The outcome of the Board's managed succession process resulted both in the appointment of an outstanding CEO and proved the strength and depth of Shell's leadership talent. I look forward to working with Wael as we accelerate the delivery of our strategy."

Wael Sawan said: "It's been a privilege to work alongside Ben and I'm honoured to take over the leadership of this great company from him. I'm looking forward to channelling the pioneering spirit and passion of our incredible people to rise to the immense challenges, and grasp the opportunities presented by the energy transition. We will be disciplined and value focused, as we work with our customers and partners to deliver the reliable, affordable and cleaner energy the world needs."

Commenting on Ben van Beurden, Sir Andrew said: "Ben can look back with great pride on an extraordinary 39-year Shell career, culminating in nine years as an exceptional CEO. During the last decade, he has been in the vanguard for the transition of Shell to a net-zero emissions energy business by 2050 and has become a leading industry voice on some of the most important issues affecting society.

"He leaves a financially strong and profitable company with a robust balance sheet, very strong cash generation capability and a compelling set of options for growth. These were all enabled by bold moves he has led, including the 2016 acquisition of BG and the transformational $30 billion divestment of non-core assets that followed. He took firm, decisive action to marshal the company through the global pandemic, seizing the opportunity for a major reset to ensure we emerged fitter, stronger and equipped to succeed in the energy transition. Powering Progress, Shell's detailed strategy to accelerate our profitable transition to a net-zero emissions energy business by 2050, was unveiled in February 2021 and was quickly followed by moves to simplify both our organisational and share structures. Ben's legacy will frame Shell's success for decades to come."

African phosphate producer and developer Kropz says that outgoing CEO **Mark Summers** and COO **Michelle Lawrence** have agreed to remain in their positions until the company concludes a recruitment process for their successors. Summers and Lawrence agreed under short-term consulting agreements to stay with Kropz to assist with a handover to a new CEO and ensure continuity of the operations across the company.The Kropz board says that it has identified and is in the process of engaging with a potential candidate to take over the role of CEO and executive director of Kropz and its subsidiaries – an endeavour it plans to finalise by early January 2023.

Calendar 2023

FEBRUARY

1-3
SulGas Conference 2023,
MUMBAI, India
Contact: Conference Communications Office,
Three Ten Initiative Technologies LLP
Tel: +91 73308 75310
Email: admin@sulgasconference.com

20-23
Laurance Reid Annual Gas Conditioning Conference,
NORMAN, Oklahoma, USA
Contact: Lily Martinez, Program Director
Tel: +1 405 325 4414
Email: lmartinez@ou.edu

27-MARCH 1
CRU Phosphates 2023 Conference,
ISTANBUL, Turkey
Contact: CRU Events
Tel: +44 (0)20 7903 2444
Email: conferences@crugroup.com

MARCH

13-16
The 8th Sulphur and Sulphuric Acid Conference 2023,
CAPE TOWN, South Africa
Contact: Conference Organiser, Gugu Charlie,
Southern African Institute Of Mining And Metallurgy
Tel: +27 73 801 8353
Email: gugu@saimm.co.za

APRIL

2-5
2023 Australasia Sulphuric Acid Workshop,
BRISBANE, Australia
Contact: Cathy Hawyard, Sulfuric Acid Today
Tel: +1 (985) 807-3868
Email: kathy@h2so4today.com

25-27
TSI Sulphur World Symposium 2023,
EDINBURGH, UK
Contact: Sarah Amirie, The Sulphur Institute
Tel: +1 202 296 2971
Email: SAmirie@sulphurinstitute.org

MAY

8-12
REFCOMM 2023,
GALVESTON, Texas, USA
Contact: CRU Events
Tel: +44 (0)20 7903 2444
Email: conferences@crugroup.com

23-25
Ninth International Acid Gas Injection Symposium,
CALGARY, Canada
Contact: Alice Wu, Spheretech Connect
Email: alicewu@spheretechconnect.com
Web: www.spheretechconnect.com

JUNE

9-10
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

PHOTO: BRIAN BROWN/ALAMY STOCK PHOTO

The impact of Ukraine on sulphur markets

Last year saw global trade in all commodities have to take into account the potential loss of supply from Russia, a key exporter of many commodities. Sulphur was no exception, with prices swinging wildly across the year.

Above: Piles of phosphate ore at the Monsanto phosphate mine processing facility near Soda Springs Idaho, USA. The phosphate market continues to be the key driver for sulphur demand.

We are now approaching the first anniversary of president Putin's 'special military operation' in Ukraine. Though the front lines have moved back and forth, there seems no immediate prospect of any end to the terrible fighting, and the likelihood for 2023 is more of what we saw in 2022. The immediate impact was a price rise in all major commodities supplied by Russia on anticipation of future shortages. Because of its importance to farmers globally, there have been no sanctions on food exports or fertilizer itself, although the US has created a licensing scheme for fertilizer imports from Russia, and the EU introduced a quota for potash and NPK imports from Russia in July 2022. However, the impact of financial sanctions and Russian companies' consequent inability to access the global SWIFT payments system means that purchases have become more difficult and complicated, and some shipping companies have suspended routes to and from Russia.

Russia has also been restricting exports of fertilizer and agricultural products through export taxes, licensing requirements, and actual bans. Russia put export licensing requirements in place in 2021 for nitrogen-based fertilizers (including NPKs). It has also been unable to export ammonia via the Togliatti pipeline across Ukraine to Odessa.

Table 1: **Russia's share of key fertilizer markets, 2021**

Product	Volume, million t/a	Export market share	Export market rank
MOP	11.8	27%	3rd
Ammonium nitrate	4.3	49%	1st
Urea	7.0	18%	1st
NPKs	5.9	38%	1st
Ammonia	4.4	30%	1st
DAP/MAP	4.0	14%	4th
Sulphur	1.8	9%	3rd

Source: Argus

Fertilizer markets

Fertilizer markets had already been suffering from supply disruptions that had followed the covid pandemic, and prices were already high going into 2022. The invasion of Ukraine and the sanctions and trade disruptions that followed merely pushed prices even higher. As Table 1 shows, Russia was the leading exporter of many key fertilizers in 2021, and the third largest exporter of sulphur.

Potash markets had the greatest potential to be affected; just under one third of global potash production is accounted for by Russia and Belarus, and the two countries represented around 40% of total potash exports in 2021. Belaruskali relied on exports via the Baltic Sea, with 85% of its exports using that route, and losing access to the Lithuanian rail network meant this could no longer be exported that way. Although producers such as Nutrien, Mosaic, and K+S have announced potash capacity additions, there is a long lead time for new supply and the market remains very tight.

In the event, it is nitrogen markets that have been worst affected, with supplies of natural gas from Russia to Europe being drastically reduced, pushing up gas prices in Europe and severely curtailing ammonia and downstream nitrogen production. European gas prices had already been high in early 2022 because of a cold winter in 2021-22 and dislocation to renewable electricity supplies. This has had a knock-on effect on phosphate markets, crucial to sulphur demand, with high prices for ammonia affecting diammonium phosphate (DAP) production. Phosphate markets have also faced reduced supply from China, which normally supplies around 25% of all internationally traded phosphate. China has extended quotas on phosphate exports to try and keep control of domestic prices and supply to its own farmers. The country has faced reduced MAP/DAP production due to high coal prices curtailing domestic ammonia production. Overall, China's exports in 2022 were down about 60% on 2021. In the longer term, this reduction will be offset by additional production elsewhere. OCP in Morocco is adding 3 million t/a of MAP/DAP capacity over the 2022-23 period, and in Saudi Arabia the Ma'aden Phosphate 3 expansion project will be fully operational in 2025. Mosaic also has some scope to increase operating rates in Florida. Nevertheless, it has had a major impact on phosphate demand. The International Fertilizer Association (IFA) says that global fertilizer use declined 2.4% in 2021-2022 due to affordability issues, changes in crop mixes, and the war in Ukraine, with phosphate demand in particular falling more than 4%, and IFA estimates that the figure for 2022-23 will be another fall of 5%. This will have a knock-on effect on food production, especially the fall in nitrogen demand. The effect may not be so pronounced for phosphate and potash, which can tolerate a year of under-application, but nitrogen, the key building block for plants, remains crucial and yields will fall in its absence.

Sulphur

As Table 1 shows, Russia was also a significant sulphur exporter prior to the conflict. Russian sulphur exports totaled 1.8 million tonnes in 2021. This was actually significantly down from the usual figure of over 3 million t/a – Russian exports in 2020 were around 3.6 million tonnes. The fall in 2021 was due to an increase in demand within Russia for sulphur for phosphate production, as well as a dip in production. Even so, a loss of 1.8 million t/a could cause major disruption to the market and fears of this helped drive prices higher in the first half of 2022. At the time that the conflict began, there was also concern that exports from Kazakhstan might be affected. Kazakhstan exported 3.9 million t/a of sulphur in 2021, and more than 90% of that was taken via rail through Russia. However, as the year progressed, it became clear that sulphur was still being exported normally from Kazakhstan, and that Russian exports had not been as badly affected as feared, and this helped the relaxation in sulphur markets in the second half of 2022.

Sulphur prices rose throughout the first half of 2022, with Middle Eastern f.o.b. prices reaching $470-480/t. However, the second half of the year saw an equally rapid fall, with the high prices causing demand destruction and contraction in demand from the phosphate industry. Indeed Middle East prices dropped by almost $400/t, and bottomed out around $100/t at the end of 2022, lower than they had been going into the year. Though prices have risen slightly since then, a full recovery awaits an upturn in the phosphate industry. Support has mainly come from the metals sector, with record prices for nickel driving demand for sulphur to feed HPAL projects in Indonesia.

In August, Russia imposed a quota on the export of sulphur. The quota ran from August 10th to December 31st, and set an export ceiling of 1.1 million tonnes. The quota did not apply to sulphur produced outside of the Eurasian Economic Union (Russia plus Armenia, Belarus, Kazakhstan and Kyrgyzstan) prior to August 10th, or for which there was an existing order for delivery by ship or which had been accepted by Russian Railways for transportation. Furthermore, sulphur exported to the Donetsk and Lugansk People's Republics, Abkhazia and South Ossetia were also not subject to the quotas. The decree which initiated the quota also fixed maximum prices for sulphur supplied to Russian fertilizer producers at a level no higher than the average f.o.b. prices from May-July 2021. This follows the same model of an existing price cap on mineral fertilizers.

New sanctions

However, new sanctions are still being progressively imposed. In December the UK and EU imposed a ban import of a variety of materials and equipment from Russia and Belarus, including machinery for oil production and exploration; and the agreement also banned the purchase of several chemicals, including sulphur. So far, major buyers of Russian sulphur like Morocco are not part of the sanctions, however, nor are major importers of Russian fertilizer such as Brazil and India.

A price cap was also agreed on Russian oil in early December by the G7 group of nations, plus Australia and the EU. The cap prohibits countries from paying more than $60/bbl for Russian oil. In response, Russia has now said its oil and oil products will not be sold to anyone imposing the price cap for five months from 1st February until 1st July. Furthermore, in February, the EU will ban the purchase of oil and petrochemical products from Russia. This could have a significant impact on diesel markets. Previously Russia had been a major supplier of diesel for Europe, whose refineries tend to produce more gasoline than the continent requires (with a surplus going to the US) and less diesel. Europe had been importing 2.5 million tonnes of diesel per month. There is some slack for European refiners to raise crude runs to compensate, but this will also lead to further surpluses for gasoline and other products and consequent price falls – winter is historically a time of lower gasoline demand in Europe.

Higher crude runs could mean higher sulphur production from European refineries, but the ban on purchases of Russian crude will be problematic for some of Europe's refiners. PCK at Schwedt and Total at Leuna rely heavily on Russian crude imports, while the Priolo refinery in Sicily is owned by Russia's Lukoil. All three face reduced capacity or even closure. High natural gas prices – thankfully now coming back down to normal levels – have also weighed heavily on the cost of producing hydrogen and hence operating hydrocrackers and hydrotreaters for sulphur removal.

Insurance

In another blow to trade from Russia, major insurance companies have said that they will cancel war risk coverage across Russia, Ukraine and Belarus from January, leaving cargo and freight companies liable for any losses linked to the ongoing conflict. At least 12 of the 13 Protection

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and Indemnity (P&I) clubs - which cover 90% of the world's ocean-going ships, have said that they will no longer be able to provide coverage to clients because reinsurers were exiting the region as a result of financial losses. The cancellations mean it will be harder for ship owners or charterers to secure insurance this year, resulting in higher prices and some shipping firms either deciding to avoid the region or even sail without coverage. In response, the Japanese government has asked insurers to take on additional risks to ensure LNG can be shipped from Russia, particularly the Sakhalin project in eastern Siberia, which supplies 9% of Japan's LNG imports.

Phosphate demand still key

The direction of sulphur markets in 2023 will depend crucially upon demand from the processed phosphates sector, which remains the largest slice of sulphur demand. One major issue remains China's system of inspection certificates and export quotas, which have seen phosphate exports fall by around 45% in 2022. On the other hand, a relatively mild winter so far in Europe has seen natural gas prices fall to the (admittedly high) levels that prevailed prior to the invasion of Ukraine, which has benefitted nitrogen markets and hence DAP producers. So far this does not seem to have impacted upon sulphur import demand in countries such as Morocco, but it may do so as the year progresses. Likewise the falling sulphur price has helped DAP producers and may rescue demand somewhat.

Chinese domestic phosphate production will also be the key to Chinese imports of sulphur this year. China's domestic production of sulphur has been rising steadily over recent years due to new refinery construction and rising sour gas production. Two large new refineries started up at the end of 2022 at Lianyungang and Jieyang with a combined sulphur capacity of 1.4 million t/a, and these will be ramping up production throughout 2023. The relaxation of covid restrictions in China, which had been a severe brake upon the Chinese economy, is expected to see gasoline demand rise as people return to driving more, increasing refinery run rates in China. China imported 8.5 million t/a of sulphur in 2021 and an estimated 7.4 million t/a in 2022. Recent figures from Argus predict the 2023 figure to reach 7.8 million t/a this year, but much depends on phosphate export quotas.

The sulphur market also faces increased supply from the Middle East, with the continuing ramp up of the new refineries at Al Zour in Kuwait and Jizan in Saudi Arabia. Higher run rates at refineries in Europe and the US to make up for loss of oil and petrochemical supply from Russia will also boost sulphur output, though this of course offsets reduced sulphur supply from Russia. Russia exported only 1.1 million t/a of sulphur in 2022, and the figure for 2023 is likely to be similarly low.

As global GDP recovers, led by a recovery in China, demand for sulphuric acid and hence sulphur for industrial uses will also rise. There is also continuing expansion in the metals processing sector. Indonesia's imports of sulphur for HPAL processing of nickel is increasing, and may reach 2 million t/a this year.

Overall, sulphur demand growth is expected to rise in 2023, probably more than offsetting increases in supply. But the outlook remains clouded by international sanctions, logistic issues, the rebalancing of global trade flows, and export restrictions, to name a few, and volatile prices are likely over the coming months. ■

PHOTO: BOLIDEN

A looming sulphur shortage?

Left: The Harjavalta smelter sulphuric acid plant, Finland.

Last year attention was drawn to the potential for large scale decarbonisation to leave the world short of the key resources of sulphur, and hence sulphuric acid. But is there a global sulphur shortage on the distant horizon?

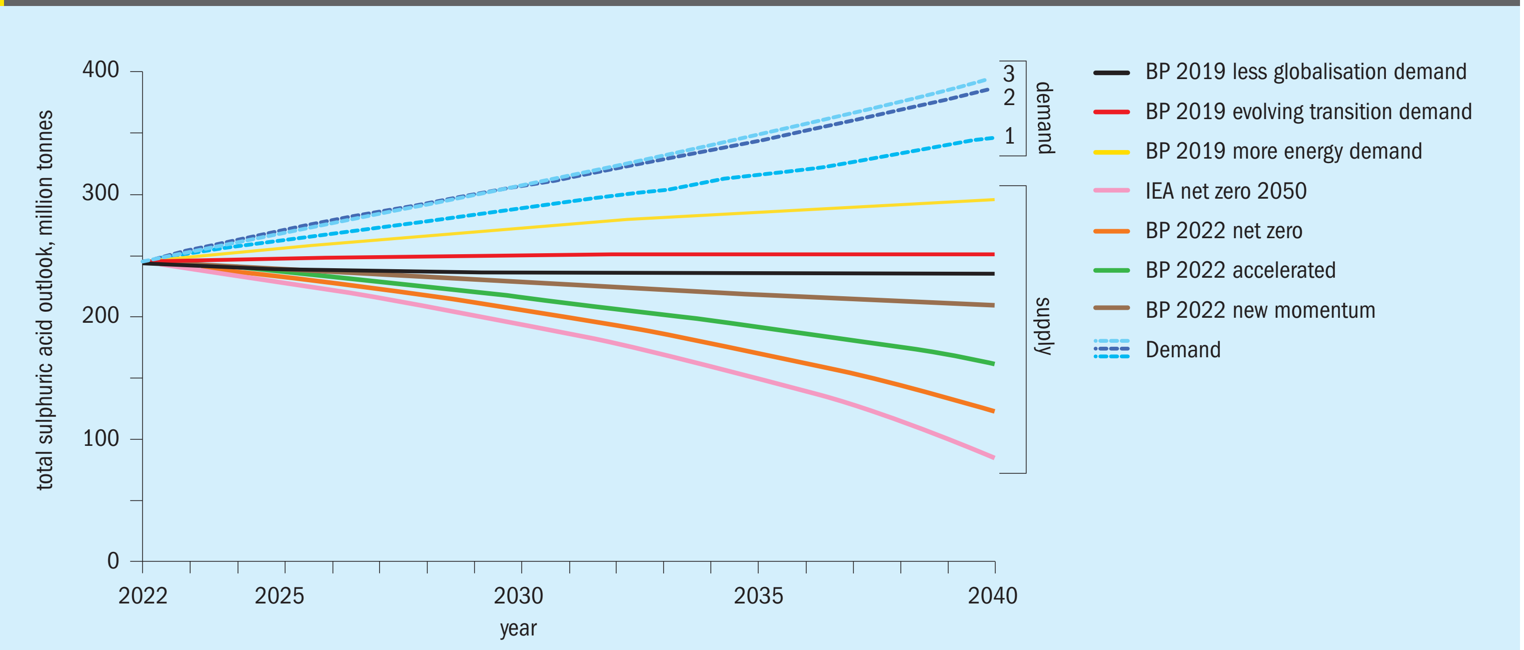
The article was written by professor Mark Maslin of University College, London, and published in The Geographical Journal; the journal of the highly regarded Royal Geographical Society[1]. It projected forward sulphuric acid demand to 2040, ending up at a figure of 400 million t/a, and looked at what the reduction in sulphur supply from oil and gas might be under various future scenarios being examined by BP as part of its transition away from being a fossil fuel company. The conclusion was that under an optimistic forecast there would be a shortfall of 100 million t/a of acid supply, and under a pessimistic one up to 320 million t/a, or 80% of the requirement by 2040.

This is certainly a worrying prospect, and it echoes other warnings, including ones from within the industry. In 2012 at the CRU Sulphur Conference, Dr Peter Clark of Alberta Sulphur Research highlighted the potential shortfall in sulphur from reduced oil consumption[2], and this was followed up with a joint paper with Angie Slavens in 2018[3]. Dr Clark's forecast was in some ways less gloomy, but mainly because he forecast a far slower phaseout of fossil fuels than the studies used by Maslin. Even so, he foresaw a shortfall by 2030. So how worried should we be?

Sulphuric acid demand

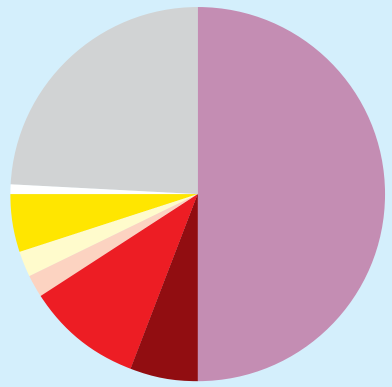
Sulphur remains one of the key raw materials for the modern world. Its main derivative, sulphuric acid, is the largest global industrial chemical by volume, with over 260 million t/a consumed in 2021. Its primary use is in the fertilizer industry, for extraction of phosphates from phosphate-bearing ores, but it also performs a similar function in the copper, nickel, uranium and other metal extraction industries, as well as titanium ore for paints and pigments. Other major uses are as a catalyst in refinery alkylation of gasoline, manufacture of hydrochloric acid, water treatment, and in

Fig. 1: **Projections of long-term sulphuric acid production and demand**



Source: Maslin et al[1]

Fig. 2: **Consumption of sulphuric acid by end use**



a wide variety of industrial and pharmaceutical processes. At present, around 55% of acid goes to make phosphates – most of that destined for fertilizer use, 10% to metal processing, 2% to titanium dioxide, and a similar amount to hydrochloric acid production, 5% to production of various fibres, and 24% to the many industrial processes using it (Figure 2).

Nor is this demand for sulphuric acid likely to go away soon. Indeed, projections for this decade indicate that its use could rise to over 300 million t/a by the end of the decade, an annual rise of around 2%. If this rise were to continue at that rate, demand would have reached 370 million t/a by 2040, and 440 million t/a by 2050 (the Maslin study used a higher growth rate of 2.3% year on year to reach its figure of 400 million t/a by 2040). However, it is possible that this 'steady state' projection may underestimate the potential for demand growth.

Phosphates

Rapid growth is unlikely to come from the phosphate side; phosphate fertilizer demand growth has been relatively steady and has actually slowed over the past couple of decades. During the 2000s phosphate demand increased by around 3.5% year on year, but in the 2010s this slowed to an average of around 1.8% AAGR. It is also subject to short-term setbacks such as the disruption to the fertilizer market caused by high prices and lack of availability seen in 2022, leading to an approximately 9% year on year fall in phosphate fertilizer consumption last year. Nevertheless, on a long-term basis it continues to grow, albeit perhaps at around 1.5% year on year for the rest of this decade, following a correction in 2023 to bring demand back up to around the 2021 level.

It remains to be seen how long phosphate fertilizer consumption will continue to rise. Many major global markets such as the US and Europe are already relatively mature in terms of consumption, and may see falls due to increased efficiency of use and, in Europe, regulations on sourcing phosphates from sewage and other forms of nutrient recycling. China has actually seen falling fertilizer applications as it moves to greater nutrient use efficiency and tries to tackle overapplication of fertilizer and consequent deleterious environmental effects. Chinese phosphate production has also fallen due to measures to tackle pollution and overcapacity. Likewise the rate of increase of global population, which was a major driver of fertilizer consumption in the late 20th century, continues to slow. Estimates of when peak global population will be reached used to cluster around 2100 according to UN estimates, but these estimates were contingent on fertility rates in China and Japan picking up, which has not happened -if anything the reverse. Current estimates put peak global population at around 2060-65, and it may even be as soon as 2050. Conversely, industrialisation continues to increase, and this has driven higher calorie consumption and more intensive agriculture, requiring more fertilizer. Greater disposable income is correlated with increased protein consumption and higher fertilizer demand in developing countries. And while some markets are mature, there is still room for growth in South America, especially Brazil, and Africa in particular still has some way to go both before population levels settle to replacement values, incomes near global norms and fertilizer applications match global averages. Much of the coming growth in phosphate demand may eventually come from Africa. There is thus still long-term potential for increased phosphate fertilizer demand, and a figure of a 1.5% year on year increase may not be far wrong even out as far as 2050.

Electrification

The same is not true of metals processing, however. As the world makes greater use of electricity, especially for vehicle power trains, so demand for transition metals for batteries grows, almost exponentially at present. The International Energy Agency has estimated that global copper demand is likely to increase by 2.1-3.4 times by 2050 compared to its 2020 value, and demand for nickel and cobalt will increase by a factor of 10 times and lithium 20 times its current value. Industry figures are more conservative. BHP forecasts a 4-5 fold increase in nickel demand by 2050. Even so, that would mean that consumption would rise from just over 2 million t/a to over 11 million t/a.

How will all of this metal be extracted? Nickel processing employs a variety of forms, from pyrometallurgical processes which often leave it alloyed with iron (ferronickel and 'nickel pig iron') to smelting of sulphide ores. But deposits of sulphides are relatively rare compared to the abundance of oxidised laterite ores. Production of large volumes of the high purity nickel that will be required for the battery industry has increasingly looked to high pressure sulphuric acid leaching of the ore – the HPAL process, and the current expansion in electric vehicle manufacture has already seen a number of large scale HPAL plants built in Indonesia, with the potential for other large projects to be developed in Australia and elsewhere. This could see sulphuric acid requirements increase dramatically over the next decades.

Increased production of copper may not be as dramatic for acid demand because for copper the abundance of sulphide vs oxide ores is reversed compared to nickel. While acid leaching of copper will increase, this only accounts for around 20% of copper production, and there presumably will also be a corresponding increase in copper smelting, which generates sulphuric acid as a by-product and which will presumably be able to feed some of the new nickel extraction.

There is also the question of battery recycling. As global use of EVs increases, there will be increased pressure, and presumably increased cost incentive, to recycle more of these strategic metals. At the moment recycling electric vehicle batteries is an expensive process involving high temperature melting and recovery, but most forecasts assume that there will be much greater use of recycling of scrap nickel, perhaps as much as 40% by 2050.

This would reduce the need for new mined nickel and HPAL processing.

Long term acid demand

Taking these factors together, how much extra acid demand could we see? A growth in phosphate demand of 1.5% per year would mean an increase in demand of 35% from 2020 to 2040, or around an extra 50 million t/a of acid. Metal leaching could add 25 million t/a under even fairly conservative forecasts for nickel and copper, and assuming an increase in recycling. Other industrial uses would add another 70 million t/a, assuming they tracked average long term global GDP growth rates of 3% year on year. This combined would take acid demand to 415 million t/a by 2040 – higher, though not by a long way, of the projections used by the Maslin paper, which assumed 370 million t/a, and averaging around 2.35% growth per year.

Sulphur supply

Production of sulphur 'in all forms' was just over 90 million t/a last year. This includes sulphuric acid generated in the smelting of metal sulphide ores and acid generated from the thermal breakdown of iron pyrites. However, the majority; around 65 million t/a, came from elemental sulphur recovered from oil at refineries and from natural gas at gas plants. It is future use of these commodities which will determine the long-term supply situation for sulphur.

Future oil demand

Oil has dominated the world's primary energy mix for nearly six decades. Although its share peaked in the mid-1970s, when it accounted for almost half of the world's energy consumption, its demand continues to grow in absolute terms. For instance, in 2019, the world consumed more than three times the number of oil barrels per day than it did in 1965. Oil demand growth in the first two decades of the 21st century – aside from the dip caused by the covid pandemic – was just under 2% year on year. While some oil goes to heating or the production of petrochemicals, about 60% of it is used as a liquid fuel, following refining, and so it is vehicle use that dominates and will dominate demand. Within the transport sector, however, there are trends which are likely to see the rate of increase in demand fall over the next two decades. The main three are improvements in the fuel efficiency of vehicles, slower population growth and increasingly saturated markets for vehicles, similar to what we discussed earlier with the phosphate market, and, increasingly, the electrification of the transport sector.

The greatest impact may be decided by the rate of penetration of EVs into the transport market. In 2012, only 130,000 electric vehicles (EVs) were sold worldwide, accounting for 0.01% of total cars sold. By 2021, the figure was 6.6 million, representing 9% of the global car market and more than tripling the market share from just two years earlier, according to the International Energy Agency (IEA). Many developed nations are no looking to phase out the sale of new diesel or gasoline cars. The US has a target of making 50% of all new vehicles sold in the country in 2030 zero-emissions vehicles while the UK and several other European countries have announced a ban on the registration of new gasoline and diesel cars and vans by 2030. Nearly 30 countries have committed to a ban on new gasoline/diesel vehicles by 2040.

What this will mean for oil consumption depends upon whose figures you believe. BP has an optimistic forecast of up to 70% EV use by 2050, while OPEC puts its 2045 figure at only 20%. OPEC believes that global oil consumption will rise from 97 million bbl/d in 2021 to 110 million bbl/d in 2045, and puts 2035 as the time when oil demand will plateau – other forecasters have progressively brought their prediction of peak oil demand closer to the present, and 2030 is now a favourite time for this. If oil demand does peak in 2030, what matters most is how fast it falls thereafter. Most forecasts expect a prolonged plateau of several years, which would mean that sulphur recovered from oil may only rise from 35 million t/d at present to about 38 million t/a by 2040.

But some projections call for a faster decline in the use of oil in order to meet targets for carbon dioxide emissions and keep the resulting increase in global temperatures to a minimum.

Natural gas

Natural gas was the fastest growing source of energy for the second half of the 20th century, mainly for electrical power generation. It has progressively replaced coal-fired generating capacity in North America and Europe, and become the favoured energy source in the Middle East. The development of a large international market for liquefied natural gas (LNG), removing the need for long and often expensive pipelines, has allowed the gas boom to spread to new regions. Recovery of sulphur from sourer natural gas fields, beginning in Europe and North America, but now spreading to the Middle East, Central Asia and China, has been the fastest growing source of new sulphur over the past few decades.

From 1980-2000, gas demand increased by about 2.6% year on year, rising from 1.5 trillion cubic metres (tcm) to 2.5 tcm. From 2000 to 2020 the increase was 2.4% year on year, and gas demand touched 4 tcm in 2019. Gas has benefited from being seen as a cleaner form of energy than coal or oil, and thus preferred for investment decisions by government policy in various countries. The past couple of years, however, have seen something of a change in attitudes, partially due to increased pressure to decarbonise power generation and concentrate more on renewable energy, and partially because of the price hikes to gas worldwide, and especially in Europe, caused by the invasion of Ukraine and consequent attempt by Europe to boycott Russian gas. Currently the International Energy Agency is only forecasting an average annual demand increase of 0.8% out to 2025, with industrial demand, for production of hydrogen, ammonia and methanol, for example, accounting for 60% of incremental demand as compared to power generation or domestic heating. China, India and southeast Asia remain the largest growth markets. There is expected to be a shift towards more renewable power generation, especially in Europe and North America, but China has also been a pioneer in this regard. Nevertheless, urbanisation, global wealth and GDP and use of electricity in transport increases, so demand for power will rise rapidly and it is likely that demand for gas will continue to increase overall. The Gas Exporting Countries Forum (GECF) – a sort of gas equivalent of OPEC – projects that global gas demand will continue to rise, by a total of 46% from 2020 to 2050, reaching 5.6 tcm. While this is a substantial jump, it is only a 1.1% rise per annum, reflecting the increasing use of renewables.

Where this gas will be sourced from will determine how much sulphur is generated from its production. In the Middle East and China, a lot of sulphur is coming from new sour gas reserves which have remained untapped hitherto because of the extra expense and difficulty in exploiting them. On the other hand, in Central Asia gas developments have often preferred to reinject acid gas into wells because of the lack of local sulphur demand and difficulty of transporting it from a remote land-locked region. Greater use of shale gas, generally lower in sulphur content, may also affect the sulphur balance of gas production. Saudi Arabia is soon to begin tapping its large shale gas field at Jafura and projects that it will be producing 2 bcm/day from this source by 2030. Overall, it may be a reasonable assumption that the sulphur balance from gas production will remain roughly constant, with new shale gas developments balancing sour gas exploration and production. This then might mean that sulphur production from sour gas rises by about 10 million t/a out to 2040.

The acid balance

At the moment, then, combining the projections for both oil and gas, our outlook would see sulphur recovery from oil and gas rise by about 13 million t/a from 2020 to 2040, equivalent to about 40 million t/a of additional sulphuric acid production. Set against the increase in acid demand of 100-140 million t/a that we have projected, this would indeed lead to a significant shortfall in acid capacity, as the Maslin paper has argued. Prof Maslin concludes that this would mean rising acid prices, possibly pricing fertilizer production out of the market and making food production more expensive.

However, this figure does not take into account any additional acid produced by copper and other metal smelting. Remembering that copper demand is forecast to more than double over the period as the transport system electrifies, then a consequential doubling in smelter acid production would reduce that shortfall almost to nothing. If the price is right, and in the event of any shortfall, acid can also be produced, as it still is to a small extent in China, by iron pyrite roasting. Furthermore, as Maslin argues, increased use of recycling of fertilizer nutrients, more efficient fertilizer use, or switching to industrial processes that avoid intensive use of sulphuric acid could also reduce any potential acid supply shortfall. Nitric acid produced from ammonia using hydrogen generated from renewable electricity for example could be a substitute in some industrial processes.

The conclusion then would seem to be that – for the moment – there is no need to worry about a sulphur shortfall, or at least a sulphuric acid shortfall, for the next couple of decades. Beyond that, as oil use falls and gas use peaks, that situation may begin to slowly change, but we are not about to run out of sulphuric acid just yet. ■

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SULPHUR index 2022

A complete listing of all articles and news items that appeared in *Sulphur* magazine during 2022.

Sulphur in Central Asia (Jan/Feb 2022, p18).

PHOTO: GAZPROM

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	Itafos begins producing hydrofluorosolicic acid	Jul/Aug	14
	Joint venture to make electronic grade acid	Nov/Dec	12
	Mosiac reports strong results	Mar/Apr	12
	Process to sequester CO2 while producing acid	Jul/Aug	14
	Sulphuric acid from carbon sequestration	Sep/Oct	12
World	Copper smelting activity down	Nov/Dec	14
	Nickel production up in spite of Ukraine crisis	May/Jun	15
Zimbabwe	Acid plant due for 2024	Sep/Oct	14

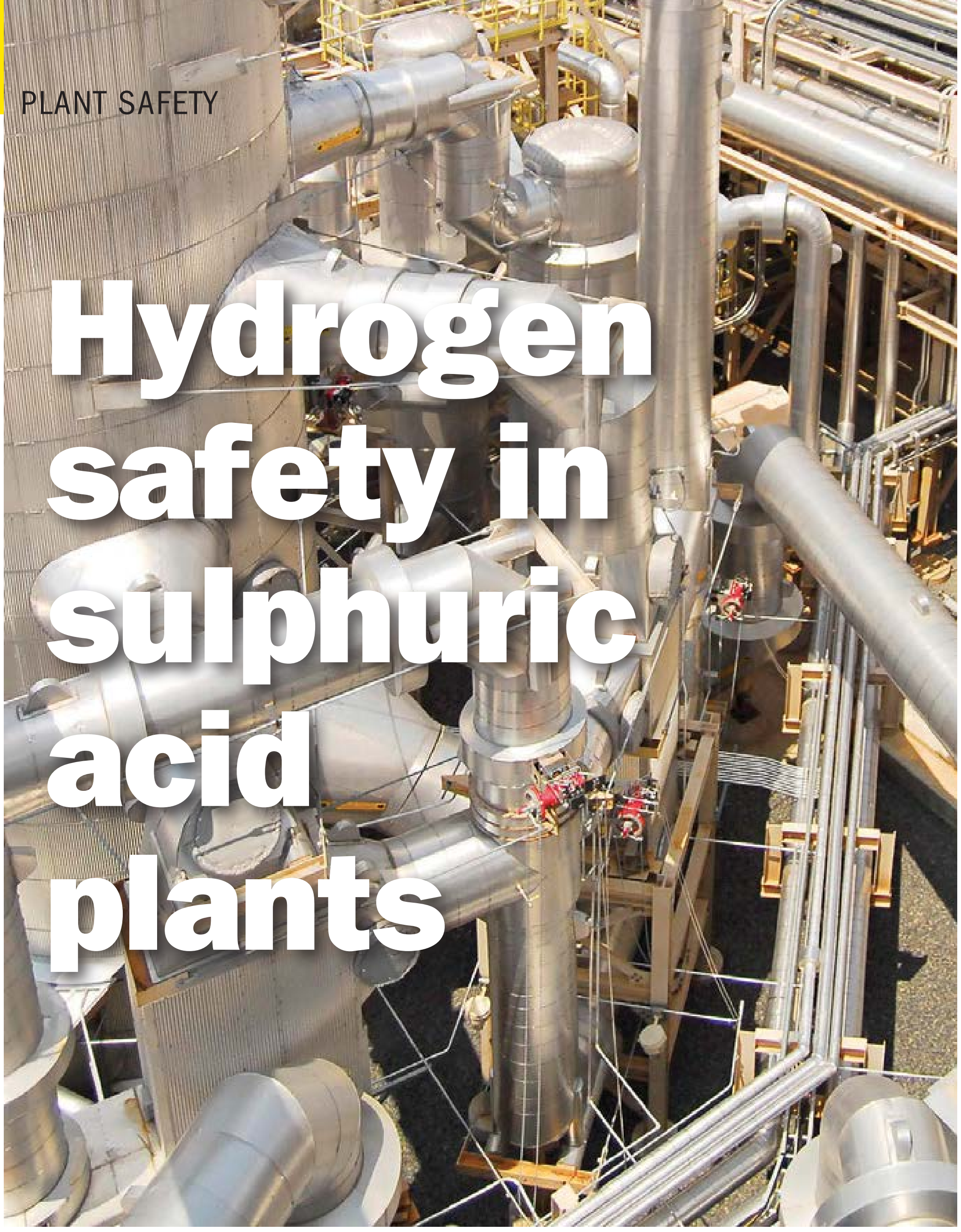


PHOTO: ELESSENT CLEAN TECHNOLOGIES

Hydrogen safety in sulphuric acid plants

Safety in sulphuric acid plants is a well-known and widely discussed topic. Industry turnover is a reality, and keeping new employees informed of hydrogen safety procedures is key to keeping plants fully operational and incident free. **Walter Weiss** of Elessent Clean Technologies discusses the steps facilities need to take to prevent hydrogen incidents.

Hydrogen is a chemical element that is a gas at normal temperature and pressure. It is the lightest of all elements on the periodic table and is highly combustible. On Earth, hydrogen occurs naturally in compound form with other elements. For it to stand alone, it must be produced in different ways. In a sulphuric acid plant, hydrogen can be formed through an electrochemical reaction in which there is an exchange of electrons. The following electrochemical reaction is responsible for hydrogen formation:

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$

In this formation specifically, the iron loses two electrons after coming in contact with sulphuric acid. This electrochemical reaction can partially be described by its two half-cell reactions involving the electron transfer as follows:

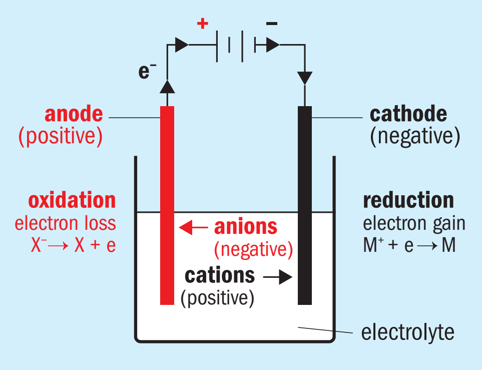
$$Fe \rightarrow Fe{+}{+} + 2e^-$$

$$2H + 2e^- \rightarrow H_2$$

When iron loses its electrons, also known as its oxidation reaction, it occurs at the anode or metal surface where the acid contacts iron, nickel or chromium equipment. The hydrogen reduction reaction occurs at the cathode. In a sulphuric acid plant, the cathode is in the bulk solution. Electrons are able to move more freely in the bulk solution because of its conductivity, so the transfer of electrons occurs more easily. Acid with weaker strength has higher conductivity, and the higher the acid conductivity, the more rapidly the reaction can take place. Fig. 1 shows the classical electrochemical cell in simple form.

In sulphuric acid plants, the strong acid system is made up of a variety of steels, which are made primarily of iron. A plant's design and operation govern the acid condensation from the gas phase and maintenance of the right acid concentration in the liquid phase within the sulphuric acid plant environment. Corrosion is minimised if this is done properly, and corrosion is the culprit in hydrogen evolution which left unattended can result in reduced plant safety. That said, there are always certain baseline levels of corrosion and hydrogen evolution that occur on a continuous basis. But with stringent concentration control, this level of hydrogen generation in comparison to the gas flowrate is insignificant and almost undetectable. Generally speaking, the majority of plant operators are not aware of its presence.

Fig. 1: **Classical electrochemical cell in simple form**



Source: Elessent Clean Technologies

The impact of process technology changes

Since the 1970s, advances in process technology have been made to address evolving EPA requirements. Some of these changes are directly related to the surface area of steel within an acid plant. Over the last several decades, the relative surface area of steel within an acid plant has increased.

The introduction of new flow schemes and new equipment design has led to the creation of high points where hydrogen can collect if not continuously removed. While these industry changes have made significant improvements to acid plant operations, they have also generated a new set of risk concerns and requirements which require operator attention.

As previously noted, corrosion from condensation in sulphuric acid plants leads to the generation of hydrogen. When metal surfaces come into contact with weak acid, it can increase the corrosion rate of the metals by several orders of magnitude, and as corrosion rates rise, the risk of hydrogen generation becomes greater. Over time, increased rates of hydrogen can lead to gas bubbles forming in the acid. When the hydrogen gas bubbles move through the acid, it disturbs the passive oxide or sulphate film that builds up on surfaces containing sulphuric acid which further accelerates corrosion rates within the plant.

Limiting corrosion

Within the plant environment, there are acceptable rates of corrosion that occur within relatively small concentration ranges and temperature changes. However, it is important to implement procedures to ensure that rates of corrosion do not rise. Equipment and piping must be kept within their prescribed operating window to keep corrosion rates low. Proper monitoring and attention to instrumentation maintenance is paramount for leak detection around equipment, like acid coolers that have water and acid on opposing sides of metal tubes, vulnerable to corrosion. Responding to acid leaks as quickly as possible is essential in minimising equipment damage and hydrogen generation. Not only will the water rapidly dilute acid outside the desired concentration range for the acid cooler materials, but additional heat will also be generated. Because acid dilution produces heat and corrosion rates increase with rises in acid temperature, corrosion rates intensify drastically in the event of an acid cooler leak.

Similarly, the loss of acid system concentration control caused by a control loop failure or an upstream steam system leak, can cause corrosion rates to intensify. Here again, the best course of action includes quick detection and then rapid separation of the water source from the acid and swift de-inventory of acid plant equipment. Corrosion rates should subside, and hydrogen generation should return to more acceptable levels immediately upon removal of the weaker acid from the system, and the system is re-inventoried with circulating strong acid.

Noting that the above describes acid plant incidents which likely entail full attention from the plant operators – draining, isolating, purging, cooling, etc. – attention to simultaneous generation of hydrogen can be readily overlooked without proper training and drills for these operators.

Preventing hydrogen ignition

The elements needed for a fire, which happen to be the same as those needed for an explosion, are a fuel, an oxidant and an ignition source. The difference between a fire and an explosion lies in where these elements meet. An explosion occurs when the fuel and oxidant are mixed in a confined space.

Hydrogen is a very effective fuel, and it is extremely buoyant and diffusive. In order for it to ignite at its lower explosive limit (LEL), the energy required is very low, nearly undetectable. Under normal circumstances, in a plant with adequate air circulation, hydrogen will flow normally through the plant with the bulk gas and be carried out the stack in low concentrations. However, in a stagnant plant, or plant with little air flow, it is possible for hydrogen to accumulate in high points like the tops of acid towers. Because hydrogen is diffusive, it mixes well with process gases which contain oxygen. Normal process gases like NO_2, NO and SO_2 can take part in the reaction resulting in a reduction in the LEL and increase in the energy release. Once hydrogen builds up to a value exceeding its lower explosive limit of 4% (or less), an ignition source will start a fire. As already mentioned, an ignition source will cause an explosion if these elements are located within a confined space, and there are many confined spaces within an acid plant. Also worth noting, the ignition source required for initiating hydrogen combustion in air is infinitesimally small – such as static charges associated with droplets.

Continued operation of the main compressor in the acid plant while the operators respond to the incident will help reduce hydrogen concentrations by maintaining proper air flow. This will also help minimise the confined space risk factor. That said, if the main compressor is shut down, either by intent or by interlock, the risk of fire and explosion increases significantly. Thus, a key to maintaining hydrogen safety measures includes maintaining air flow to purge the plant.

Over the last decade or so, there have been an average of one or two hydrogen explosion incidents per year, occurring almost entirely when the plant has been shut down. The energy release at the LEL concentration is significant enough to cause damage to important plant equipment which can cause extensive down time and severe repair costs.

When planning for a shutdown, purging the plant to flush out the hydrogen should be at the top of the to-do list. Other preventative measures include installing high point vents in accessible locations and opening those vents after purging the plant to aid in the release of hydrogen that continues to form. Using automated valves is also recommended to speed response time and to distance workers opening valves from the explosion potential. Additionally, isolating equipment, draining acid and water from equipment and rapidly reacting to concentration or temperature upsets can help minimise hydrogen generation. Some final measures to help reduce the occurrence of a hydrogen incident include ensuring effective concentration controls, dilution water interlocks and process alarms.

Conclusion

While plants are designed to minimise all potential risks related to hydrogen, accidents still happen. It is imperative that facilities take steps to proactively prevent hydrogen incidents, such as:

- drilling emergency procedures;
- conducting operator training focused on hydrogen awareness;
- reconsidering the presence of hydrogen for general work or hot work permitting;
- implementing a mechanical integrity programme;
- conducting routine turnaround inspections and equipment repairs;
- replacing equipment prior to a failure;
- carefully monitoring process conditions.

Maintaining sulphuric acid plants by safely starting up, operating and shutting down are key to minimising the presence of hydrogen, thus minimising the risk of a hydrogen incident. ■

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

Do you have a plan for a weak acid incident?

The world has seen a number of hydrogen explosions in double absorption plants mostly in the intermediate absorption tower (IAT). To review this increase and to determine the causes, an International Hydrogen Safety Workgroup was formed including major acid plant contractors, major acid producers, and consultants in the sulphuric acid arena. Workgroup member **Rick Davis** of Davis & Associates Consulting explores some of the findings.

I have been involved in the sulphuric acid industry for over 40 years and I have found the process secret. The secret is that without water the production of sulphuric acid is impossible. This is the primary reason that the process gas is dried to a very low water dewpoint using 93-98% sulphuric acid in the drying tower. This allows the use of carbon steel for most of the plant equipment. Over the years, the increase in sulphur dioxide (SO_2) feed gas concentrations have been increasing the use of stainless steel in process equipment such as the converter. This change is not based on any corrosion consideration. Stainless steel is stronger than carbon steel at high temperatures and produces less high temperature oxidation.

How hydrogen can be generated

The workgroup has determined that the major factors causing hydrogen explosions are:

- weak acid incidents;
- failure of timely detection of weak acid conditions;
- failure to react.

There is no mystery of how sulphuric acid can generate hydrogen. I remember in chemistry lab in high school my teacher mixed hydrochloric acid and some zinc and collected the off-gas in a glass bottle and then covered the bottle lid and lit the gas with a small piece of burning wood. When the stick was introduced into the covered bottle it went poof and pop when the hydrogen ignited. The chemical reaction is:

$$Zn + HCl \rightarrow ZnCl + H_2$$

This is the same reaction for Fe, Ni and many other similar elements, but with H_2SO_4 the reaction is:

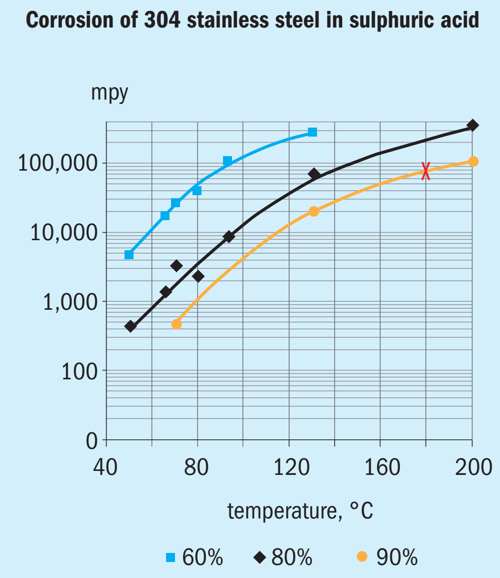
$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$

Normally, the acid concentration and temperature range routinely handled in acid plants are:

- 93% H_2SO_4, <150°F (66°C)
- 97-99% H_2SO_4, 110-240°F (43-116°C)
- 99-99.5% H_2SO_4, max. 397°F (203°C)

Acid below the above range will be considered as weak acid.

Fig. 1: **Time taken for a weak acid excursion to lead to a hydrogen incident**



Source: MECS

Basis:
100 m² (1,075 ft²) surface area
90% acid at 180°C = 85,000 mil/yr or 0.25 mm/hr

Metal loss:
Density of 304L SS – 8.3.g/cm³ (0.3 lb/in³)
0.25 mm/hour X 1 cm/10 mm X 1,000,000 cm² X 8.3 g/cm³ X kg/1,000 g = 208 kg Fe/hr per 100 m²/hr

Therefore:
208 kg Fe/hr X kg-mole/56 kg X 1 H_2/Fe X 22.4 Nm³/kg-mol = 83 Nm³/hr H_2 per 100 m²

Worse case time to reach 4-vol% LEL with a tube leak in a 600 m² acid cooler:
For a 3,000 t/d plant with a hanging Brownian movement mist eliminator, a typical volume of the mist eliminator housing area is:
7.5 m diameter X 5 m high = 220 m³.
Volume of H_2 to reach LEL is: 220 m³ X 4.0 vol-% = 8.8 m³
The H_2 generation calculation determines 83 Nm³/h of H_2/100 m² metal in contact with weak acid.

Hydrogen generation rate: $83\ \frac{m^3}{hr} \times \frac{600\ m^2}{100\ m^2} \times \frac{1\ hr}{60\ min} = 8.3\ \frac{m^3}{min}$

Time to reach LEL: 8.8 m³ needed to reach LEL $* \frac{1\ min}{8.8\ m^3}$ H_2 generation rate = ~1 min

This calculation shows a considerably shorter amount of time than we've seen in practice.
It's most likely due to variables like mass transfer of acid through sulfates on the surface of the metal and the actual acid temperature. Even a failing acid cooler will still cool the acid for a period of time.

To illustrate how the corrosion of 304 stainless steel is affected by temperature and concentration, remember when water is added to concentrated acid, heat is generated. So, if you start with 93% H_2SO_4 at 110°F, which is within the normal range and dilute to 90%, the temperature will increase to over 150°F. With only a 3% drop of concentration there will be an increase in corrosion and hydrogen generation.

In the scenario shown in Fig. 1, a committee member estimated how much time it takes for a weak acid excursion to lead to a hydrogen incident in a 3,000 t/d plant. The square footage of metal in contact with weak acid and time will affect the overall quantity of hydrogen generation. While this scenario most likely would not exactly match your plant configuration, it provides a scalable benchmark that illustrates the time range for hydrogen generation. Each plant must review their situation to determine standard operating procedures (SOPs) to address the actions required to mitigate the situation.

This establishes one rate of generation of hydrogen. The rate can be greater or less dependent on the actual conditions. The workgroup has reviewed incidents where the acid concentration dropped to as low as 80 wt-% H_2SO_4. In these situations the corrosion rate was greater, therefore, the hydrogen generation rate is greater.

Hydrogen will migrate to the highest point possible. Most of the incidents brought to the workgroup have occurred in the mist eliminator volume region in the interpass tower, but incidents have also occurred in drying towers and in the converter stage connected to the interpass tower.

The development of hydrogen gas is time dependent, therefore, your plant operations response should be timely. The operators must be trained with SOPs and reinforced through continuing education.

A weak acid incident can originate from the following water sources:

- High pressure steam generation components like:
  - waste heat boiler (furnace and converter boilers)
  - steam superheaters
  - economisers
  - unintentional water addition due to leaking dilution water valves during a shutdown

Fig. 2: Sulphate and scale can plug the drain line.

- Acid cooler issues including:
  - tube leaks
  - maintenance procedures
  - operating procedures

Weak acid incidents detection

Steam leaks

Routine acid condensate observations from the economisers should be conducted. Routine should mean at least once per shift. Many plants with previous steam equipment leaks should consider increased frequency or additional instrumentation due to the reduced mechanical integrity of the equipment due to previous water leaks. Opening a drain valve on an economiser should produce dry white smoke. Typically, there may be a few drops of condensate. These observations should be documented and used as a point of reference for future observations.

If there is no white smoke that normally means the plant is not routinely monitoring the economiser for condensate. Sulphates and scale can gather on the economiser floor. These deposits can plug and restrict the drain nozzle as shown in Fig. 2. No smoke means the line is plugged.

Some economisers are designed with a centre point drain with a line extending to the outside perimeter of the economiser to allow access to the valve for observation and draining. Many economisers have a sidewall drain located close to the economiser floor with a short connecting nozzle.

I have seen that some plants have installed a condensate collection pot with instrumentation to detect the accumulation of condensate. These collection pots should not eliminate the need for routine drain observations plus early detection between observations.

One of the many issues the Hydrogen Workgroup reviewed was the detection of the acid dewpoint entering the intermediate absorption tower. Acid dewpoint analysers have been marketed for years to monitor the acid dewpoint for fuel fired steam boilers. The analytic equipment can provide continuous reading of the dewpoint. The application of an acid dewpoint analyser on a fuel-fired steam boiler is far different than the outlet of the economiser before an intermediate absorption tower. Two investigations into the technology for continuous monitoring of the dewpoint showed that this is not feasible. It was found to be maintenance intensive, but there is an answer.

Acid dewpoint analysers can be effective to detect sudden changes in the acid dewpoint of the process gas, but not relied on for an absolute indication of acid dewpoint. Most HP steam leaks will cause a sudden change to the acid dewpoint. Leaks in superheaters may lead to an increase of acid dewpoint but may not be a sudden change. The observations at the economiser will show change. Usually, more condensate is observed.

The early detection of the weak acid incidents in steam systems in your plant should be developed into your plant standard operational procedures (SOPs) based on your plant specific configuration.

Acid coolers

Cooling water is responsible for the majority of acid cooler leaks. When stainless steel acid coolers were first introduced to the sulphuric acid industry back in in the early 1970s it was realised that controlling the cooling water quality and the tube wall metal temperature are critical for the control of corrosion. When Chemetics first marketed anodically protected coolers, they insisted that the cooling water flow must be maintained at the designed flow rate and acid temperature to the acid tower would be controlled bypassing hot acid around the cooler. There was no means or way to throttle cooling water which meant water-side fouling was minimised. Maintaining the acid pressure greater than the cooling water pressure allows for quick detection of tube leaks by monitoring the pH of the cooling water. A small acid leak will change the pH of the cooling water. There should be one pH and a conductivity probe in the outlet cooling water line of each cooler to allow for quick detection of an acid leak. Maintenance of pH probes unfortunately has not received the required priority to maintain an accurate indication in many plants.

PHOTOS: CHEMETICS

Fig. 3: The increasing size of acid coolers.
Left: 800 t/d plant, 0.8 m shell ID, 5.3 m^3 acid, 2.4 m^3 water. Right: 4,400 t/d plant, 1.8 m shell ID, 18 m^3 acid, 7.5 m^3 water.

Reaction to weak acid conditions

The workgroup suggests that the plant response should be:

- timely;
- included in plant specific SOPs;
- weak acid SOPs should be written, and the operating staff should be trained and tested.

The key issues that should be included in the reaction plan are:

- maintain air flow by slow rolling the compressor to prevent the accumulation of hydrogen;
- stop the source of water;
- removal of the weak acid.

Steam system incidents

Waste heat boilers

The major cause is tube to tubesheet leaks. It has been determined that poor quality tube rolling and welding at this critical weld has been the cause of many leaks.

Economisers

The design purpose of the economiser is to reduce the sensible heat of the process gas entering the acid system to recover the energy into the steam system versus the cooling water. This requires the cooling of the process gas close to the acid dewpoint. When the actual plant conditions are not as designed, condensation of acid will occur in the economiser. After several drifts away from design conditions, it can lead to tube leaks causing corrosion.

Acid coolers

The majority of hydrogen incidents reported to the workgroup were caused by tube leaks, but there has been an incident involving acid cooler washing procedures and an incident that occurred while the plant was shut down.

Reaction plan

The reaction plan should consider addressing the above issues and plant specific issues.

Steam system

Waster heat boilers

A leak in a waste heat boiler will require a plant shutdown to access. Do not shut down the blower. This will prevent the accumulation of hydrogen and that can lead to explosions. The air flow can be reduced, but not stopped.

Economisers

When a leak in an economiser is quickly detected the plant may not require a complete plant cool down. One issue the workgroup found is that many plants cannot by-pass boiler feedwater around the leaking economiser to continue to provide feedwater to a boiler exposed to the heat of a sulphur furnace. Can your plant isolate the water side of the economiser?

Waste heat boiler

Maintain air flow for plant cool down. Can air flow be maintained with steam production shutdown due to the leak?

How will the energy input to the blower be maintained? With a steam driven blower, can alternative steam production be provided in a timely manner?

Acid coolers

Early detection is required, but when detected the reaction plan should include the isolation of the water source cooling water and the removal of weak acid from the cooler. These reactions will reduce the generation of hydrogen. How will your plant do it?

Acid coolers have got larger with increasing plant capacities. The photos in Fig. 3 show how acid coolers are being designed with increased plant capacities.

The requirement to isolate the source of water and the removal of weak acid to reduce the generation of Hydrogen is very plant specific.

Some issues of your weak acid incident may include:

- Can your plant isolate each of the acid coolers from the cooling water system?
- Acid coolers are significantly larger than the original design. Can your plant drain the acid cooler in a timely matter? Are the drains and vent nozzles large enough? Do you have a location to contain the volume of acid and water?
- Are the drain valves covered with a blank flange (which take time to remove)?

Summary

Weak acid will generate hydrogen and if hydrogen accumulates, an explosive range can be reached quickly. Timely detection of a weak acid incident is essential.

Ensure that your plant has procedures (a plan) to respond to weak acid conditions as failure to plan often results in plan to fail.

Many isolation valves may not have been moved for several months or even years. Some isolation valves are not quickly accessible leading to a delay of the isolation of the water and acid system. This issue is plant specific and should be a part of the development of your SOPs review.

The International Hydrogen Safety Workgroup has written over nine articles and have made several presentations at Sulphur conferences, Sulphuric Acid Today Workshops, and at the Central Florida AIChE Clearwater conferences. If your plant has not started to plan for a weak acid incident you can find the past publications on Sulphuric Today website: www.h2so4today.com/hydrogen-safety.

If you have questions concerning hydrogen safety please contact the workgroup. My e-mail is rick@consultdac.com.

Sulphur recovery in the energy transition

In the current energy transition era, the oil and gas industry is focusing on lowering its carbon footprint while generating green energy resources such as blue hydrogen. In this article, **Thomas K. Chow**, **Marcus Weber** and **Denny Li** of Fluor Solutions/Goar, Allison & Associates, L.L.C. demonstrate how SRU/TGTU plants within sour gas facilities can facilitate the capture of CO_2 and generate H_2 by implementing advanced sulphur recovery technologies.

In an effort to suppress current dramatic global weather changes, scientists and policymakers around the globe are advocating and striving to minimise the use of fossil fuels and maximise the use of "green" energy resources. The oil and gas industry is also doing its part in focusing on lowering its carbon intensity footprint while also investigating the use of alternative green energy resources such as hydrogen. Undoubtedly both carbon capture and hydrogen generation processes that are commonly pursued are capex and opex intensive; however, there is an opportunity to accomplish some of these tasks cost effectively via advanced sulphur recovery technology and processes.

Sulphur recovery units associated with sour natural gas facilities must contend with unique operational challenges associated with the acid gas feed produced from a sour gas facility. Compared to typical refinery acid gas, the acid gas produced from a sour gas plant is typically leaner in H_2S with higher concentrations of CO_2; various hydrocarbons; and benzene, toluene, ethylbenzene, and xylene (BTEX). Higher reaction furnace temperatures are necessary to totally destruct the BTEX and hydrocarbons; however, the lower H_2S concentration in the acid gas makes it difficult to achieve the desired flame temperature without co-firing with fuel gas or utilising oxygen-enriched air.

The use of high-level oxygen enrichment in the SRU presents an opportunity in terms of CO_2 capture and H_2 production in any facility but is especially well suited for SRU/TGTUs in sour gas plants for the following reasons:

- There is already a relatively high concentration of CO_2 in the feed that will pass through to the Claus tail gas.
- Any hydrocarbons in the acid gas feed are converted into CO_2.
- Oxygen-enrichment elevates the amount of H_2 produced in the reaction furnace from side reactions and eliminates additional presence of undesired nitrogen.

As shown in Table 1, the tail gas treatment unit (TGTU) absorber overhead stream of an SRU converted from air-based operations to high-level oxygen is heavily concentrated with CO_2 and H_2 and minimum nitrogen.

In this article, Fluor discusses the results of case studies investigating how a high-level, oxygen-enriched SRU within sour gas facilities can be optimised to facilitate an owner's CO_2 capture goals and H_2 generation potential.

Table 1: **Tail gas absorber overhead comparison**

	Air-based SRU operation	O_2-enriched SRU operation
Reaction furnace temperature, °C	1,150	1,150
Sulphur capacity, t/d	3,000	3,000
Oxygen or air need, Nm^3/h	220,200	42,200
TGTU absorber overhead, Nm^3/h	260,900	50,600
H_2, mol-%	1.7	24.2
CO_2, mol-%	11.8	60.2
N_2, mol-%	65.8	1.7
H_2O, mol-%	19.9	13.8
COS, ppmv	110	230
H_2S, ppmv	270	270

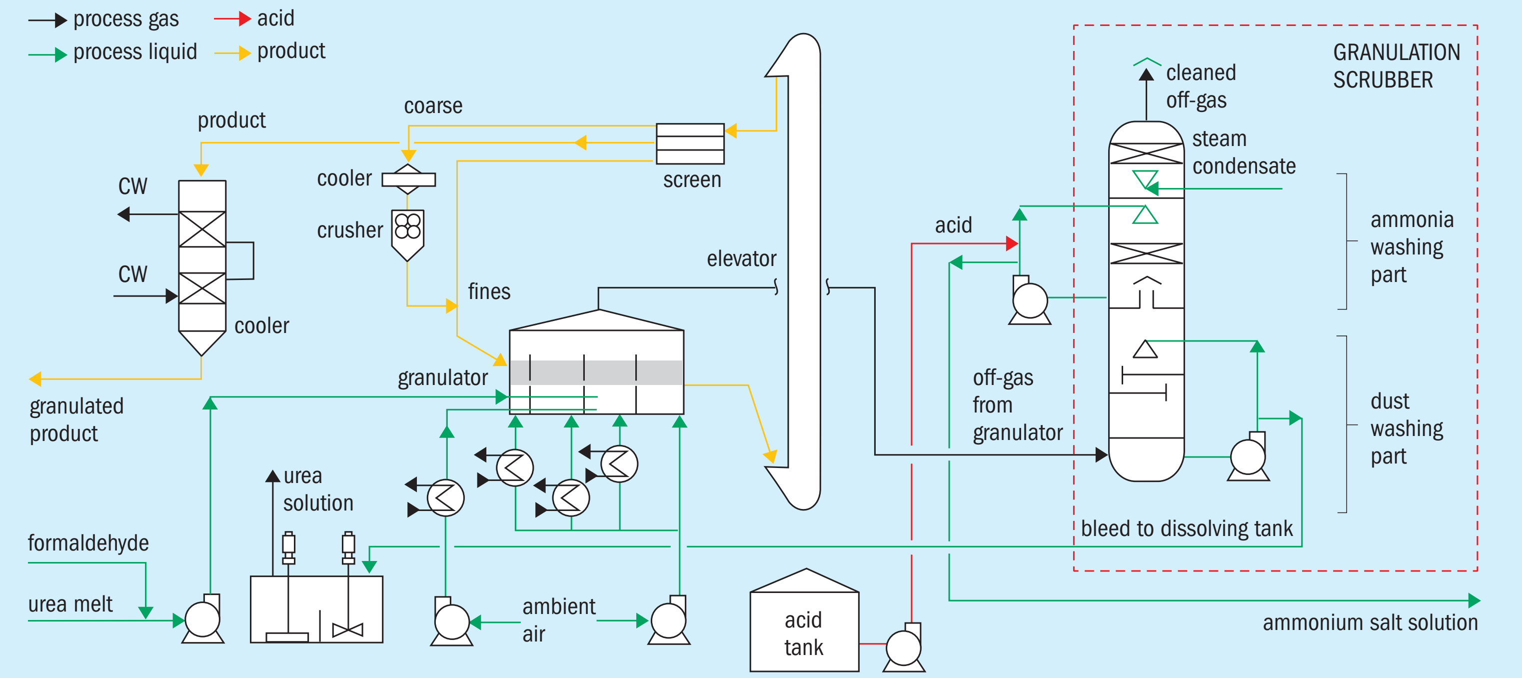
Source: Fluor

Oxygen enrichment and COPE II process

Oxygen enrichment is the utilisation of a purer source of oxygen molecules that replace all or a portion of the nitrogen molecules within the combustion air in the reaction furnace and thus reduce the volumetric gas flow in downstream SRU/TGTU equipment. As a consequence, the design processing capacity of an existing SRU/TGTU is increased proportionally or sizes for equipment of a new SRU/TGTU can be reduced compared to those of an air-based Claus operation. A dedicated oxygen production unit (OPU), like an oxygen

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

Fig. 1: **COPE II™ SRU thermal section**



Source: Fluor

VPSA, could be employed to deliver the oxygen source of typically 90-95% purity. Alternatively, oxygen from a cryogenic air separation unit (ASU) could be utilised if high capacity is needed at the facility. Currently over 400 operating Claus SRUs worldwide effectively utilise various levels of oxygen enrichment.

In existing SRU equipment, increases in the oxygen enrichment level correspond to higher capacity increases. Low-level enrichment in the 21-28% oxygen concentration range yields an increase of 25-30% of design capacity, medium-level (28-45% enrichment) yields increase of 50-70% of design capacity, and high-level enrichment (up to 100%) yields increase up to 150% of design capacity[1]. Oxygen enrichment levels can be manually adjusted by an operator to accommodate the processing capacity needs of the facility from original design capacity up to the desired revamped capacity.

With the lower diluent (nitrogen) content in the oxidant, the exothermic combustion reaction results in a higher temperature in the reaction furnace. One benefit of the higher furnace temperature is the assurance of the destruction of ammonia and BTEX which require minimum temperatures of 2,450°F (1,350°C) and 2,000°F (1,100°C) respectively[2]. Destruction of ammonia and BTEX is essential as these components can form ammonia salts and carbon deposition that causes plugging in piping and Claus catalyst deactivation. The primary concern with the increase in furnace temperature is that the operation could approach the design temperature limits of the refractory. Typically, existing equipment design limits will determine the allowable oxygen enrichment level.

Implementation of Fluor/GAA's COPE™ II Technology allows for higher levels of oxygen enrichment to be utilised while remaining below refractory design temperature limits of the reaction furnace (thermal reactor) refractory. A portion of the SRU process gas from the outlet of the first sulphur condenser is recycled back to the reaction furnace burner by way of the COPE™ II recycle ejector. The recycled process gas is mostly inert which helps to reduce the furnace temperature. The ejector is simple to operate with medium-pressure steam, adjustable for different oxygen enrichment levels, and has a small footprint compared to a blower or compressor (Fig. 1).

Fluor has developed a patented process that leverages the COPE™ II Technology to produce high purity CO_2 from the SRU, named the Oxygen Enhanced Claus CO_2 Recovery Process (OEC²RP). This process requires near 100% oxygen enrichment to ensure low nitrogen content in the Claus tail gas[3]. The Claus tail gas would be treated in a hydrogenation-amine tail gas treating unit (TGTU) to remove the residual sulphur compounds.

The overhead from the amine absorber would comprise primarily CO_2, H_2, and water. Depending on project goals, the H_2 could be recovered as by-product or oxidised to generate high-pressure steam and CO_2 dehydrated to obtain a high purity CO_2 product stream.

Case study objective

Fluor's OEC²RP implemented with COPE™ II Technology was evaluated in a recent study for the Middle East region. The objective was to optimise hydrogen production and produce a high purity CO_2 stream for sequestration from an SRU/TGTU in a large-scale sour gas facility. Optimisation studies were performed on the COPE recycle and the reaction furnace operating temperature.

Case study parameters

The basis for the case study is as follows:

- sulphur recovery unit capacity is 3,000 t/d of sulphur;
- two-stage Claus with a hydrogenation/Flexsorb TGTU;
- amine acid gas feed:
  - CO_2 22.16 mol-%
  - H_2S 69.22 mol-%
  - H_2O 8.23 mol-%
  - COS 0.0003 mol-%
  - hydrocarbons 0.17 mol-%
  - BTEX 0.16 mol-%
  - mercaptans 0.06 mol-%

Table 2: **Air, COPE II, direct steam injection comparison**

Case	Air-based SRU operation	COPE II operation	Direct steam injection
Reaction furnace temperature, °C	1,150	1,150	1,150
Sulphur capacity, t/d	3,000	3,000	3,000
Oxygen or air need, Nm^3/h	220,200	42,200	42,200
COPE recycle, Nm^3/h	-	48,200	-
Steam injection or motive steam, kg/h	-	24,800	68,600
SRU tail gas (From 3rd condenser), Nm^3/h	340,400	180,700	235,000
TGTU absorber overhead, kmol/h	11,640	2,260	2,320
Nm^3/h	260,900	50,600	52,100
H_2, mol-%	1.7	24.2	22.4
CO_2, mol-%	11.8	60.2	58.4
N_2, mol%	65.8	1.7	1.1
H_2O, mol-%	19.9	13.8	18.0
COS, ppmv	110	240	210
H_2S, ppmv	270	270	270
H_2, kmol/h	198	546	520
CO_2, kmol/h	1,379	1,360	1,360

Source: Fluor

- oxygen purity of 98 vol-% utilised as the oxidant in the reaction furnace to minimise ingress of nitrogen diluent;
- TGTU Flexsorb performance targeted 270 ppmv H_2S on the absorber outlet to meet the CO_2 product specification.

Case study 1: Optimisation of recycle media for hydrogen production

A simulation case study was undertaken to ascertain the effect of the composition of the recycle gas on the amount of hydrogen produced. The COPE recycle is typically a mixture of steam from the ejector and various gases from the SRU/TGTU process of which CO_2 is the primary component since N_2 is minimised in this study case.

Hydrogen has been known as a valuable product, especially in this "green" energy era. An evaluation of H_2 production in the reaction furnace was then performed. Since general observation indicates that steam not only lowers the reaction furnace flame temperature but also enhances production of H_2, an investigation was carried out by replacing the COPE recycle gas with a pure steam injection as the temperature moderating medium to the reaction furnace.

As shown in Table 2, the steam injection model showed a two-fold increase in the amount of steam injected into the reaction furnace compared to the steam required for the COPE II recycle ejector to maintain the same temperature in the reaction furnace. Additionally, unconverted steam in the process was carried downstream until being condensed in the TGTU direct contact condenser. This steam increases volumetric flowrate by 30% resulting in larger SRU and TGTU hydrogenation equipment. The large opex associated with the increased steam injection along with the larger equipment make the "steam-only" option uneconomical considering the COPE II benefits and slightly higher H_2 production. However, this presents an option for manipulating the desired amount of H_2 production by increasing the amount of steam injection in an optimisation case if maximisation of H_2 production is desired by a client. Such an option helps to eliminate the need for installing a capex intensive hydrogen production unit.

Case study 2: Reaction furnace operation for hydrogen production

A second case study was undertaken to evaluate the effect of the reaction furnace temperature on the amount of hydrogen produced in the SRU. While a minimum of 2,000°F (1,100°C) is required in the reaction furnace for BTEX destruction, a higher operating temperature can be achieved through reduction of the COPE recycle flow. A higher operating temperature has an effect on hydrogen formation. While the upper reaction furnace temperature limit in this evaluation is set at 2,650°F (1,455°C) to protect the reaction furnace refractory, the operating temperature in the reaction furnace without COPE recycle was slightly lower than this limit, at 1,425°C, due to the lean acid gas feed.

As shown in Table 3, the lower the reaction furnace temperature is brought down, the amount of H_2 produced specifically in the reaction furnace rises. However, the lower reaction furnace operating temperatures benefit in H_2 production is negated at the tail end of the sulphur plant as H_2 and CO_2 are brought to equilibrium in the hydrogenation bed.

Additionally, the higher operating temperature is not favourable in terms of the CO and COS formation in the reaction furnace. While the hydrogenation reactor can reduce the CO and COS because it promotes water-gas-shift and hydrolysis reactions, the residual amounts from the higher reaction furnace temperature cases still may exceed certain stringent tail gas specifications.

Ultimately, there is little benefit in controlling the reaction furnace temperature in regard to influencing the H_2 production. The reaction furnace temperature should be set higher rather than lower to minimise the COPE II recycle requirement.

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

Table 3: **Reaction furnace temperature results**

Case	No recycle	1,350	1,300	1,250	1,200
Reaction furnace temperature, °C	1,425	1,350	1,300	1,250	1,200
Oxygen or air need, Nm³/h	42,200	42,200	42,200	42,200	42,200
COPE recycle, Nm³/h	-	8,500	15,700	24,700	36,100
Motive steam, kg/h	-	4,500	8,300	12,900	18,700
Reaction furnace H_2 flow, Nm³/h	11,800	12,500	12,900	13,100	12,700
SRU tail gas H_2 flow, kmol/h	300	316	334	354	364
Nm³/h	6,710	7,090	7,490	7,940	8,160
TGTU absorber overhead, kmol/h	2,210	2,210	2,220	2,220	2,220
Nm³/h	49,600	49,600	49,700	49,800	49,800
CO_2, mol-%	60.1	60.1	60.1	60.2	60.2
CO, mol-%	0.4	0.3	0.3	0.2	0.1
H_2, mol-%	24.0	24.0	24.0	24.1	24.1
H_2S, mol-%	0.03	0.03	0.03	0.03	0.03
COS, mol-%	0.05	0.04	0.04	0.03	0.03
H_2, kmol/h	540	540	542	544	545
CO_2, kmol/h	1,352	1,354	1,355	1,358	1,360

Notes: TGTU overhead sulphur content would translate into SO_2 content if the CO_2-rich gas is passed through a thermal oxidiser. *Source: Fluor*

Economics

Fluor recently completed an evaluation comparing OEC²RP with post-combustion CO_2 capture of incinerator stack gas at a large Middle East sour gas plant. The evaluation indicated that the ROM capital cost (capex) of an amine-based CO_2 capture system producing a similar CO_2 stream to OEC²RP was 75% more. While there was significant capex savings, the evaluation also showed that the OEC²RP had a high operating cost (opex) primarily because the oxygen to the SRU was treated as an operating cost. If the oxygen is readily available, the economics would favour OEC²RP much more. (Table 4)

The evaluation showed the payback period for negating the capex savings provided by OEC²RP against the higher operating cost for an amine-based CO_2 capture was over ten years.

Table 4: **Relative capex/opex**

Configuration	Capex change relative to OEC²RP	Opex change relative to OEC²RP	Reduced opex payout (years)
OEC²RP	Base case	Base case	Base case
Amine CO_2 capture on absorber overhead	+75%	-67%	11
Amine CO_2 capture on incinerator outlet	+251%	-43%	57

Notes:
1. Capex/opex analysis assumed that the SRU using OEC²RP did not increase sulphur production rate. Increasing the sulphur production to the full potential of OEC²RP would require the addition of sulphur capacity in the form of more or larger units for the other two cases.
2. OEC²RP operating costs includes the oxygen required for operation as a capital cost recovery adder on top of the operating cost of the oxygen plant. No further capital cost associated with the oxygen plant.
Source: Fluor

Conclusion

An ever-increasing percentage of the capital expenditures of many major corporations in oil and gas are planned around the "energy transition" of the world. Carbon capture and hydrogen are key cornerstones of that transition. Fluor has leveraged commercialised technologies in the form of OEC²RP to facilitate the upgrading of a SRU into a platform for future H_2 production and CO_2 capture. With the patented OCE²RP and the carbon capture technologies within its portfolio, Fluor can readily assist its clients with their plans to reduce their carbon footprint and realise the benefits of some "free" H_2. ■

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CO_2 recovery options in sulphur plants

CO_2 emission abatement strategies have become increasingly important as the world strives to combat global climate change. **Mahin Rameshni** and **Stephen Santo** of Rameshni & Associates Technology & Engineering (RATE USA) discuss carbon capture options available for sulphur recovery units.

The global concentration of CO_2 in the atmosphere is increasing rapidly. CO_2 emissions have an impact on global climate change. Power generation from fossil fuel-fired power plants (e.g. coal and natural gas) is the single largest source of CO_2 emissions. However, fossil fuel-fired power plants play a vital role in meeting energy demands. For instance, coal-fired power plants can be operated flexibly to meet varying demand. With growing concerns over the increasing atmospheric concentration of anthropogenic greenhouse gases, effective CO_2 emission abatement strategies such as carbon capture and storage (CCS) are required to combat this trend.

CCS is a process consisting of the separation of CO_2 from industrial and energy-related sources, transport to a storage location and long-term isolation from the atmosphere. The three basic stages of CCS can be summarised as:

- separation of CO_2;
- transportation;
- storage.

There are three major approaches for CCS:

- post-combustion capture;
- pre-combustion capture;
- oxyfuel process.

Post-combustion capture offers some advantages as existing combustion technologies can still be used without the need for radical changes to them. This makes post-combustion capture easier to implement as a retrofit option compared to the two other approaches. For this reason, post-combustion capture is most likely to be the first technology that will be deployed.

A number of separation technologies can be employed for both pre- and post-combustion capture. These include:

- adsorption;
- physical absorption;
- chemical absorption
- cryogenic separation;
- membranes;
- RATE technology CO_2 liquefaction.

Several advanced and improved configurations are available for amine-type designs and will be discussed in this article.

RATE recently filed a patent application that covers the combination of CO_2 recovery and hydrogen generation in SRUs but it has not yet been published by the US Patent office.

Pre- and post-combustion capture

RATE offers several options for pre-combustion and post-combustion CO_2 removal.

Amine-type CO_2 removal has been used widely in pre-combustion and post-combustion units. In post-combustion capture, due to the presence of oxygen, the type of solvent selected should tolerate oxygen, like MEA, and a thermal reclaiming system is required to remove degraded components. Post-combustion capture and storage (PCCS) units comprise CO_2 absorption by 30 wt-% monoethanolamine (MEA) solution and CO_2 compression at 150 bar for permanent storage or enhanced oil recovery.

However, PCCS amine type technology needs substantial amounts of thermal energy for absorbent regeneration and electricity for carbon capture, CO_2 compression as well as for the operation of other parasitic electricity consumers. The PCCS energy requirements vastly affect the overall plant performance. It produces more CO_2 by supplying thermal energy for CO_2 removal, resulting in insignificant net CO_2 removal.

One option to optimise the amine configuration to reduce the thermal energy consumption is to have multiple stages of the flash drum to remove the CO_2 before the regeneration system (see Fig. 1).

This configuration uses a physical solvent and works best when both the acid gas concentration and the operating pressure is high. It is a non-reactive process with no degradation product and no reclaiming. It is a non-corrosive process using primarily carbon steel construction. The feed gas is contacted with the cool regenerated solvent, which removes CO_2 and H_2S from the gas phase and the absorbed gases are removed by thermal regeneration in a stripper.

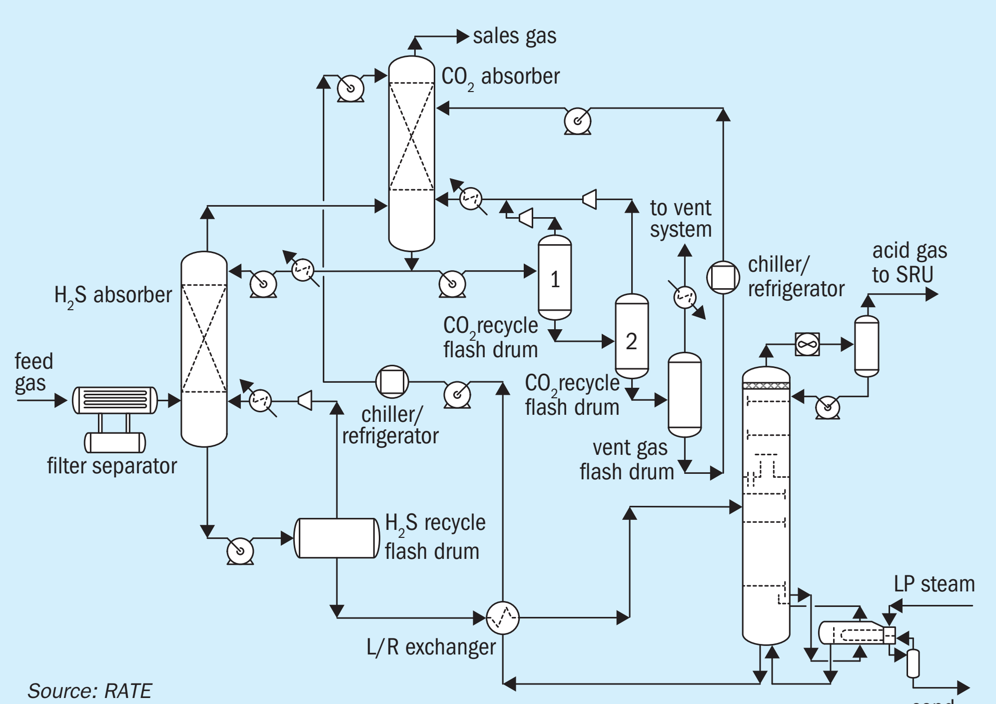
A substantial amount of CO_2 is removed in the multiple flash stages before entering the regeneration which significantly reduces the thermal energy required for regeneration.

In the pre-combustion process chemical solvents like MEA, MDEA based, aMDEA and physical solvents like Selexol, Rectisol or similar are commonly used.

Fig. 1 represents pre-combustion CO_2 removal where the CO_2 is removed before the acid gas enters the sulphur recovery unit (SRU). There are several advantages to this scheme. By removing the majority of the CO_2 upstream of the SRU, the size of the sulphur plant is reduced significantly, resulting in lower capital and operating costs. Other advantages are that the CO_2 is removed without increasing the thermal energy for the regeneration reboiler and by adding an extra absorber the CO_2 is removed.

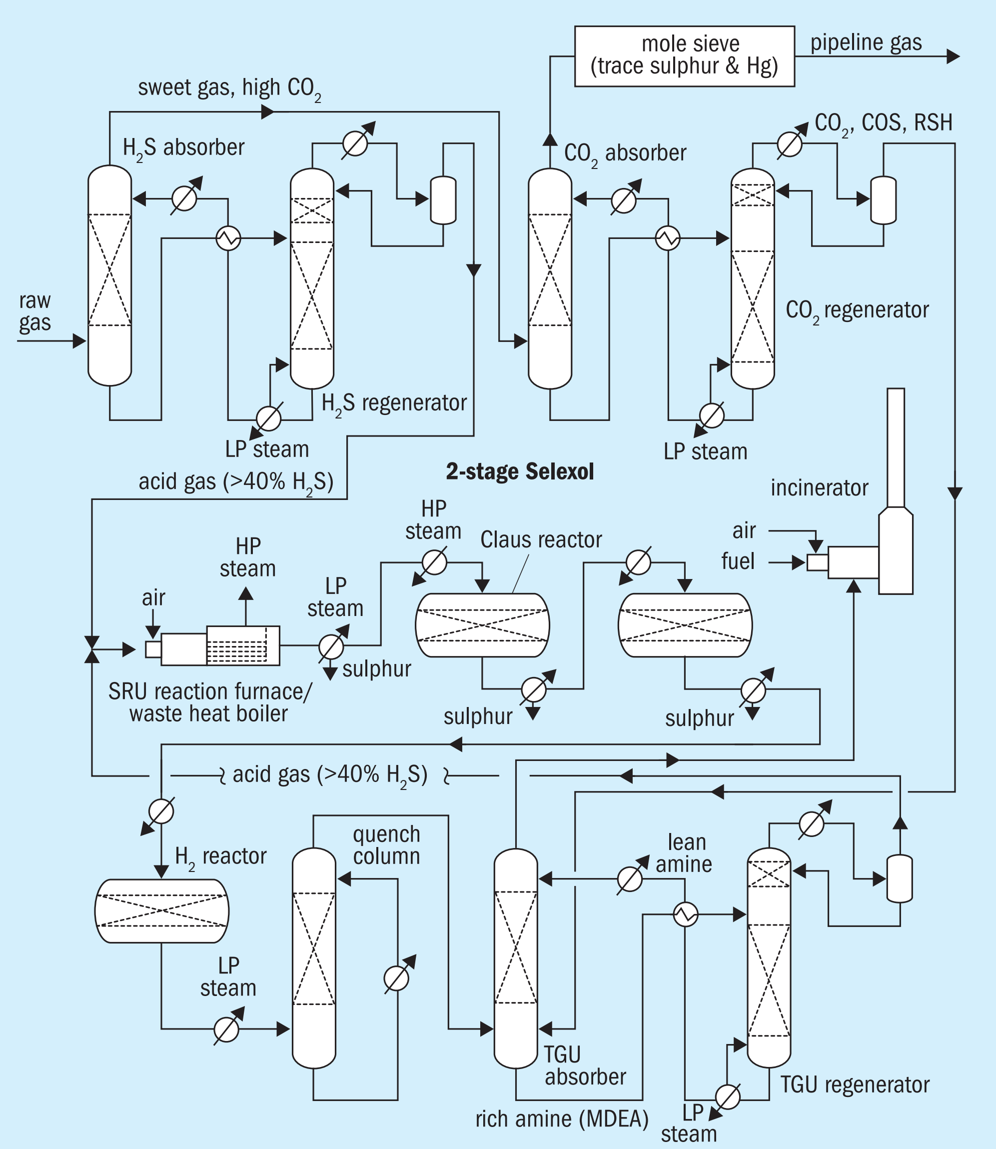
This configuration is evaluated based on the feed composition to the amine gas regeneration unit (AGRU) for the new facilities. The new sulphur recovery and tail gas unit will have less volumetric flow, the H_2S

Fig. 1: **CO_2 removal with muti-stage flash**



Source: RATE

Fig. 2: **Two-stage Selexol with molecular sieve, and SRU/TGTU**



Source: RATE

concentration is richer and will achieve better operation while the CO_2 has already been removed and the unit is designed based on new carbon capture. This scheme has been in operation in USA gas plants.

Another option, shown in Fig. 2, represents pre-combustion capture upstream of the sulphur recovery units, where H_2S and CO_2 are separated by using a physical solvent such as Selexol and a molecular sieve as summarised below:

- Stage 1: CO_2 removal using a two-stage physical solvent
  - H_2S absorber – overhead contains sweet gas and high CO_2 goes to stage 2
  - H_2S regenerator – overhead goes to SRU to process H_2S to sulphur
- Stage 2: CO_2 absorber and CO_2 regeneration
  - CO_2 absorber – overhead goes for water dew point control, Hg removal by molecular sieve and then to pipeline
  - CO_2 regenerator – overhead goes to the TGTU absorber
- Conventional two-stage Claus unit and tail gas treating unit.

A third pre-combustion CO_2 removal configuration is shown in Fig. 3 and described below.

The acid gas removal scheme in this option is Selexol or Rectisol and the sulphur recovery is designed based on 100% oxygen enrichment. The tail gas treating unit contains an additional reactor for COS hydrolysis and to process the feed stream directly to maintain a high temperature in the SRU.

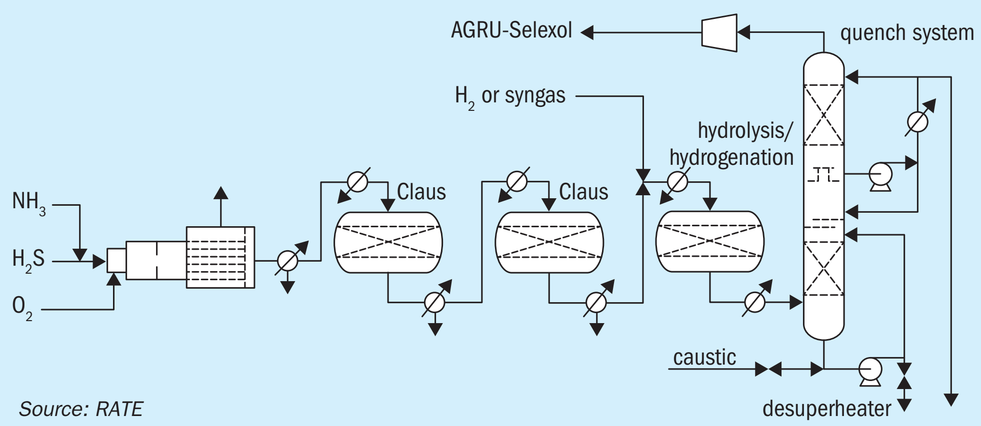
The tail gas unit is designed to recycle the quench overhead to the acid gas removal (Selexol, Rectisol) where the tail gas amine portion is eliminated and to achieve zero sulphur and CO_2 emissions. The H_2S and CO_2 are sent to a unit using a physical solvent where CO_2 is separated from H_2S. The H_2S is recycled to the SRU, and the CO_2 is sent to another unit for compression.

CO_2 removal from natural gas

RATE offers the combination of CO_2 liquefaction with a two-stage membrane system for CO_2 removal from natural gas as a pre-combustion configuration (see Fig. 4). If the H_2S content is low, adsorbents are used upstream of the unit to remove the H_2S, if the H_2S content is high, the addition of a membrane is required to separate the H_2S from the CO_2. The recovered H_2S is sent to the sulphur recovery unit.

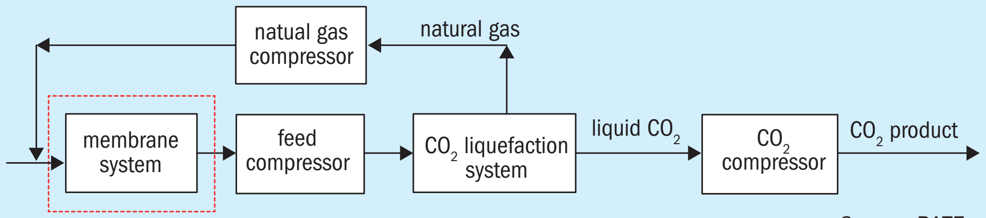
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52

Fig. 3: **Stack-free CO_2 and SO_2 process**



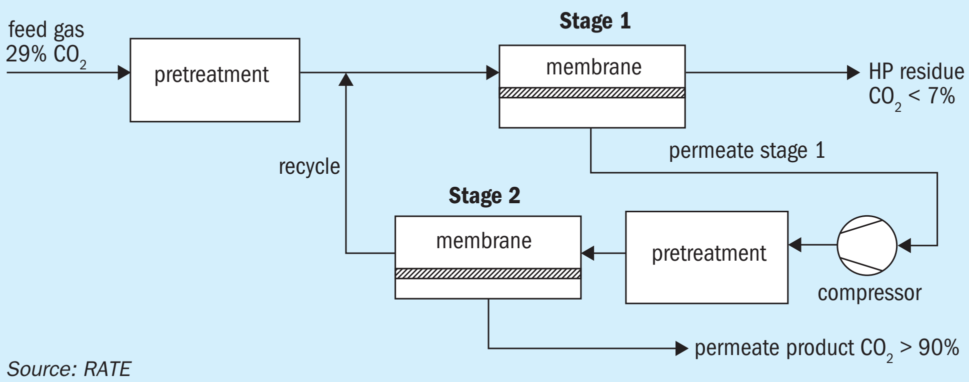
Source: RATE

Fig. 4: **RATE CO_2 liquefaction with membrane**



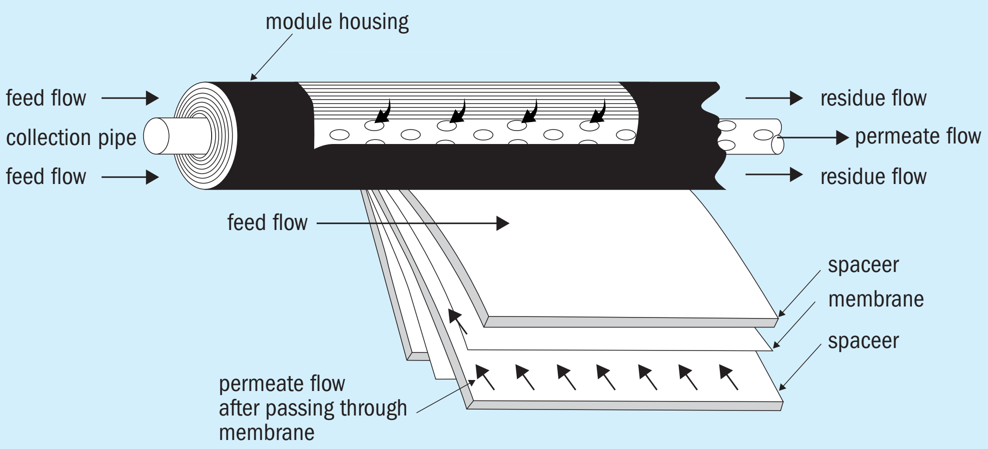
Source: RATE

Fig. 5: **Two-stage membrane system**



Source: RATE

Fig. 6: **Membrane details**



Source: RATE

This combination of CO_2 liquefaction with a two-stage membrane system for pre-combustion capture requires only one-third of the energy compared to a conventional amine-type unit and provides a very reliable scheme with minimum capital costs.

For a project with 950 million std ft³/d of the feed stream entering the membrane system, about 200 million std ft³/d of the gas was processed in the CO_2 liquefaction. The capital cost saving from the combination of CO_2 liquefaction and the two-stage membrane system versus CO_2 removal using an amine solvent is about 40 to 45%.

Key advantages of CO_2 liquefaction with a two-stage membrane system compared to conventional CO_2 removal are:

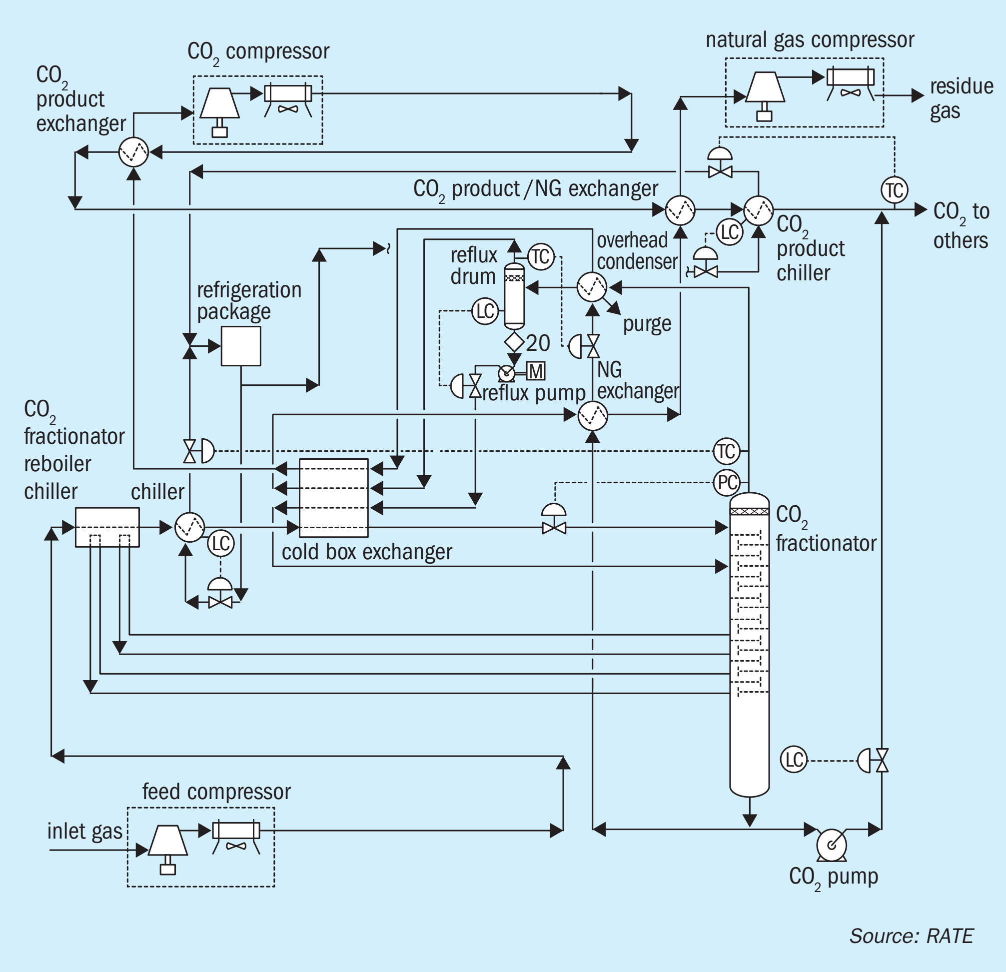
- eliminates high amine circulation rate;
- significant reduction of consumption steam or fuel to provide heating media;
- reduces the number of items of equipment, especially large equipment;
- eliminates large absorber and regeneration columns;
- reduces plot space by providing a compact and modular unit;
- at least 40-45% saving in capital cost;
- reduces labour and time during construction.

A two-stage membrane process scheme is shown in Fig. 5. The feed gas is first passed through a pre-treatment section consisting of a filter coalescer, carbon bed, particulate filter, and heater. The heated gas is then routed to the first membrane stage, which separates the inlet gas into two streams:

- LP permeate stream: The membranes preferentially permeate CO_2 and the resulting LP permeate stream, enriched in CO_2, is compressed and sent to the second membrane stage for further CO_2 recovery.
- HP residue stream, depleted in CO_2 and more concentrated in the heavy hydrocarbons, is routed to the sales pipeline at high pressure.

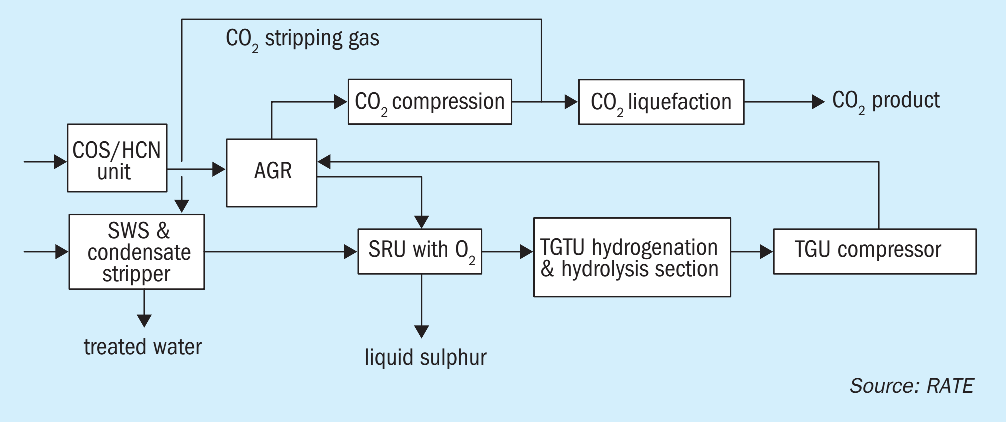
For use in CO_2 recovery processes, the design incorporates spiral-wound membrane modules. These modules consist of a densely packed sandwich of membrane envelopes and spacers in a spiral wound configuration around a central collection pipe (as shown in Fig. 6). Mesh spacer materials create channels through which the feed gas and permeate vapours travel with minimum pressure drops. As a feed

Fig. 7: **RATE CO_2 liquefaction process**



Source: RATE

Fig. 8: **Post combustion CO_2 removal from SRU**



Source: RATE

gas stream containing organic vapour passes across the membrane surface, CO_2 passes preferentially through the membrane and enters the permeate channel. The permeate vapour spirals inward through the permeate channel to the central collection pipe.

To provide the driving force for permeation, a pressure difference is maintained across the membrane between the feed and the permeate stream. The pressure difference can be obtained by compressing the feed or by using a high-pressure feed stream and maintaining the permeate at a lower pressure by connecting it to a lower pressure point. This pressure difference directly affects the rate at which CO_2 permeates the membrane. The larger the pressure difference, the greater the flux of CO_2 through the membrane and reduction in the number of membrane modules needed to perform a desired separation.

CO_2 liquefaction is a process to separate CO_2 from a mixture of hydrocarbons, mostly methane, to generate two streams, one is the CO_2 and the other is the residue or natural gas. The residue is recycled back to the membrane system for further separation.

The dried gas enters the CO_2 liquefaction unit where it is chilled by heat integration with the fractionation column (furnishing reboiler duty for the column). The gas is then further chilled and partially condensed in the refrigerant chillers using an external refrigerant. Next, the inlet stream is totally condensed and partially sub-cooled through further heat integration with streams leaving the cold section of the plant. Finally, it is flash expanded to the fractionation column at an optimum pressure designed for effective CO_2/methane separation while avoiding CO_2 freezing issues.

Vapour leaving the column overhead is further chilled and partially condensed in the overhead condenser with CO_2 refrigerant. The resultant CO_2-rich liquid is pumped back to the fractionation column following further heat integration within the process.

The refrigerant for the overhead condenser is a portion of the CO_2 product from the bottom of the fractionation column. This liquid CO_2 is then flashed to a relative low pressure where it chills and partially condenses the overhead vapour stream. The volume fraction of CO_2 in the gas leaving the reflux accumulator is approximately 21%. The CO_2 used as refrigerant in the overhead condenser is then compressed, cooled, and returned back to the fractionation column where it is recovered in liquid form.

A distillation process for removing CO_2 is designed with a feed gas stream under pressure that is cooled by heat exchange with other streams of the process and/or external sources of the refrigeration system. The gas is condensed as it is cooled, and the high-pressure liquid is expanded to an intermediate pressure, resulting in further cooling of the stream due to the vaporisation occurring during expansion of the liquids.

The expanded stream, comprising a mixture of liquid and vapour, is fractionated in a distillation column to separate residual methane, nitrogen, and other volatile gases as overhead vapour from the CO_2 and the heavier hydrocarbon components as bottom liquid product. A portion of the liquid CO_2 can be flash expanded to lower pressure and thereafter used to provide low level refrigeration to the process streams if desired.

Fig. 7 presents the process flow diagram for the CO_2 liquefaction process developed by RATE. A portion of the produced CO_2 is used as the chiller to eliminate an external chiller and save energy.

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

Post-combustion CO_2 removal in SRUs

In a post-combustion amine unit, a suitable solvent can be used for CO_2 removal, however, the main issue is the use of energy for the AGRU which can result in insignificant or uneconomical net CO_2 capture.

Recently, RATE has been working on a project for CO_2 recovery and SO_2 emission control in Europe. Fig. 8 shows the major units in the project.

Using CO_2 liquefaction instead of an amine type unit is very economical and the required energy is significantly reduced.

In the COS/HCN hydrolysis section, COS and HCN are catalytically converted into H_2S, CO_2, NH_3 and H_2O which can be further removed from this plant. The conversion is described in the following hydrolysis reactions:

$$COS + H_2O \rightarrow H_2S + CO_2$$

$$HCN + H_2O \rightarrow NH_3 + CO_2$$

In the CO shift reactor, CO is converted to H_2 according to the water gas reaction:

$$CO + H_2O \rightarrow H_2 + CO_2$$

The gas stream from the hydrolysis section flows to the AGRU where a physical solvent, such as Selexol or similar, is used. In the AGRU, the treated gas containing high CO_2 is sent to the RATE CO_2 liquefaction unit for further purification.

The hydrolysis reactor after the hydrogenation reactor in the TGTU, so-called TG-MAX, is RATE's patented technology (US 10,752,505 B2).

The purified CO_2 can be reinjected or used in other applications such as a transport medium for solid waste conveying, a pressure medium for the lock hopper system, seal gas for feeding and withdrawing screw feeders or as a stripping gas. In this project, the CO_2 is used as a stripping gas in a two-stage SWS design.

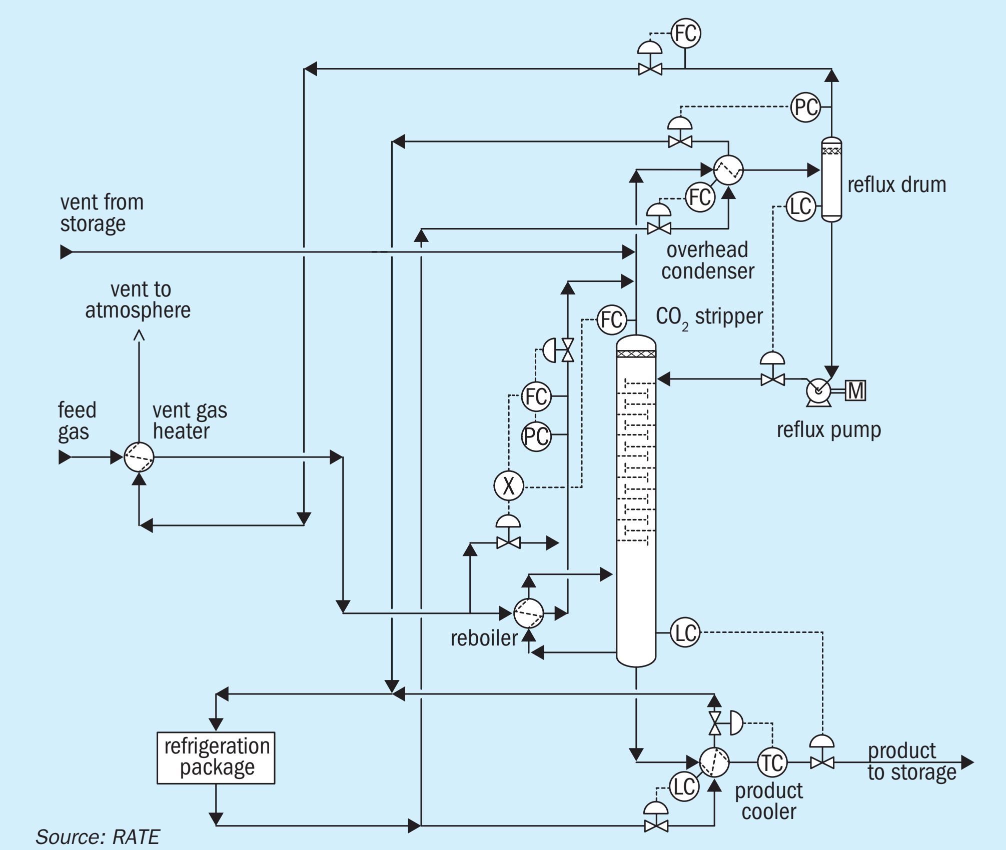
The H_2S acid gas stream from the AGRU is converted to sulphur in the SRU using oxygen enrichment technology.

Fig. 9 shows the RATE CO_2 liquefaction process for flue gas decarburisation, which is simpler than the pre-combustion CO_2 liquefaction and membrane system.

The proprietary RATE process condensate stripper uses CO_2 as the stripping gas to strip H_2S. This design is unique for this application.

The SWS and condensate stripper comprises two separate columns: the process condensate stripper and the NH_3 stripper.

Fig. 9: RATE CO_2 liquefaction flue gas decarbonisation



Source: RATE

The first treatment step is the removal of sour gases and volatile components in the RATE process condensate stripper. The liquid phase of the process condensate flash drum is preheated and fed to the stripper column in between the upper and middle packing. the process condensate stripper column consists of two sections.

In the upper section, CO_2 stripping gas is utilised to remove H_2S and minimise stripping of NH_3.

In the lower section, volatile components and CO_2 are removed by means of uprising steam. Additionally, any dissolved carbonates are thermally decomposed. The stripped water is routed to the NH_3 Stripper where NH_3 is removed and mixed with H_2S from another stripper and then routed to the sulphur recovery unit.

As already described, the design includes a COS/HCN hydrolysis unit, however, there is still some HCN and COS not fully hydrolysed which flows to the AGRU and eventually reaches the SRU. HCN can be washed as well as combusted in the reaction furnace and an additional feature has also been provided in the TGTU unit to hydrolyse all the remaining of COS.

In summary:

- The acid gas removal scheme uses Selexol physical solvent or similar.
- The SWS and condensate stripper is a unique design where CO_2 was used as the stripping gas.
- The SRU is designed based on 100% oxygen enrichment single combustion.
- The tail gas treating unit (TGTU) contains an additional reactor for COS hydrolysis and to process one the feed stream directly to maintain a high temperature in the SRU.
- The TGTU is designed to recycle the quench overhead to the acid gas scrubber whereby the tail gas amine portion is eliminated and zero sulphur emissions are achieved.

CO_2 removal in existing SRUs

Existing sulphur recovery and tail gas treating units are required to meet SO_2 emission limits according to the local environmental regulations or world bank and various solutions are commercially available and have been used. In some places the stack is sulphur free, but CO_2 is emitted. The easiest way to minimise the flue gas decarburisation is to add a unit to capture the CO_2 before the stack.

One solution is to have an amine-type unit using a solvent that is suitable for the presence of oxygen, like MEA or similar. However, due to the significant energy required for the regeneration reboiler and electrical consumption resulting in additional CO_2 being produced, the net decarburisation is not significant.

Adsorption is a physical process that involves the attachment of a gas or liquid to a solid surface. The adsorbent is regenerated by the application of heat (temperature swing adsorption, TSA) or the reduction of pressure (pressure swing adsorption, PSA). Adsorbents which could be applied for CO_2 capture include activated carbon, alumina, metallic oxides and zeolites. Current adsorption systems may not be suitable for application in large-scale power plant flue gas treatment. At such scale, the low adsorption capacity of most available adsorbents may pose significant challenges. In addition, the flue gas streams to be treated must have high CO_2 concentrations because of the generally low selectivity of most available adsorbents.

Cryogenic separation separates CO_2 from the flue gas stream by condensation. At atmospheric pressure, CO_2 condenses at -56.6°C. This physical process is suitable for treating flue gas streams with high CO_2 concentrations considering the costs of refrigeration. This is typically used for CO_2 capture for oxyfuel processes.

When membranes are used in gas absorption, membranes act as contacting devices between the gas stream and the liquid solvent. The membrane may or may not provide additional selectivity. These offer some advantages over the conventional contacting devices such as packed columns as they are more compact and are not susceptible to flooding, entrainment, channelling, or foaming. However, they require that the pressures on the liquid and gas sides are equal to enable CO_2 transport across the membrane. Their separation efficiency depends on the CO_2 partial pressure. As such, they are suitable for high CO_2 concentration applications (well above 20 vol-%) such as flue gas streams from oxyfuel and IGCC processes.

Conclusions

Pre- and post- combustion CO_2 removal or decarbonisation options have been discussed. The required energy for CO_2 removal is very important where CO_2 is produced to remove the CO_2, resulting in an insignificant net CO_2. It is crucial to carefully evaluate the CO_2 removal case by case and to select the most economic option.

Based on a case-by-case evaluation, if a pre- or post-combustion amine-type scheme is selected it is advised to provide multi-stage flashes to reduce the CO_2 to the regeneration and to lower the energy consumption.

If the amine-type process is selected for post-combustion capture CO_2 removal, the selected solvent should be able to tolerate the oxygen from combustion like incineration and a thermal reclaimer should be provided to remove the degraded materials which also requires additional thermal energy.

The RATE CO_2 liquefaction option for flue gas decarbonisation in post-combustion requires minimum energy and minimum capital costs. The presence of oxygen from combustion will not cause any harm. This scheme can be added to existing SRUs after the incineration and before the stack.

For new SRUs, the CO_2 can also be removed by pre- or post-combustion capture depending on the facilities.

RATE CO_2 liquefaction with a two-stage membrane system as the pre-combustion option requires only one-third of the energy of a conventional amine-type unit. ■

Sulphur run-down liquid level prediction

Sulphur run-down lines are typically sized by referencing past projects and 'rules of thumb'. Very little analysis is performed to identify the impacts of slope, fittings, valves, etc. It is critical to maintain an open vapour path from the condenser to the sealing device. CSI has observed problems in the field which appear to be caused by undersized run-down lines.

CSI developed a method of predicting the liquid level in a run-down line that considers the most common elements. This was accomplished by building a full-scale model of a run-down line that evaluated pipe NPS, pipe slope, rod-out-cross elbows, rod-out cross elevation drops, and liquid viscosity. This article* presents the testing and development of the predictive method as well as the predictive method itself.

In a Claus sulphur recovery unit, sulphur is continuously produced in a series of condensers (typically four per train). These condensers operate at an elevated pressure (typically 1 to 8 psig/0.07 to 0.55 bar). The sulphur is continuously drained from the condensers via the run-down lines. These lines run from the condenser drain to a sealing device, and from the sealing device to a sulphur storage container. It is critical that the process gas remains in the condensers so it can continue through for further processing. The sealing device is a passive device that allows the sulphur to pass through, while preventing vapour from escaping. The sealing device operation is comparable to the function of a steam trap.

Flow in a sulphur run-down is effectively 'open channel' flow. It is critical that these lines have open channel flow for three reasons:

- Having a continuous downward slope ensures that the lines will drain. This is convenient for maintenance operations, and, more importantly, avoids the accumulation of debris at low points resulting in obstruction. Open channel flow results.
- Sulphur accumulation in the condenser is to be avoided. The run-down lines must be sized for something greater than the maximum production rate. Open channel flow results.
- Vapour displaced from the sulphur sealing device must have an open path to the condenser to prevent vapour locking. The vapour space of the sealing device must operate at the same pressure as the condenser and a vapour path from the sealing device to the condenser must be maintained to ensure this. Note that this is true of all popular sealing devices including traditional seal legs, SulTraps manufactured by SOS, and SxSeals manufactured by CSI.

The sulphur industry typically sizes run-down lines based on rules of thumb, past experience, and occasional theoretical calculations performed by engineering companies. No best practice approach exists for either the philosophy (vapour path opening size, debris accumulation safety factor) or for the method. The industry would benefit from a more rigorously developed approach.

Approach

CSI's goal was to develop a general method of predicting the liquid level and maximum capacity of sulphur run-down lines. This was accomplished using a combination of predictive calculations and physical testing. Predictive calculations can be applied to steady, open channel flow in a straight run, but predictive calculation is difficult when applied to flow through fittings and transitional regions. The work performed to develop the general method consisted of:

- development of a predictive calculation method for straight runs;
- assembly of a full-scale model of a run-down line incorporating common elements;
- testing with water of varying viscosity from which sulphur flow predictions could be extrapolated;
- validation of the predictive calculations for the straight runs;
- identification of empirical 'multipliers' that predict the liquid level in the fittings and transition regions.

Fig. 1 shows a visualisation of the development approach. Much of the work was performed by a five-person team of University of North Carolina, Charlotte undergrad students as their senior design project. The team designed and assembled the apparatus, conducted the test runs, and gathered the data. The team also performed some data analysis, though the final data analysis was performed by CSI engineering.

Test apparatus

The test apparatus was a full-scale run-down line configurable to evaluate the various items of interest. The material used

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Fig. 1: **Visualization of the development approach**

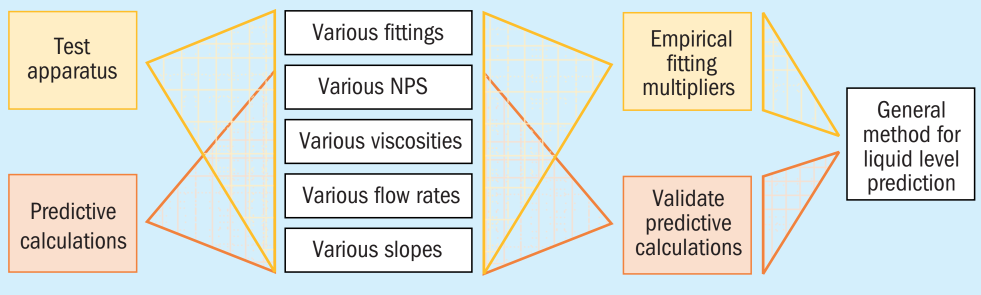

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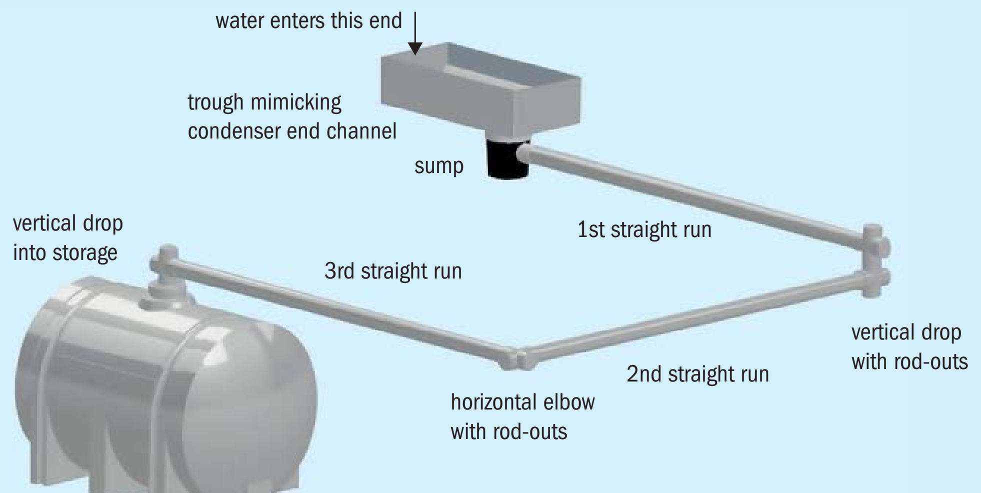
Fig. 2: **Test apparatus layout**



Source: CSI

was primarily clear PVC which enabled measurement of the liquid level within. The test apparatus was configurable to include the following:

- pipe sizes ranging from 2 inches to 4 inches NPS;
- a straight section sufficiently long to produce fully-developed flow;
- various pipe slopes from $^1/_8$ in/ft to $^5/_8$ in/ft;
- an entrance region representing a typical sump-style condenser connection;
- a vertical drop made with rod-out crosses;
- a horizontal 90° elbow made with a rod-out cross;
- an exit region representing a vertical drop into a sulphur pit.

The use of clear PVC prevented testing with sulphur. Instead, thickened water was used to mimic the flow characteristics of sulphur. Thus, the fluid conditions that could be evaluated included:

- water at various viscosities;
- various flow rates.

Fig. 2 shows the test apparatus layout.

Without the ability to test sulphur directly, it was necessary to manipulate the water viscosity to mimic the flow characteristics of sulphur. Reynolds number is strongly predictive of flow characteristics. Thus, the target water viscosities were based on achieving the same Reynolds number in testing as will be seen in sulphur. Specifically, the same density/dynamic viscosity ratio (rho/mu).

Sulphur's viscosity increases dramatically above 318°F (159°C) when the sulphur molecules form polymer chains. The presence of H_2S in the sulphur has the effect of capping those chains and reducing the sulphur viscosity. As a high-end viscosity, CSI considered a first condenser condition of 350°F (177°C), 500 ppm H_2S, and 50 cP. At the low end, CSI considered a fourth condenser condition of 280°F (138°C), 25 ppm H_2S, and 9 cP. These viscosities were arrived at using work published by ASRL (Rheometric Properties of Liquid Elemental Sulphur and Modifying Effects of Hydrogen Sulphide; Alberta Sulphur Research Ltd. 2019). CSI conducted testing across a larger viscosity range to extend the applicability of the results. A water viscosity range of 1 to 36 cSt was tested, which is equivalent to a sulphur viscosity range of 3 to 115 cP. A total of 91 test runs were conducted.

The test apparatus provided control of the inputs: pipe NPS, pipe slope, fluid flow rate, fluid viscosity, and fitting configuration. The primary measured parameter was the liquid level at various locations along the line. At ten locations holes were drilled in the top of the pipe and a depth gauge was used to measure the liquid level. Additionally, a clear window was installed on each 'blind' of the rod-out fittings; this was used to observe the flow characteristics and to measure the liquid level against the window (see photos).

Uncertainty

Through the course of testing and analysis, three areas of uncertainty were identified. These are unlikely to have a significant impact on the conclusions of the study but need to be acknowledged.

Inconsistent slope: For the majority of the test runs, the slope was measured referencing the concrete slab on which the apparatus was assembled. This was later identified as a source of significant error as the slab was not level. The tests were not re-run, rather the slope data was corrected for the analysis. As a result, for each test run, each of the three pipe runs in the test apparatus was set to a different slope. This differed from the intended test setup and may have introduced some amount of error as each of the fittings had a slightly different slope entering vs exiting the fitting.

Fully developed flow: The straight run pipe lengths were chosen to ensure fully developed flow. This analysis was based on L/D recommendations for internal flow. But during testing it was observed that the open channel would form standing waves and other flow variability that extended for the full length of the pipe. The pipe lengths were not sufficient to ensure fully developed flow. The impact of this was most significant in the first straight run as discussed in the next point.

Sump region flow pattern: The first section of the test setup was intended to mimic a sump on the bottom of a sulphur condenser. In a sulphur condenser the sulphur waterfalls down the tubesheet and forms a river of sulphur in the ends channel heading towards the sump. It is speculated that this 'river' has relatively even flow distribution. But in the test setup, the

PHOTO: CSI

Test apparatus.

PHOTO: CSI

Imitation condenser end channel.

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Example of liquid flow through the vertical drop; view from above.

Example of liquid turbulence exiting the vertical drop.

water was delivered to the 'end channel' via a pipe. The flow of water discharging from the pipe created currents and standing waves in the end channel and sump that carried through to the run-down line. To mitigate this, baffles were inserted in front of the pipe discharge to create a more even distribution of flow entering the sump. This successfully eliminated the standing waves and other flow variations in the first straight pipe. But the original intention of accurately representing the condenser sump was not achieved.

Predictive calculations

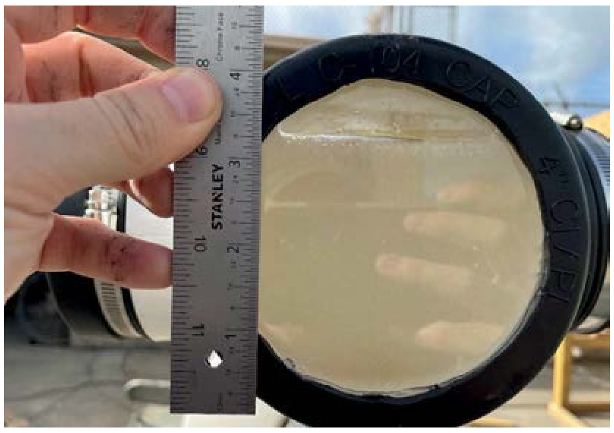
For steady-state conditions in straight pipe, the liquid level can be predicted using fluid theory (Fig. 3). At steady state, the energy of the system balances. In the case of gravity-driven flow, the two energy paths in balance are energy loss due to friction with the pipe wall, and energy gain due to elevation drop (liquid head).

The liquid head is calculated as elevation drop per unit length of pipe. The frictional loss is calculated using the Darcy-Weisbach equation with modification to consider the partial cross-section of the fluid in the pipe. Specifically, the liquid-vapour interface surface is considered to have no frictional losses and is therefore omitted from the calculation.

The conventional presentation of Darcy's equation is re-arranged to solve for the pipe slope:

$$\frac{h}{L} = f \cdot \frac{1}{D} \cdot \frac{V^2}{2 \cdot g}$$

where:
h = elevation drop per unit length
L = unit length of pipe
f = pipe wall friction factor calculated from Reynolds number where Reynolds number uses the fluid hydraulic diameter D
D = fluid hydraulic diameter = 4* (liquid

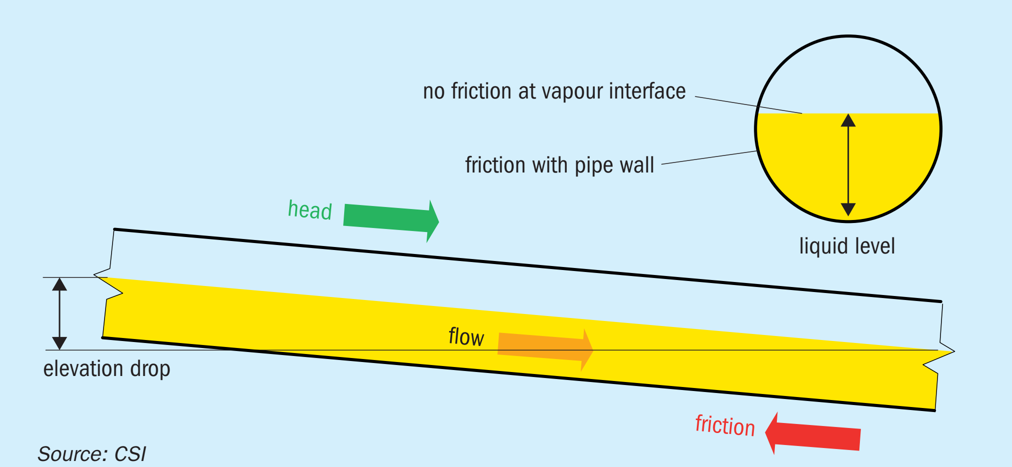


PHOTOS: CSI

Left: Example of liquid level rise at entrance to horizontal elbow fitting. Right: Example of liquid level viewed through sight glass on elbow.

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

Fig. 3: **Open channel flow energy balance**



Source: CSI

cross section)/(liquid arc length contacting the pipe wall)
V = fluid velocity
g = gravity constant

CSI's approach was to consider a fixed slope and flow rate; then to find the liquid level by iteration. f, D, and V on the right side of the equation are all functions of liquid level and change with each iteration. The liquid level is iterated until both sides of Darcy's equation balance. This approach is valid for straight pipe with a constant slope and fully developed flow.

CSI did not attempt to predict the liquid level in the fittings, choosing instead to depend empirically on the test results. It is likely that modelling the liquid level in the fittings would require sophisticated CFD modelling. This was beyond the capabilities of the group working on the project.

Test results

The test results for straight pipe all trend as expected. Pipe NPS, fluid viscosity, fluid flow rate, and pipe slope all have the expected effect on the liquid level. Overall, the formula tends to slightly under-predict the liquid level. The under-prediction is minor for most of the tested range, becoming significant only for lower viscosities running at higher flow rates. The graphs in Figs 4 and 5 show this comparison for 4-inch NPS pipe at two different viscosities. Points are observed data; dotted lines are the prediction. The other NPS/viscosity combinations follow the same trends.

The test points shown in the graphs in Figs 4 and 5 are all below the 50% liquid level. This is because the liquid level in the fittings was roughly 2x higher than the liquid level in the straight pipe. The test flow rate was limited by the fittings. This is expected as the fluid tends to slow down and 'pile up' in the fitting before it changes direction and starts flowing again. Interestingly, the liquid level observed in the fittings is higher than one would expect based solely on conservation of energy (Bernoulli's equation). This indicates that fluid momentum creates highly dynamic flow conditions in the fittings. Indeed, the liquid movement in the fittings was considerably more turbulent than in the straight runs.

The liquid in the fittings would slosh around and bounce up and down making it difficult to determine the true liquid level. Liquid level measurements were taken at the fittings with the intention of capturing the average liquid level; it is felt that this was accomplished reasonably well. Even though the data has a lot of scatter, the trends of the averages still follow a logical pattern.

To analyse the fitting data, the observed fitting liquid level was divided by the predicted straight pipe liquid level to product a 'fitting ratio'. It was found that the fitting ratio was dependent on the fluid viscosity and the pipe slope, but not on the fluid flow rate or the pipe NPS. Formulas for the fitting ratios were developed from the data.

Horizontal rod-out elbow:

$\text{Ratio} = (-0.02) * \text{viscosity} + 0.54 * \ln(\text{slope}) + 3.25$

where viscosity units are cP and slope units are in/ft

Vertical drop elbow:

$\text{Ratio} = (-0.02) * \text{viscosity} + 0.59 * \ln(\text{slope}) + 3.49$

where viscosity units are cP and slope units are in/ft

The vertical drop tended to produce a slightly larger liquid level. This is reflected in the last term of the two formulas. The charts in Figs 6 and 7 show the observed fitting ratios compared to those predicted by the formula.

A similar analysis was conducted for the sump nozzle. It was expected that the transition from low velocity in the sump to higher velocity in the pipe would result in liquid level drop as energy is conserved. This was observed, but the data was very scattered, and trends were difficult to establish. This was likely due to the inconsistent flow characteristics in this region as previously discussed. A fitting ratio formula was derived from the data, but its accuracy is questionable considering the uncertainty surrounding this area of the test.

$\text{Ratio} = 0.98 * \text{slope} + 1.04$

where slope units are in/ft

The test setup also included a vertical drop into the collection vessel mimicking a typical discharge into a sulphur pit. As expected, there was never any backup of liquid in this region; a clear vapour path was always present in all test runs.

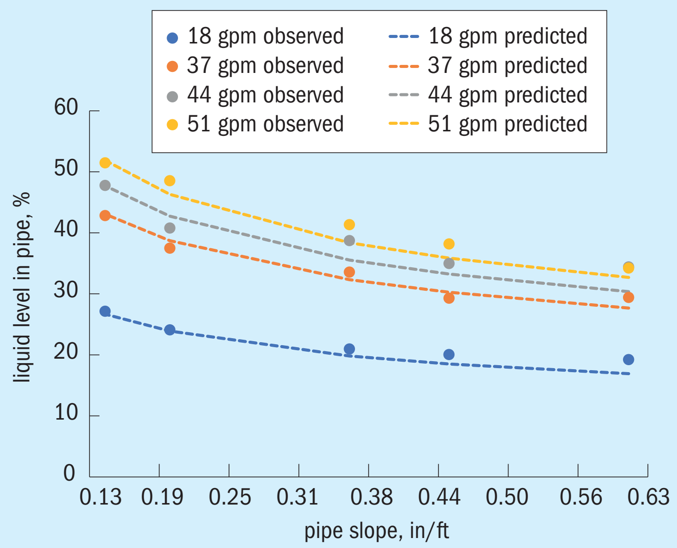
Application

The test data and analysis provided formulas that can be used to predict the liquid level in sulphur rundown lines of various configurations. In theory, when the liquid level reaches 100% at any point in the line, vapour can no longer exchange between the sulphur condenser and the sealing device, and a vapour lock scenario becomes possible. This should provide an engineer with the ability to determine the maximum liquid capacity of a given line. But the real-world application is a bit fuzzier. The following factors should also be considered by any engineer endeavouring to apply these findings:

Sloshing vapour exchange: The test did not directly evaluate the ability of vapour to travel through the line. From the observations, it is speculated that even when the fitting liquid level is at 100%, the 'sloshing' of the fluid in the line opens intermittent vapour paths that are sufficient for pressure equalisation under normal conditions. This is an argument for more aggressive line sizing.

Debris accumulation: Accumulation of debris in the form of tar-like material buildup on the pipe walls is relatively common in SRUs. This accumulation effectively reduces the cross-section of the pipe resulting in diminishing capacity over time. This is an argument for more conservative line sizing.

Fig. 4: Straight pipe liquid level formula prediction and observations for 4-inch NPS with 22.5 cP water



Source: CSI

Fig. 5: Straight pipe liquid level formula prediction and observations for 4-inch NPS with 1.0 cP water

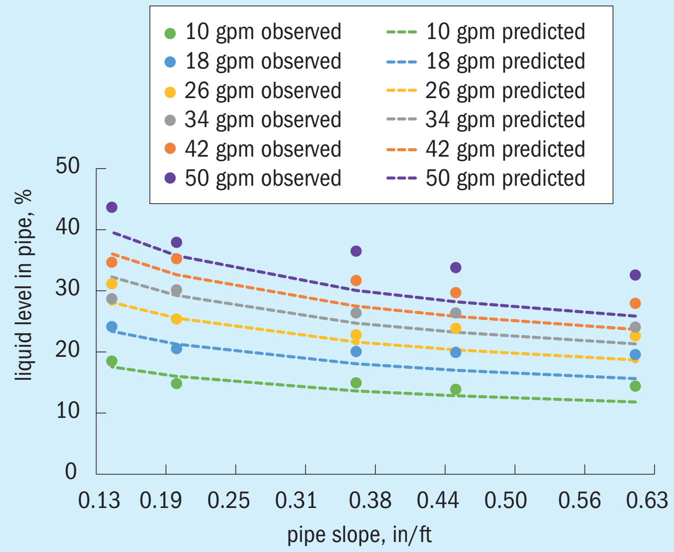


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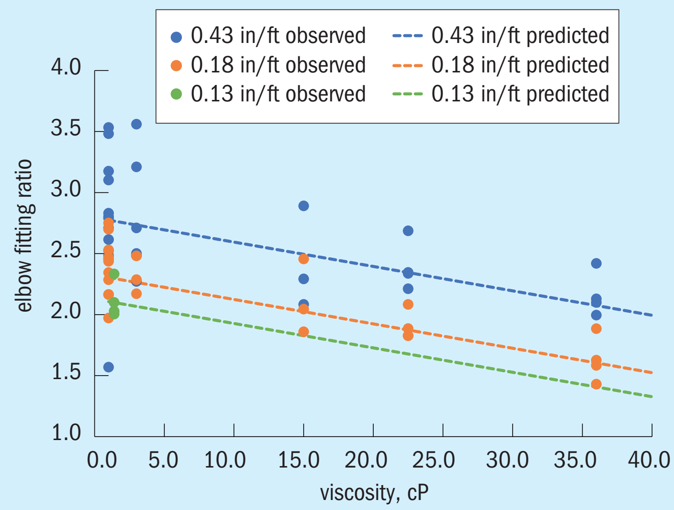
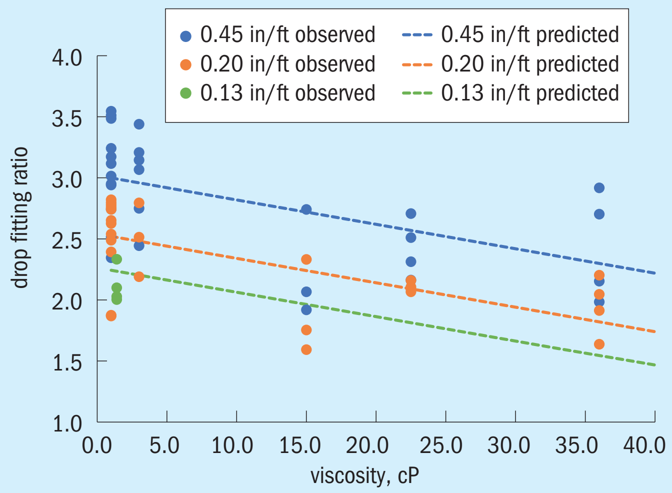
Fig. 6: Horizontal rod-out elbow liquid level formula prediction and observations



Source: CSI

Fig. 7: Vertical rod-out drop liquid level formula prediction and observations



Source: CSI

Valve design: Industry best practice is to use full-port plug or ball valves in run-down lines; these should have minimal effect on the fluid level in the pipe. But other valves are often encountered; any reduction in the line cross-section will create a restriction point. This is an argument for more conservative line sizing when valve choice is sub-optimal.

Fitting frequency: The test was constructed to evaluate the fittings in isolation. A series of fittings in close succession would result in slower fluid velocity and a higher liquid level in the pipe. This is an argument for more conservative line sizing when fittings density is high.

Varying slope: The test was conducted with relatively consistent slope throughout. Many real-world applications have multiple section of pipe with varying slope. This is acceptable provided the calculations are based on the shallowest slope. But many run-down lines include short sections of near-level pipe. This is an argument for more conservative line sizing when there are near-level sections of pipe.

Experience: CSI has observed several running plants that appear to be operating without issue despite having run-down lines that would be considered under-sized based on this test data. It is speculated that, in most real-world applications, intermittent vapour exchange provides sufficient pressure equalisation between the sulphur condenser and the sealing device. This is an argument for more aggressive line sizing.

Summary

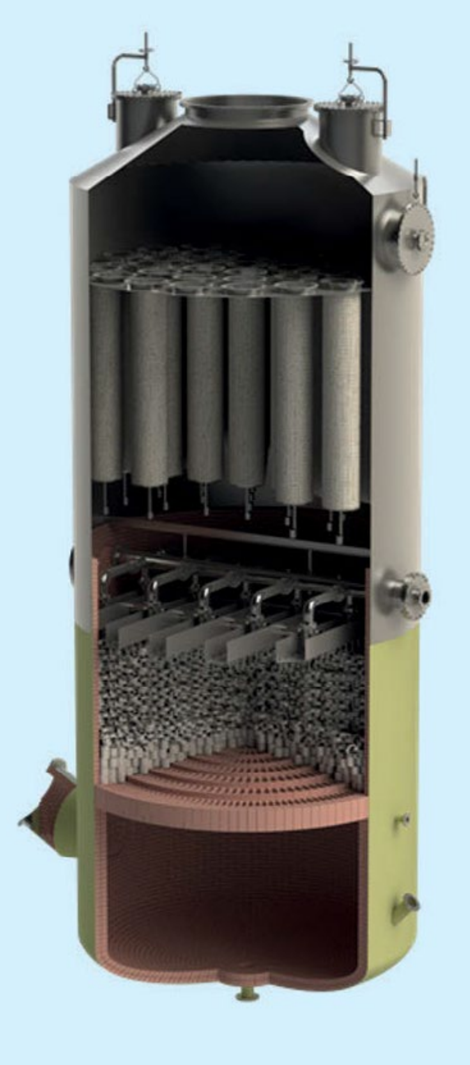
A series of test was conducted to characterise the liquid level in run-down line piping. The purpose was to establish a method of sizing these lines to ensure proper vapour pressure equalisation between the sulphur condenser and the sealing device. The tests considered many of the common elements of a rundown line. The results led to the development of a set of formulas that can be applied to a variety of rundown line configurations to predict the liquid level. The formulas should not be applied blindly as there are several over factors to consider when sizing run-down lines. These factors are briefly discussed and require engineering judgement for their application. ■

The art of candle filter wetting

When candle filter mist eliminators installed in the absorption towers in sulphuric acid plants are not sufficiently wet, problems can occur such as free SO_3 at the stack, NOx issues and emission non-compliance. **Craig Cassells** of Begg Cousland Envirotec discusses how these problems can be overcome by the installation of an annular wetting ring solution.

Candle filter mist eliminators are used widely in the sulphuric acid industry across the world. Located in the absorption towers as well as drying towers, they play a pivotal role in reducing air pollution as well as operational problems caused by the formation of sulphuric acid mists. Their successful operation is vital for achieving a plant's operational capacity, protecting downstream equipment, and reducing the need for stoppages and maintenance interventions.

Fig. 1: **Typical hanging type candle arrangement in the IAT/FAT**



Source: Begg Cousland

Fig. 1 shows a typical hanging type candle arrangement in an intermediate or final absorption tower.

Brownian diffusion mist eliminators are normally installed in the intermediate absorption tower (IAT) and in more recent times the final absorption tower (FAT) for achieving lower emission standards. Their use relies on the fibre media being sufficiently wetted, but what issues can arise when the candle filters are not sufficiently wet?

Case 1 – Free SO_3

One of the main reasons for installing a wetting system in a sulphuric acid plant is in the event of free SO_3, which can cause a visible plume at the stack. This will occur:

- at sulphuric acid plant start-up;
- in cases where there is an interrupted power supply and stopping and starting of the plant;
- in plants that have oleum production.

The best solution is to irrigate the candle filters with sulphuric acid to ensure the fibre bed is sufficiently wet.

Case 2 – NOx (nitrous oxides)

Nitrous oxides can form nitrosyl sulphuric acid which will cause problems within the candle filter fibre bed (Fig. 2). It is dependent on the operating temperature and concentration build-up. This leads to operational issues, such as higher than expected pressure loss, loss of removal efficiency and product contamination. To solve this NOx issue, the following steps can be taken:

- irrigate the candle filters with fresh H_2SO_4;
- increase the tower temperature to above 73°C to dissolve the nitrosyl crystals;
- segregate the acid collected within the filter from the final product acid.

Case 3 – Free SO_2

The final case is free SO_2, which can result in emission non-compliance. Begg Cousland's experience has been with single contact wet sulphuric acid plants and the solution has been to irrigate the filters with a mixture of sulphuric acid and hydrogen peroxide to remove the SO_2.

How to wet a candle filter

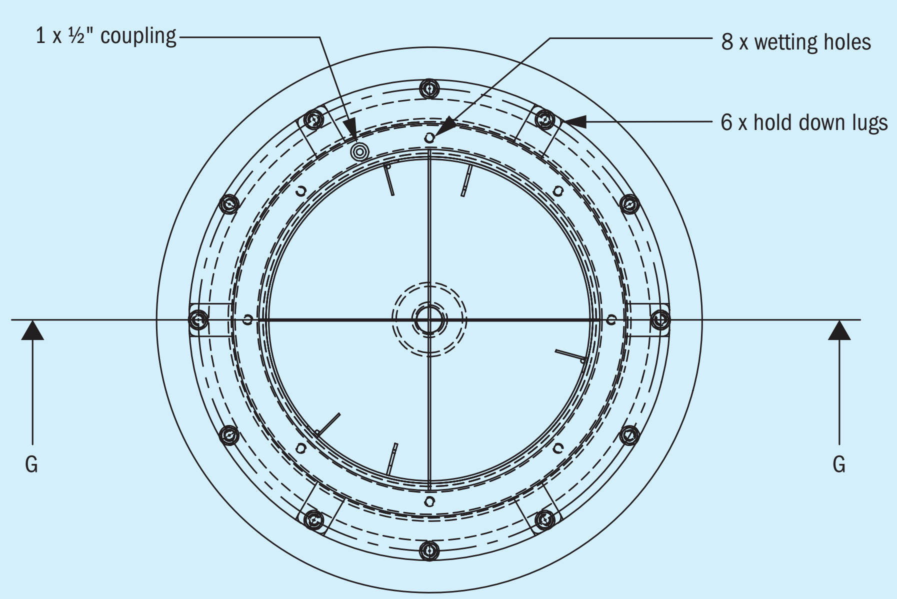
Traditionally, candle filters have been wetted using spray nozzles. This can be done by spraying from beneath the installed filters using a series of spray bars and manifolds, or in the case of standing type filters, by fitting the spray nozzle into the

PHOTO: BEGG COUSLAND

Fig. 2: Removed candle filters contaminated with NOx.

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

Fig. 3: **Wetting ring example**



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top plate. There are some drawbacks to this method:

- A relatively high supply pressure (3-5 bar) is needed which may require a secondary acid pump, as the pressure supplied to the acid distributor is too low.
- These methods rely on the gas to carry the sprayed liquid into the fibre bed of the candle which does not always provide uniform coverage, particularly in the case of longer length filters. In some cases, spraying from below and above is necessary to solve this problem.

Improving the introduction of liquid to the fibre bed

Begg Cousland considered several options to improve the wetting of a candle filter and settled on an annular wetting ring solution fitted to the top of the filter (Fig. 3). The main advantages of this design are that it is a low-pressure liquid feed with fully controllable flowrates to suit the candle filter size. The ring allows the liquid to be fed directly into the fibre bed providing uniform liquid addition.

The optimal configuration for a wetting ring system is with the candle filters in a hanging type orientation to ensure easier access to the tubesheet above. In this case there is a series of circumferential manifolds and flexible hoses connected to the wetting ring. It is worth noting that the wetting ring system can be installed as part of a new supply of candle filters, but can also be retrofitted to existing candle filter installations.

Recent case studies

Case study 1: A Southern African customer having issues with free SO_3. This was an existing installation in a plant that was having issues with interrupted power, causing multiple restarts. Begg Cousland looked at how to retrofit a wetting ring in the final absorption tower and came up with a bolt-on solution where the existing candle filters were drilled with holes and retrofitted (Fig. 4). Following the wetting ring installation, stack emissions were improved significantly.

Case study 2: A North American customer having issues with stack opacity when producing oleum. In this case it was slightly more difficult as the customer had X-TRA FLOW candle filters with both an inner and outer fibre bed, meaning two sets of wetting rings had to be produced for each filter (Fig. 5). Again, the filters were drilled with holes to be retrofitted with wetting rings. Both the inner and outer fibre bed were fed from a central circumferential manifold feeding both rings.

Fig. 4: **Retrofitted wetting ring system**

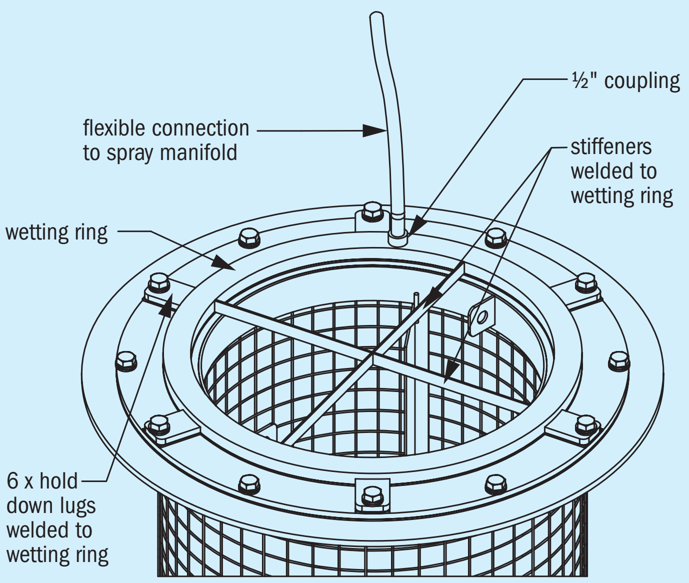

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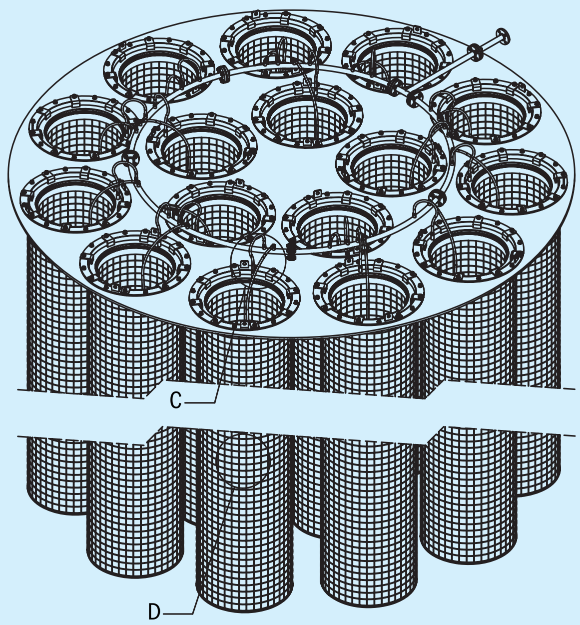
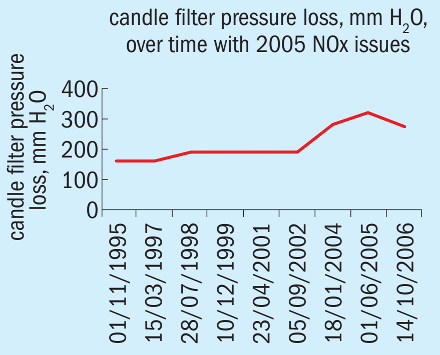
Fig. 5: **XTRA-FLOW candle filter wetting ring installation**



Source: Begg Cousland

Case study 3: This was one of Begg Cousland's first experiences of increased fibre bed pressure loss due to NOx in 2004 when a European customer changed the old set of candle filters, like-for-like. When the new candle filters went into operation the pressure loss was higher than the old set, which should not have been the case. The plant sourced zinc concentrate from the Century mine, which has high levels of NO. As shown on the pressure loss trend graph (Fig. 6) the use of some Century concentrate began in 1997-8, which led to an increase in pressure loss. A higher percentage was used from 2002, leading to another increase.

Fig. 6: **Pressure loss increases due to presence of NOx**



Source: Begg Cousland

Nitrosylsulphuric Acid ($NOHSO_4$) forms crystals below 73°C when insufficient H_2O is present to prevent (or to dissolve) them. The fibre, when removed, was hard to the touch and when sent for analysis high levels of nitrogen were discovered.

It was not possible to visually see the build-up of nitrosyl crystals in the tower/fibre bed as the crystals themselves are white. It only became apparent when the filters were removed from the tower, and they fumed an orange/brown colour.

Where NOx is an issue, the tower needs to be operated at an elevated temperature (75-77°C) to solubilize the crystals. The use of a wetting ring is imperative, with the candles pre-wetted before start-up and continuous wetting in operation.

In the case of NOx, the high levels of nitrogen still remain an issue as the collected contaminated acid from the filters must be segregated from the final product acid. A flanged drain pipework can be introduced into a central manifold, as well as the use of a drip tray at the base to minimise NOx drips into the acid below (Fig. 7).

Case study 4: The reduction of SO_2 in a European single contact wet sulphuric acid plant. In this installation, there were fluoropolymer candle filters in a standing-type orientation. The mixture of hydrogen peroxide and sulphuric acid was introduced using PFA flexible hoses and wetting rings at the top of the candle. Once again, the stack opacity was greatly reduced.

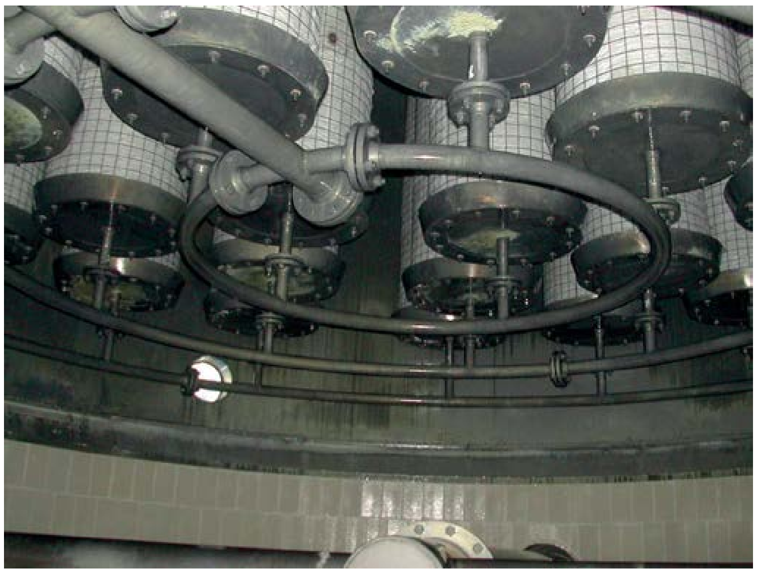


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Fig. 7: Flanged type collection system with drip trays.

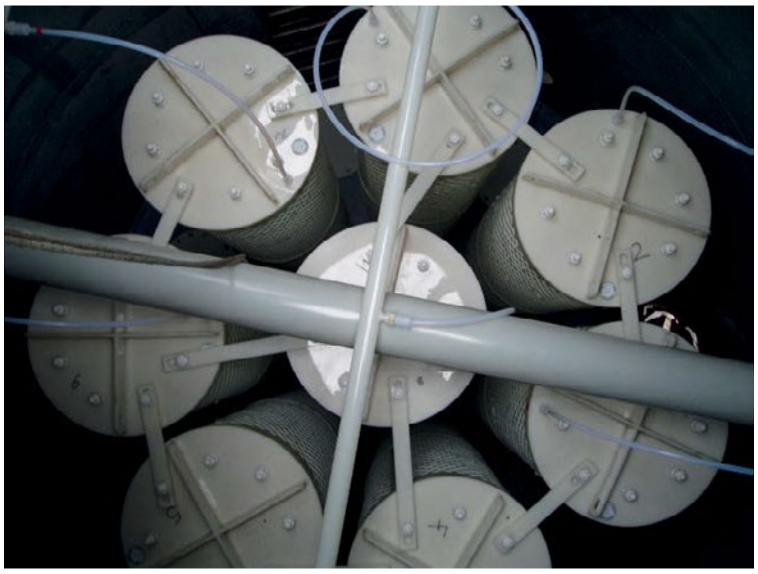

PHOTO: BEGG COUSLAND

Fig. 8: WSA candle filters with wetting ring system.

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

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