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SULPHUR

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Sulphur in Central Asia

Sulphuric acid catalysts

SRU optimisation

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Protectionism casts a shadow over the new year

Cover: *Crystal of Nickel Sulphate. Photo: Patrick Kormendy / ShutterStock*

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Protectionism casts a shadow over the new year

The start of a new year is a traditional time to take stock of the previous 12 months and look ahead to the next. In this regard, CRU's most recent annual client survey, conducted at the end of December last year, makes interesting reading as to your own concerns for 2025 and beyond. There were numerous responses across commodity and financial sectors, and broadly based worldwide, if slightly skewed towards Europe and North America, but across all of these the key worry for the coming year clearly emerged as trade tariffs and protectionism. This is perhaps unsurprising, given incoming US president Donald Trump's avowed intent to impose blanket 20% tariffs on all goods entering the US, and up to 60% on China. While most clients did not think tariffs would rise as much as some of Trump's rhetoric might suggest, most expect rises of 5-10% across the board, and Asian businesses are most concerned. CRU's most recent position paper on US tariffs highlights some of the internal political and legal challenges in implementing these, but does acknowledge that some rises will be inevitable, and may well produce the kind of reciprocal measures last seen in the previous Trump administration's trade war with China and the EU in 2018.

> **"Most clients were cautiously optimistic that 2025 will see continued steady growth..."**

Of course protectionism comes in many forms, and many respondents were also concerned about trade and trade restrictions based on sustainability criteria, such as the EU Carbon Border Adjustment Mechanism or US Inflation Reduction Act. A number of other issues – including carbon pricing, reporting requirements and supply chain issues – were of roughly equal importance. Additionally, and perhaps unsurprisingly in a world where war in Ukraine has led to its own sanctions regime against Russia and Houthi rebels take potshots at passing shipping in the Red Sea, war and geopolitics were also cited as major downside risks to growth.

Even so, most clients were cautiously optimistic that 2025 will see continued steady growth, falling interest rates and further progress towards decarbonisation. A clear majority expected global growth to be between 2-3% in 2025. This is in line with CRU's own forecast of 2.6%, and similar to growth in 2024 (which is expected to have been 2.7%). A figure of 3% is widely acknowledged as being the trend rate of growth that can be expected from the world in 'normal' times. Most respondents also agreed with CRU's view that interest rates will fall this year in most major economies, with respondents in North America being the most dovish.

There was also optimism on the green transition in spite of the scepticism of the incoming US administration. Most customers expect fossil fuel demand to have peaked by 2030, and a significant minority of respondents – almost one-third – in both Europe and Asia believe that consumption of fossil fuels in their region has already peaked, and the majority expect it will have peaked by 2030. Even in the Americas almost 60% of respondents believe fossil fuel consumption will peak by 2030. Asked to name the most important commodities and technologies for the coming years, copper was the single most popular commodity, while hydrogen and solar were the most popular technologies. However, it was noteworthy that responses were spread across a wide range of technologies, and that most were linked in some way to decarbonisation. Half of the respondents expect global EV sales to grow between 0–10% year on year in 2025, and most of the remainder expect double-digit growth rates.

Overall, the survey results paint a picture of a year in which there are significant risks and challenges – most of all around trade and geopolitics. However, clients are also focused on the many opportunities that will exist if we see continued growth, and as decarbonisation continues to rise up the agenda. ■

Richard Hands, Editor

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Price Trends

SULPHUR

Global sulphur prices were mostly assessed flat in mid-January, with only slight changes for China, Indonesia and India, while the first quarter contracts for the Middle East, North Africa and Tampa increased from the previous quarter. Overall, the number of transactions taking place globally has declined as subdued demand has limited trading activity in most delivered markets. The current sulphur price environment has been shaped by the combination of rising Chinese demand and higher Middle East f.o.b. prices in the second half of last year. As a result, some consumer markets such as Indonesia and India have been subject to upward pressure in order to remain attractive destinations. But demand remained lacklustre across delivered markets, leaving prices relatively stable.

The sulphur price into China has narrowed slightly to $183-185/t c.fr. Import transactions into China have been limited. The latest reported purchase was of 30,000 t by a phosphate producer at a level of $185/t c.fr, with shipment to the Yangtze River expected in February. Another cargo of non-mainstream sources was reported as sold to southern China at a level of $184/t c.fr. However, this transaction could not be confirmed at the time of writing. Indonesian buyer PT Lygend closed a tender at $187/t c.fr for 50,000 tonnes on 10th January 2025. This price level has supported an overall positive market sentiment in China. The sulphur port spot transaction price is reported at around $214/t. The port price indicates a netback price at around $181/t c.fr. This is $4/t lower than the current price for fresh import products. This has led to end-users preferring to purchase port products rather than fresh import cargoes. Chinese sulphur prices are relatively steady despite the bearish sentiment in the phosphate market. Phosphate producers continue to show a consistent demand for sulphur as end-users still require sulphur in order to prepare for the spring application season. Port inventory is decreasing as activity has focused on domestic stocks. Total sulphur port inventories in China decreased by 61,000 tonnes to 2.04 million tonnes on 15 January 2025. This is the lowest stock level since 20 July 2023. The volume at Yangtze River ports increased 11,000 tonnes to 722,000 t while the Dafeng port inventory declined 60,000 tonnes to 406,000 t.

The spot price for sulphur cargoes into Indonesia has widened and is now assessed at $180-187/t c.fr after holding at $180-185/t c.fr for five weeks. The price has widened as a PT Lygend tender for 50,000 t was awarded at around $187/t c.fr on 10 January. Additionally, reports suggest a tender in Taiwan, China, was awarded at $175/t f.o.b. to Saudi Aramco and is headed to Indonesia, though this could not be confirmed at the time of writing. The lower end of $180/t c.fr is considered as still viable, according to multiple market participants. Transactions into the country had been limited as the market has been experiencing upward pressure as a result of recent Middle East price hikes and Chinese demand for sulphur towards the end of last year. The market is considered to have stable demand, according to market sources.

Sulphur prices in India were assessed slightly lower at $175-185/t c.fr this week, down from the previous assessment of $180-185/t c.fr, as activity in the market was limited by existing stocks and subdued demand. Importers are refraining from purchasing additional cargoes, while major Middle Eastern suppliers maintain high c.fr offers, despite the market's muted appetite. Recent offers from the Arabian Gulf are reported in the range of $160-170/t c.fr, but no transactions have been concluded at those levels. Offers from the Middle East have been heard at $170-185/t c.fr. As a result, the current market assessment has reduced slightly to $175-185/t c.fr. Market participants consider that this downward trend could persist through March, supported by stable inventory levels and lower downstream demand due to anticipated plant shutdowns in March and April. The pricing dynamic is further influenced by a strategic shift among suppliers, with some transitioning into trading roles. Notably, ADNOC and other major suppliers are increasingly bypassing traders to engage directly with buyers. This shift has created ripples across the trader community, with reports of a Middle Eastern supplier cancelling a 1 million tonne annual allocation with a prominent trader, significantly impacting their operations.

India had imported approximately 61,500 tonnes of sulphur by 10th January 2025, with 78% sourced from Oman and the remainder from Bahrain. The Omani cargoes were delivered to IFFCO Paradip, while the Bahraini shipment was destined for FACT. For January 2024, total imports stood at around 120,000 tonnes, with 73% of the volume loaded from Ruwais and the rest from Ras Laffan, according to the latest Interocean vessel data.

Spot prices in the Middle East were assessed unchanged. A lack of transactions out of this region has left prices flat. This is in contrast to the Mediterranean where there has been an uptick in activity and prices have been increasing since the end of last year. Prices remained flat, but the bullish sentiment persists as demand remains constant from countries like Egypt and Libya. Middle East quarterly contract prices for 2025 Q1 have been settled at $150-160/t f.o.b., which is an increase from the 2024 Q4 prices. The average Q1 price of $155/t f.o.b. is an increase of $33/t from the midpoint of the 2024 Q4 price level of $122/t f.o.b.

The contract price range for supply of sulphur to North Africa in the first quarter of 2025 increased to $160-170/t c.fr based on market feedback, up from $120-140/t c.fr for 2024 Q4. Contract prices have increased for two consecutive quarters after the price range for Q3 was published at $94-103/t c.fr, which was a slight decrease from Q2's price of $95-105/t c.fr. Origins of contract supply to North Africa are the UAE and a range of other Middle East sources as well as Kazakhstan, Poland and Spain.

The US Tampa quarterly contract prices for the first quarter of 2025 were settled up $49/lt from the 2024 Q4 settlement, market sources confirmed. This leaves the published contract price at $165/lt f.o.b. Tampa for 2025 Q1. The Q4 2024 price was settled at $116/lt f.o.b., the Q3 2024 price was $76/lt f.o.b., the Q2 2024 was $81/lt f.o.b. and the Q1 2024 price was $69/lt f.o.b.

SULPHURIC ACID

Benchmark prices for sulphuric acid were assessed mostly unchanged in mid-January. Europe remains tight on availability while Asian supplying markets have become increasingly tight following sales towards the end of last year and the beginning of this year. Price movements have failed to gain traction as tight availability is being offset by subdued demand in delivered countries. This has kept prices largely stable since the beginning of the year. European supply is expected to increase by mid- to-late Q1, aligning with a potential recovery in demand. As a result, the

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global sulphuric acid market remains at a standstill, with market participants awaiting either a shift in demand or supply to gain a better price direction.

Acid prices for Northwest Europe were assessed flat at $110-120/t f.o.b. for the third consecutive week amid tight supply. The price previously held at $100-110/t for twelve consecutive weeks. Availability remains tight in the region and although expected in Q1, it is possible that the supply does not materialise until the middle or end of the quarter, according to market participants. The price could soon decrease as several market participants consider the current price to be too high for market activity to take place. However, no transactions were confirmed at lower levels. The current midpoint of $115/t f.o.b. is the highest since the week of 18 August 2022.

In Japan/South Korea the published price has changed on the lower end as quarterly contracts for delivery to China from South Korea were settled at a price level of low $30s/t. The spot price in the region remains assessed unchanged at a level of $50-55/t f.o.b. The market is now under conditions of tightening supply, being mostly sold out for Q1 and with reports of availability expected to be tight for the first half of the year.

Export prices for sulphuric acid in China were assessed unchanged at $50-55/t f.o.b. after narrowing from $45-55/t at the start of the year. Market participants anticipate that the market will remain relatively stable, while others consider that activity could pick up ahead of the Chinese New Year celebrations. Chinese producers ended last year making an effort to maintain low inventories ahead of the upcoming Chinese New Year holidays, according to market participants. As a result, sales were made towards the end of last year with prices below the currently published range. Following a number of sales made at the $45/t f.o.b. level towards the end of last year and the beginning of this year, the price narrowed to its current range. China's sulphuric acid exports for January-November decreased 3% year on year to 2.1 million tonnes, while its acid imports decreased by around 50% from the same period in 2023.

India's sulphuric acid market conditions remain unchanged at $105-110/t c.fr as weak demand and sufficient inventories from earlier imports have kept activity subdued. Prices have held steady, with offers from Japan and South Korea currently assessed at $50-55/t. International traders indicated that lower prices could stimulate activity in the market but no transactions have concluded at a lower price range. January 2025 imports have totalled 74,653 tonnes so far, with South Korea contributing 51% of the volume and the remainder has been sourced from Japan. Limited activity is expected to continue until later in the year, when some importers may re-engage in the market to restock, according to market participants. However, the sentiment remains bearish as domestic production is set to rise in the coming months, which could exert additional downward pressure on prices.

In Chile, prices for the spot market were assessed unchanged at $150-155/t c.fr. However, some participants have suggested that the price could be even lower as market activity is extremely limited. However, the purchasing activity is being limited by logistics and meteorological conditions instead of a pricing environment, according to other market participants. This is because the seasonal rough seas along with conditions of limited storage capacity have prevented transactions from taking place. These conditions may persist until around February, according to local buyers.

China's sulphuric acid exports for January-December 2024 increased by 7% year on year to 2.68 million t/a, according to Global Trade Tracker. Exports to Chile increased by 122% to 1.27 million t/a over the year, up from 577,000 t/a reported in the same period last year, while exports to Morocco decreased 28% to 321,000 t/a. The volume to India increased by 21% to 318,000 t/a, while volumes to Indonesia decreased 62% to 239,000 t/a. Exports to Saudi Arabia dropped 17% on year to 286,000 t/a. China's acid imports halved on year to 162,000 t/a from January to December 2024, data shows. In 2023, China's acid exports had dropped by 31% year on year to 2.51 million t/a, after exports for 2022 had increased 28% year on year to reach 3.64 million t/a, representing a new record and surpassing the previous year's record. ■

Price Indications

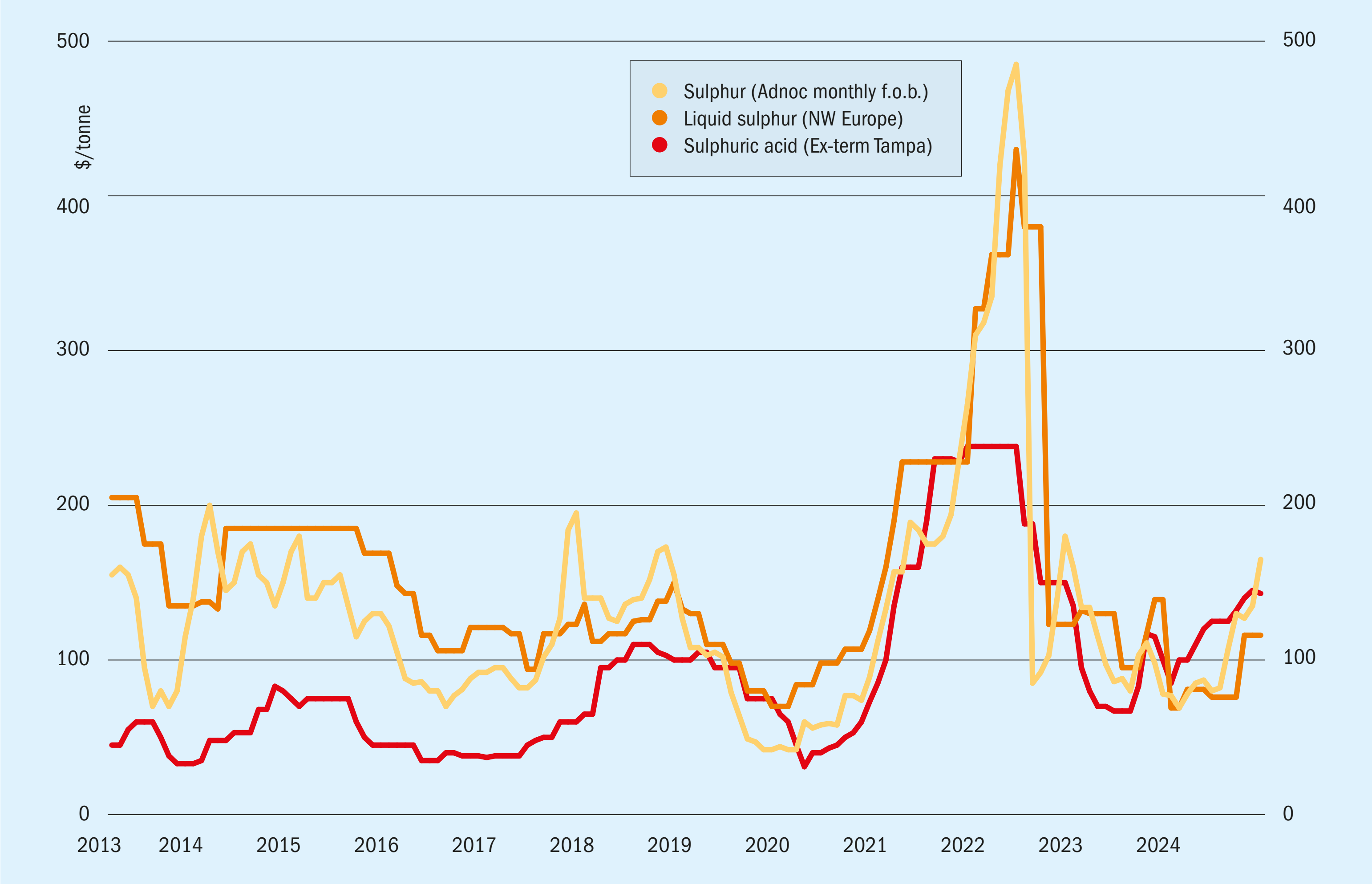
Table 1: **Recent sulphur prices, major markets**

Cash equivalent	**August**	**September**	**October**	**November**	**December**
Sulphur, bulk ($/t)					
ADNOC monthly contract	107	130	127	135	165
China c.fr spot	143	145	154	184	184
Liquid sulphur ($/t)					
Tampa f.o.b. contract	76	76	116	116	116
NW Europe c.fr	163	163	193	193	193
Sulphuric acid ($/t)					
US Gulf spot c.fr	125	132	140	145	143

Source: various

Market Outlook

Historical price trends $/tonne



Source: CRU

SULPHUR

- Sulphur prices may remain stable before decreasing on muted demand and transactions may increase in frequency contributing to price decreases in the first half of 2025.
- Price weakness in late 2023 was driven by overstocked consumers, stable supply volumes and high freights. Prices started increasing in 2024 Q2 but remained lower than the 2023 average. Slower stock drawdowns and reduced Chinese inventory has pushed sulphur prices higher.
- Sulphur supply increases are dominated by growth in the Middle East, which will allow new production to reach the traded market rapidly. High phosphate prices in 2024 H_2 has maintained support for sulphur prices.
- Demand growth is expected to exceed the supply growth rate, pushing the market balance to deficit and increasing prices. The requirement for stock drawdown will increase the marginal cost of supply and provide support to sulphur prices.
- A programme of intentional stock drawdown in Saudi Arabia and Kazakhstan, along with high Chinese port stocks, will limit how fast the market can rebalance and move to deficit. However, a return to tighter market conditions and higher sulphur prices forms the base case forecast.

SULPHURIC ACID

- The current global sulphuric acid prices are being kept largely stable by the presence of subdued demand which has offset the tight availability in regions like Northwest Europe. However, both demand and availability are set to return to more normal levels later into Q1.
- Sulphuric acid prices are expected to gradually decline in the first quarter of 2025. Subdued demand is currently offsetting tight availability. This has kept the prices largely unchanged for most of the past year. However, demand is anticipated to pick up in the initial two months of 2025, possibly coinciding with the return of supply.
- Prices for Northwest Europe have held for three weeks and could continue to do so as supply is not expected to return until later in Q1. However, a lower price could stimulate market activity, according to some market players. According to CRU's latest short-term forecast, prices are expected to average $105/t in February and $95/t by March.
- In India, Adani Enterprises is on track to commence operations at its 500,000 t/a copper smelter by the end of Q1. It is expected that the copper smelter will produce around 1.5 million t/a of sulphuric acid. Similarly, Paradeep Phosphates Ltd (PPL) is scheduled to commission its 4,000 t/day sulphuric acid plant by the end of Q2. Market participants remain cautious due to an anticipated influx of domestic sulphuric acid. In the short term, limited activity is expected to persist until later in Q1 ,after which an uptick in activity is expected. Flat demand in Chile is expected to last at least until February.

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Sulphur Industry News

GERMANY

New sulphur remelter for Duisburg

PHOTO: AGLOBIS

The existing Aglobis terminal at Duisburg.

Sulphur and sulphuric acid marketer Aglobis has signed a memorandum of understanding with logistics services company Rhenus to develop a sulphur remelter plant at Rhenus's Terminal 4 in the river Rhine port of Duisburg, operated by Rhenus Port Logistics Rhein-Ruhr. Aglobis says that the development is a result of changing sulphur supply in Europe. Declining production from refineries and sour gas is leading to less liquid sulphur availability and greater imports of solid sulphur from overseas.

"Ensuring a stable and efficient supply of this crucial material is more important than ever," said Jan Joop Alberts CEO & Chairman Aglobis AG. "That's why Aglobis, a wholly owned subsidiary of Mitsui & Co., Ltd., is taking proactive steps to support the European industry's long-term needs for molten sulphur."

Aglobis aims to increase overseas imports of sulphur, in order to address the growing demand of European chemical industries. The sulphur remelter will be operated by Aglobis and have an output of approximately 400,000 t/a, with the aim of starting the operation in 2027. Rhenus is set to support Aglobis by providing onsite sulphur warehousing and handling services at the Duisburg terminal. Aglobis is currently assessing logistics options for other stages of the supply chain, including seaport handling in Belgium and the Netherlands, as well as transportation to Duisburg via the River Rhine.

The complete supply chain will include the sourcing and shipping of solid sulphur in large quantities, transshipment to appropriately sized barges and inland waterway transport to Duisburg, remelting at the plant and distribution via low-emission transport to the industry locations in the region. Rhenus has reserved an area of circa 17,000 m^2 at its Terminal 4 in Duisburg.

"We are looking forward to starting this cooperation with Aglobis in order to provide industrial manufacturers in Duisburg and the Ruhr area with this critical raw material. As a traditional port logistics provider working with our industry customers for over a century, this project and the logistics services involved are not only part of our key competence, but also of significance for the future of this region," said Michael Petersmann, Managing Director of Rhenus Port Logistics Rhein-Ruhr. ■

MOROCCO

QatarEnergy signs sulphur supply deal with OCP

Nutricrops, a subsidiary of Morocco's OCP Group, has signed a deal with QatarEnergy for the supply of sulphur over the next decade. Over the 10 years beginning in 3Q 2024, QatarEnergy will supply up to 7.5 million tonnes of sulphur. Nutricrops says that the deal will play a crucial role in supporting its mission to provide sustainable and tailored plant nutrition solutions to farmers. The company produces a range of phosphate-based products designed to improve soil quality and optimise agricultural output. The agreement reflects the growing global demand for sustainable agricultural practices, with sulphur playing a vital role in soil management and nutrient balance. In the short term, OCP Nutricrops will continue sourcing sulphur from ADNOC in Abu Dhabi under a previous agreement that will remain in effect until early 2025.

Commenting on this occasion, Saad Sherida Al-Kaabi, Qatar's Minister of State for Energy Affairs, and president and CEO of QatarEnergy, said: "We are pleased to sign this agreement, solidifying our business relationship both with OCP Nutricrops and the Kingdom of Morocco. This agreement marks a significant step in advancing cooperation between our two companies and fostering mutual growth and value for both sides."

Qatar is one of the world's largest exporters of sulphur, with a total production capacity of around 3.4 million t/a.

ITALY

Stellantis and Zeta Energy to jointly develop lithium-sulphur batteries

Car manufacturer Stellantis and battery developer Zeta Energy have announced a joint development agreement aimed at advancing battery cell technology for electric vehicle applications. The partnership aims to develop lithium-sulphur electric vehicle batteries with gravimetric energy density while achieving a volumetric energy density comparable to today's lithium-ion technology. The companies say that this means potentially a significantly lighter battery pack with the same energy as contemporary lithium-ion batteries, enabling greater range, improved handling and enhanced performance. Additionally, the technology has the potential to improve fast-charging speed by up to 50%, making EV ownership even more convenient. Lithium-sulphur batteries are expected to cost less than half the price per kWh of current lithium-ion batteries.

"Our collaboration with Zeta Energy is another step in helping advance our electrification strategy as we work to deliver clean, safe and affordable vehicles," said Ned Curic, Stellantis Chief Engineering and Technology Officer. "Groundbreaking battery technologies like lithium-sulphur can support Stellantis' commitment to carbon neutrality by 2038 while ensuring our customers enjoy optimal range, performance and affordability."

"We are very excited to be working with Stellantis on this project," said Tom Pilette, CEO of Zeta Energy. "The combination of Zeta Energy's lithium-sulphur battery technology with Stellantis' unrivaled expertise in innovation, global manufacturing and distribution can dramatically improve the performance and cost profile of electric vehicles while increasing the supply chain resiliency for batteries and EVs."

The collaboration includes both pre-production development and planning for future production. Upon completion of the project, the batteries are targeted to power Stellantis electric vehicles by 2030. Using sulphur, a widely available and low cost component, reduces both production expenses and supply-chain risk.

UNITED ARAB EMIRATES

ADNOC awards design contract for Bab gas processing facilities

ADNOC Gas has awarded Worley Engineering the front-end engineering and design (FEED) contract for new gas processing facilities at Bab Gas Cap (BGC). The new facilities will boost ADNOC Gas' current processing capacity by 20% or over 1.8 billion scf/d with a final investment decision expected in 2026, ADNOC Gas said. The project's processing facilities will be designed to optimise production of natural gas liquids (NGL), condensate, sales gas, and sulphur, and supports ADNOC's broader gas growth strategy as it looks towards UAE gas self-sufficiency.

"Today is an important step forward for this project, which has the potential to substantially increase our gas processing capacity, unlock additional revenue and strengthen ADNOC Gas' position as a global gas supplier," Dr Ahmed Alebri, CEO of ADNOC Gas, said in a statement. "This ambitious project will deploy state-of-the-art gas processing technologies and make an important contribution to the UAE's gas self-sufficiency efforts. We are pleased to see the BGC project reach this stage," he added.

WORLD

OPEC+ postpones oil supply relaxation

At its December meeting, OPEC+; the Organisation of Petroleum Exporting Countries together with Russia, Mexico, Kazakhstan and some other nations, agreed to once again defer planned increases in oil output, this time until at least April 2025. Some further cuts, amounting to 2 million bbl/d, which were introduced two years ago and scheduled to end in December 2025, were also extended to the end of 2026, as was an additional 3.85 million bbl/d of output cuts from the 'V8' countries. Output increases of 2.2 million bbl/d will now begin in April 2025 at 140,000 barrels per month. A slowdown in global demand and rising supply from other sources have accounted for the continuing supply restrictions. Oil prices have been relatively stable at around $70-80/bbl for most of the past year.

The projects design scope includes the development of gas processing and conditioning units, acid gas recovery units, dehydration units, sulphur recovery units, NGL recovery units, and CO_2 capture facilities, ADNOC Gas said. It also includes the construction of injection facilities and associated utilities, along with the design and routing of new product pipelines for the efficient transfer of liquid sulphur to the Habshan Sulphur Granulation Plant. The facilities will receive hydrocarbons from an innovative development of the Bab field.

AZERBAIJAN

Baker Hughes partners with SOCAR to reduce flaring

Baker Hughes has signed a contract with SOCAR for an integrated gas recovery and hydrogen sulphide (H_2S) removal system that will significantly reduce downstream flaring at SOCAR's Heydar Aliyev Oil Refinery in Baku, Azerbaijan. The project is expected to recover flare gas equivalent up to 7 million Nm^3 of methane per year, and further reduce CO_2 emissions by up to 11,000 tons per year.

According to the contract signed at COP 29 in Baku, Baker Hughes will integrate its innovative gas recovery and H_2S removal system into the refinery's existing infrastructure to help abate methane and sulphur, two of the most potent greenhouse gas emissions, and remove hazardous H_2S from the site. The system will also enable SOCAR to use the recovered gas, which would have previously been flared, as fuel for the refinery. This will reduce overall fuel gas consumption and operating costs at the refinery, creating new opportunities for value enhancement and efficiency gains. Construction and commissioning is expected to take two years.

"We must reduce emissions by 45% this decade to put us on the right path to reach net zero by 2050. The industry has an imperative to act now, and we can do it with existing technology solutions that can be deployed today," said Baker Hughes Chairman and CEO Lorenzo Simonelli. "This award is a testament to our companies' shared commitment to act on emissions abatement and represents another significant milestone in Baker Hughes' journey to help customers drive more sustainable and efficient operations."

President of SOCAR, Rovshan Najaf said: "Our collaboration with Baker Hughes reflects SOCAR's commitment to advancing sustainable operations and reducing emissions across our sites. By launching this project, we are making a tangible impact on emissions abatement and setting a benchmark for environmental responsibility. This initiative aligns with our vision for a cleaner, more efficient energy future, supporting our commitment to climate goals."

PHILIPPINES

Philippines introduces 0.5% bunker fuel sulphur cap

The Maritime Industry Authority (MARINA) of the Philippines is implementing a 0.50% sulphur cap for bunker fuel consumed by the country's domestic shipping industry effective 1 January 2025, it said. MARINA Advisory No. 2024-35, published on 22 October 2024, provided supplemental guidelines on the implementation, monitoring and enforcement of a 0.50% sulphur limit on fuel oil for all Philippine registered ships in compliance to Annex VI of MARPOL. Ships which are already using distillates (MGO, MDO, IDO) or blends may shift to fuel oil with 0.50% wt sulphur content and are required to accomplish a ship-specific implementation plan (SIP). Domestic shipping firms may extend the compliance deadline based on the SIP timelines as verified by MARINA, but not to exceed five years. ■

Sulphuric Acid News

KAZAKHSTAN

Major acid plant will be part of new fertilizer complex

EuroChem's local subsidiary EuroChem Karatau has set the onstream date for its new fertilizer complex in Kazakhstan's Zhambyl region as February 2027, following a two year construction period. Construction is scheduled to begin in March 2025. The fertilizer complex will include an 800,000 t/a sulphuric acid plant, a 260,000 t/a potassium sulphate (aka SoP or sulphate of potash) plant, a 200,000 t/a calcium hydrogen phosphate plant, and a 130,000 t/a calcium chloride facility. The plant is expected to be launched in two stages. The first stage, the SoP Plant, should be commissioned at the end of 2025, while the second phase will be launched in 2027.

About half of the 800,000 t/a of sulphuric acid will be supplied to Kazatomprom for solvent extraction of uranium. The fertilizer plant will use locally-produced natural gas for its production process. According to the CEO of EuroChem Karatau Igor Georgiadi, the facility will need 130 million m3 of gas annually if it operates at full capacity. The plant will be built 14 km southwest of Zhanatas, in the Sarysu district of Zhambyl region. Potassium chloride (218,400 t/a), limestone (230,000 t/a) and solid sulphur (275,000 t/a) will be sourced from third-party producers.

CANADA

First Phosphate to license Prayon phosphoric acid technology

First Phosphate Corp. has signed a technology license agreement with Prayon for the technology to produce merchant grade phosphoric acid from igneous apatite phosphate rock as well as high-purity gypsum. Prayon will grant First Phosphate a license to use its technology to design, build, operate and maintain, within Canada, a merchant grade phosphoric acid plant with a capacity of 600 t/d (P_2O_5 terms). First Phosphate has also selected Ballestra SpA to fulfill the service agreement for the engineering services portion (FEED and EPC/EPCM) for the project. First Phosphate's relationship with Norfalco, a division of Glencore Canada remains in place for secure supply of sulphuric acid for the future phosphoric acid facility.

"With these technology, engineering and sulfuric acid supply agreements in place, First Phosphate will have the ability to implement a process to convert approximately 500,000 t/a of igneous apatite originating from its future mining operations into upwards of 190,000 t/a of value-added phosphoric acid," said Company CEO, John Passalacqua.

"Through the sale of this license, Prayon gives First Phosphate access to a world-renowned technology and highlights its commitment to transforming a critical, strategic material into high-value-added products, while recycling by-products in a well-established circular economy," said Benoît Van Massenhove of Prayon SA.

First Phosphate is developing phosphate production for the manufacture of cathode active material for the lithium iron phosphate (LFP) battery industry. It plans to vertically integrate from mine source directly into the supply chains of major North American LFP battery producers that require battery grade LFP cathode active material emanating from a consistent and secure supply source.

SAUDI ARABIA

Saudi Arabia agrees $9 billion of mining deals

Saudi Arabia has announced nine mining and metal projects worth more than $9.3 billion, in line with government policy to diversify the economy and reduce reliance on fossil fuels. India's Vedanta has agreed to invest $2 billion to build a 400,000 t/a copper smelter and refinery plus a 300,000 t/a copper rod plant at Ras Al-Khair. The project will eventually ensure domestic self-sufficiency in copper production, according to the company. A 125,000 t/a copper rod mill will form part of the first stage of the development. All necessary approvals are in place, land acquired, and equipment and technology ordered, work is likely to begin shortly. Commercial production is expected to start in Q1 2027.

Chris Griffith, CEO of Vedanta Base Metals, said: "This project ties in very nicely, both with our own ambitions as Vedanta to grow in India and the Middle East, and with Saudi Arabia's industrial strategy to secure a copper supply chain."

China's Zijin Mining Group has committed to spending $1.6 billion to build a 100,000 t/a zinc smelter with the capacity to produce 200,000 t/a of sulphuric acid as a first phase. In a second phase a lithium carbonate extraction plant capable of producing 60,000 t/a of battery-grade lithium carbonate will be built, and in a third a copper refinery with potential output of 200,000 t/a of copper cathode and around 50,000 t/a of electrolytic foil.

Hastings Technology Metals of Australia has agreed to build rare earth processing plants in several phases for a total investment of up to $1.9 billion. The rare earth elements will be sourced from mines in Saudi Arabia.

Ma'aden has also awarded three contracts worth $920 million for its third phosphate fertilizer plant. The contracts include a $330 million agreement for general construction at Ras Al-Khair with the China National Chemical Engineering Corporation. A second contract, worth $360 million, was awarded to Sinopec's subsidiary for construction at Wa'ad Al-Shamal. Tekfen Construction secured the third contract for $233 million, with work at Wa'ad Al-Shamal included.

The announced investments align with Saudi Arabia's Vision 2030 – an ambitious plan to unlock $2.5 trillion in untapped mineral resources, including phosphate, copper, gold, and bauxite. It also aims to boost the mining sector's GDP contribution from $17 billion to $64 billion by the end of the decade. Currently, Saudi Arabia imports most of its copper to meet domestic demand, estimated at 365,000 t/a. This figure is projected to more than double by 2035.

AUSTRALIA

Sulphuric acid from pyrite tailings

Cobalt Blue Holdings has signed a memorandum of understanding to work with Mount Isa City Council in Northwest Queensland to assess solutions to the region's looming sulphuric acid supply shortage. Cobalt Blue will provide advice to the city on the requirements, challenges and barriers to a potential pyrite tailings reprocessing operation to produce sulphuric acid. This solution would potentially involve Cobalt Blue's ReMine+ patented minerals processing technology for the economic recovery of elemental sulphur and metals from pyrite deposits. Mount Isa is facing a shortfall of sulphuric acid due to the announced closure of the Glencore Mount Isa copper smelter in 2030.

Mount Isa Mayor Peta MacRae said: "this MoU with Cobalt Blue aligns with the council's commitment to a sustainable future for our industries, economy, environment and communities. It demonstrates our commitment to developing a locally-made solution to the looming sulphuric acid shortage that will otherwise have a huge negative impact on many of our largest industries. Mount Isa already has expertise in the production of sulphuric acid and has existing air monitoring systems in place to ensure community safety. Cobalt Blue's technology solves the issue of dealing with old tailings as well as reinforcing the economics of the supply chain for the whole of Australia. It also reduces the sovereign risk of relying on international sulphuric acid supply."

ReMine+ technology has been demonstrated at Cobalt Blue's Broken Hill demonstration facility, producing 10 tonnes of high-purity elemental sulphur from pyrite feedstocks via a commercial rotary kiln typically operating at 150-300 kg/h throughput capacity. It can recover valuable metals (including gold, cobalt, nickel, and copper) while simultaneously generating elemental sulphur or sulphuric acid. However, it has yet to be deployed on the kind of scale that would be required at Mount Isa.

INDONESIA

GEM and Vale in HPAL project

Chinese battery metal producer GEM has signed a project investment cooperation framework agreement with PT Vale Indonesia, the Indonesian unit of the Brazilian mining company Vale, to establish a high-pressure acid leach (HPAL) facility in the central Sulawesi province of Indonesia. The $1.4 billion facility will have the capacity to produce 60,000 t/a of nickel as a mixed hydroxide precipitate (MHP) for use in electric vehicle batteries.

As announced by Indonesian president Prabowo Subianto at an Indo-Chinese business forum, the investment also includes a $40 million research and development centre for knowledge transfer and local talent development, $30 million for an environmental, social and governance (ESG) compound with green landscaping, employee dormitories, domestic water supply and waste treatment, and $10 million for community development and public facilities.

Speaking at the same event, PT Vale CEO Febriany Eddy said: "This project is not just about producing MHP – it is about creating a model for responsible resource management that benefits Indonesia and the world. By integrating advanced technology, eco-friendly practices and a commitment to net-zero production, we are shaping a future where Indonesia is recognised as a leader in sustainable industrial development."

GEM chairman Professor Xu Kaihua said: "The HPAL Project represents a vital collaboration that merges our expertise in sustainable materials with Indonesia's rich resources. This project is not only a step toward a cleaner future but a foundation for deeper cross-border cooperation in green innovation. GEM will unite with Vale to apply zero-carbon emission, intelligence, high- technology and ESG concepts in designing this project and create a world-class green demonstration park with green nickel resources, local technologies and local talents, to smelt laterite nickel ore directly into battery material."

PT Vale Indonesia already has two HPAL plants under construction in Pomalaa and Sorowako on Sulawesi island in collaboration with Zhejiang Huayou Cobalt.

CHINA

Nornickel to send concentrate, acid for processing

Russian nickel-copper producer Norilsk Nickel (Nornickel) has agreed to send copper concentrate and by-product sulphuric acid to China for processing and, in return, will receive technologies from Chinese partners to enable production of battery materials from Russia's lithium deposits, CEO Vladimir Potanin said in a broadcast interview. He described the arrangements as part of a new, four-year strategy for moderate growth. The plans are part of a strategic shift towards Asia after the company was shunned by Western equipment suppliers and selling into Western markets became more difficult after Russia invaded Ukraine in February 2022. Nornickel is not directly targeted by sanctions.

Nornickel is working with Russian nuclear power supplier Rosatom on a lithium project in the Murmansk region. The plan is to start construction of an open-pit mine at Kolmozerskoye in 2026 with completion in 2029 and production beginning the following year. Nornickel continues to invest in Russia by expanding smelting capacities in Norilsk and the Nadezhda metallurgical plant, among other projects. They are necessary to retain Russian government support, increase its tax base in the country and add 4,500 jobs by 2030, Potanin said.

In a separate statement, Nornickel said it expects to sell all of its metal production volumes next year, despite conditions remaining challenging and the nickel market forecast to be in surplus. The company gave no figures, but in October raised production guidance for this year to between 196,000-204,000 t/a for nickel and 337,000-357,000 t/a for copper, up from the previous ranges of 184,000-194,000 t/a and 334,000-354,000 t/a, following ahead-of-schedule completion of major repairs to the No.2 smelting furnace at Nadezhda.

Acid exports rose in 4Q 2024

According to customs data, China exported 256,200 tonnes of sulphuric acid in November 2024, up 34% month on month, although down 29% on a year on year basis. As of November, China's total sulphuric acid exports reached 2.16 million tonnes, a cumulative year on year decline of 12%. The top three destinations for Chinese acid in November were Chile, Saudi Arabia and India, with volumes of 126,400 tonnes, 62,100 tonnes, and 50,000 tonnes respectively.

Sumitomo Metal Mining (SMM) said that it believed that China's total sulphuric acid exports for 2024 are expected to have remained flat or slightly increased on 2023, suggesting that December's export volume would be another increase. Export business from major coastal acid plants has become an important means of balancing the domestic market, and the export operations of these key plants are also progressing steadily. As 2024 comes to an end, while domestic sulphuric acid capacity expands, downstream chemical industry demand has also slightly increased. However, the oversupply situation in the industry remains unchanged. Looking ahead to 2025, China's sulphuric acid capacity is expected to continue rising, but demand growth may lag behind supply growth. Increased competition in overseas markets adds to the uncertainty of the domestic sulphuric acid market, making the price trend of sulphuric acid in 2025 even more unpredictable.

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CHILE

Codelco charged over smelter pollution

Chile's environmental regulator SMA has filed a charge against state-owned Codelco, alleging emission violations at its Potrerillos copper smelter in the Atacama region of northern Chile. An audit showed the company had not implemented a monitoring system for sulphur dioxide emissions and other procedures in accordance with environmental standards for the plant, Reuters news agency reported. The SMA labelled the charge as serious, which could lead to a fine of around $4.1 million, and possible revocation of the environmental permit or closure. Codelco had ten days to submit a compliance plan, and 15 days to present a defence.

Glencore to test new leaching process

Glencore has signed a memorandum of understanding (MoU) with technology company Ceibo to deploy Ceibo's proprietary copper leaching technologies in Chile. The process has been validated after two years of testing at Glencore's Lomas Bayas mine and the company is moving toward scaling up the process to assess it as a way to extend mine life. Ceibo's leaching processes extract copper in all sulphides using existing leaching plants by catalysing ore oxidation through electrochemical reactions, resulting in higher recovery rates in shorter operational cycles, the company said.

Lomas Bayas' general manager Pablo Carvallo added: "Ceibo's ability to produce copper from sulphide-rich ores brings a huge value for assets like Lomas Bayas to sustain production while transitioning from oxides to sulphides."

Under the terms of the memorandum of understanding, Ceibo's technology will scale up with on-site testing through the Lomas Lab, a Glencore world-scale test site, and the company's research and development branch. This agreement opens a significant commercial avenue for Ceibo, demonstrating its unique approach with a major mining company and affirming the value that Ceibo's advanced leaching technologies bring to copper assets globally.

BRAZIL

Acid tanker spill after bridge collapse

A bridge connecting two states in Brazil's northern and north-eastern regions collapsed on Dec ember22 as vehicles were crossing, killing at least one person and spilling sulphuric acid into the Tocantins River. The National Department of Transport Infrastructure said the central span of the 533m bridge, linking the cities of Estreito in Maranhao state and Aguiarnopolis in Tocantins state, gave way in the afternoon. A tanker truck carrying the acid plunged into the water, officials said. According to the fire department, one person has been confirmed dead and another was rescued alive. Attempts by divers tor each submerged vehicles were complicated by leaking sulphuric acid from the tanker.


PHOTO: CODELCO

The Portrerillos smelter, Atacama, Chile

SOUTH KOREA

Korea Zinc completes smelter upgrade

Korea Zinc says that it has successfully completed the 'Onsen Smelter Rationalisation Project,' a key initiative undertaken throughout 2024 to strengthen the competitiveness of its Onsan Smelter. As a result, the company expects operating profits to exceed its original business targets for the year. Korea Zinc has implemented improvements in operational processes, enhanced energy efficiency, and strengthened cost competitiveness, to address issues with rising energy costs (electricity and coal), and falling treatment charges, which increased raw material expenses. The company says that Korea's domestic steel industry is struggling due to dumping by other major steelmakers, and the non-ferrous metals market faces numerous challenges with bleak prospects for 2025.

BANGLADESH

BADC signs DAP import agreement

The Bangladesh Agricultural Development Corporation (BADC), under the supervision of the Ministry of Agriculture, has signed an agreement with Banyan International Training Ltd, a Chinese company, to import 440,000 tonnes of diammonium phosphate (DAP) fertilizer for the year 2025. The agreement was signed on January 10th in Fuzhou, China by Mohammed Ruhul Amin Khan, Chairman of BADC, and Li Jin, General Manager of Banyan Group. BADC reports that the price of each tonne of fertilizer has been reduced by $2 compared to the previous rate, resulting in an estimated saving of approximately $900,000.

ALGERIA

Major new phosphate project

The Algerian Chinese Fertilizers Company (ACFC) has launched a $7 billion integrated phosphate project (PPI) in the country's Tebessa province. ACFC was formed in 2022 as a joint venture between Algerian firms Manal and Asmidal, a subsidiary of Algerian energy giant Sonatrach, and Chinese firms Wuhuan Engineering and Tian'An Chemical, a nitrogen and phosphate fertilizer producer. It was set up to develop and exploit the Bled El Hadba phosphate deposit at Djebel Onk, with the two Algerian firms owning 56% of ACFC and the two Chinese companies owning the remaining 44%.

The project incudes a large-scale phosphate rock mine with a capacity of 6 million t/a – approximately 2.5 times higher than Algeria's current national output – extracted from 2.2 billion tonnes of ore reserves. The scale of this deposit should guarantee a mine life of around 80 years.

The ACFC is also proposing to construct a state-of-the-art production and processing complex at Qued Kebrik, Energy, Capital & Power said, with 21 phosphate processing units also spread across Souk Ahras, Annaba and Skikda. The project could enter production as early as 2027, according to the current timetable, creating 12,000 construction-phase jobs and 30,000 direct and indirect jobs once operational. Existing phosphate producer SOMIPHOS is also planning a one million tonne capacity expansion at its Djebel Onk site. ■

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People

ICL has announced that **Raviv Zoller**, the company's president and CEO for the past seven years, is expected to leave the company in early 2025, following both the appointment of a replacement and a formal transition.

In a letter to the company's employees, Zoller wrote, "I feel great pride, mixed with sorrow, as I announce my expected retirement from the position as president and CEO of ICL. Over the past seven years at this amazing organization, I have come to know our employees who give their heart and soul to the company. Together, we have turned ICL into an outstanding employer, a company that strives for innovation, and a place where everyone can influence success. We have nurtured our internal and global partnerships, as we have dealt with significant external challenges. Regardless, we have focused on continuous learning and improvement and can be proud of the strength of the company, which functions as a well-oiled machine – innovative, very profitable, robust, and focused, which generates consistently strong cash flow.

"Since taking office, I have been involved in all strategic and long-term planning, including succession planning for my role, and I will be parting ways with an even stronger company than the one I joined seven years ago. I am leaving the board of directors with a talented and strong management team, a solid organizational structure, and a promising five-year plan. I expect the selection and transition processes will be quick and will be completed by the release of our annual financial statements."

"During Raviv's tenure, ICL has enjoyed unprecedented success across its key operations. The company's exceptional management team and employees – who have been the foundation of ICL's success for decades – have led significant disruption in the company's approach to innovation and sustainability. Under Raviv's leadership, the company has successfully executed against its strategy and significantly increased the profitability of its products," said ICL Chairman, Yoav Doppelt.

Eero Mäkinen (1886-1953), a pioneer of the Finnish mining industry and one of the key inventors of Flash Smelting, has been inducted into the National Mining Hall of Fame. The induction ceremony took place in Denver, Colorado on November 2, 2024. Mäkinen played an important role in the development of the modern mining industry in Finland. During his career, he made significant contributions to mining education, research and technology. Mäkinen led Outokumpu as the CEO for three decades, bringing the company to global recognition, and established institutions for mining and metallurgical engineers. Notably, Mäkinen contributed to the invention of flash smelting, an energy-efficient process for extracting metals like copper and nickel from concentrate. The groundbreaking technology was first implemented at Outokumpu in Harjavalta, Finland, and has since received the status of Best Available Technique by the EU; it has also been awarded ASM Historical Landmark status.

"Flash Smelting is one of the cleanest smelting technologies available, and Eero's legacy continues to shape the mining industry. As we speak, the same technology, but on a much larger scale, is being commissioned in Indonesia at the world's largest single-line copper smelter," said Jyrki Makkonen, Vice President, Smelting at Metso. "Metso and Outokumpu share a long history together, and we are pleased and honored that Eero and Flash Smelting will be featured in the National Mining Hall of Fame."

"We are extremely proud that our Eero Mäkinen has been so recognized for his contribution by the National Mining Hall of Fame. The same spirit of innovation is still evident at Outokumpu, as it was when Flash Smelting was first invented – not only was it totally new but an energy-efficient process to tackle the energy challenges in post-war Finland. Even though this technology is not part of our operations anymore, both innovation and energy efficiency continue to be embedded in our operations at Outokumpu today," says Jukka Sieppi, Vice President, Core Stainless Technology at Outokumpu. "Flash Smelting was the start of our technology division, which is today part of Metso, and we are proud of the shared history and continued cooperation." ■

Calendar 2025

FEBRUARY

5-7

SulGas Conference 2025, MUMBAI, India
Contact: Conference Communications Office, Three Ten Initiative Technologies LLP
Tel: +91 73308 75310
Email: admin@sulgasconference.com

24-27

75th Laurance Reid Annual Gas Conditioning Conference, NORMAN, Oklahoma, USA
Contact: Lily Martinez, Program Director
Tel: +1 405 325 4414
Email: lmartinez@ou.edu

MARCH

31 - APRIL 2

CRU Phosphates+Potash Expoconference, ORLANDO, Florida, USA
Contact: CRU Events
Tel: +44 (0) 20 7903 2444
Email: conferences@crugroup.com

APRIL

7-9

World Copper Summit, SANTIAGO, Chile
Contact: CRU Events
Tel: +44 (0) 20 7903 2444
Email: conferences@crugroup.com

8-10

TSI Sulphur World Symposium 2025, FLORENCE, Italy
Contact: The Sulphur Institute, Washington D.C., USA
Tel: +1 202 331 9660
Email: sulphur@sulphurinstitute.org

28 – MAY 2

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

JUNE

6-7

48th Annual International Phosphate Fertilizer & Sulfuric Acid Technology Conference, ST. PETERSBURG, Florida, USA
Contact: Michelle Navar, AIChE Central Florida Section
Email: vicechair@aiche-cf.org
Web: www.aiche-cf.org

Chinese phosphate exports

PHOTO: CYNTHIA LEE/ALAMY

Fertilizer loading at Lianyungang Port in Jiangsu province.

Although China remains the world's largest phosphate producer, it has been overtaken as the largest exporter by Morocco in recent years as domestic producers face continuing restrictions on exports.

China's huge domestic phosphate industry continues to set the pace for the global sulphur markets. In 2024, of a traded international sulphur market of around 36 million t/a, China was responsible for importing one quarter of that, and only Morocco is comparable in terms of import requirements. China consumes one third of all sulphuric acid produced worldwide, and its phosphate industry accounts for about half of that.

The Chinese phosphate industry grew rapidly during the first two decades of this century, as the country sought to replace its rapidly growing imports of ammonium phosphates (MAP/DAP) to feed increasingly intensive agriculture with domestic phosphate production. China has the world's second largest reserves of phosphate rock, and used ammonia produced from coal gasification to feed ammonium phosphate production. Overbuilding of capacity turned China into a large net exporter of phosphates, a position which it continues to maintain.

However, attempts to rein in domestic over-application of fertilizer and consequent environmental impacts, as well as increasing curbs on emissions from Chinese factories and tightening environmental legislation led to a fall in both domestic phosphate demand and production from around 2015.

Phosphate production

Chinese phosphate rock mining has been falling as costs of production rise. China actually became a net importer of phosphate rock in 2023, and this continued into 2024, when rock imports totalled around 2.9 million t/a. However, last year's imports look to be the peak as higher phosphate prices within China encourage more output from miners, and Chinese phosphate rock production capacity is expected to increase by 25 million t/a (product) from 2023-2029, a growth of 25% from its figure of 101 million t/a in 2023. Net import volumes are expected to fall from 2025 and end by around 2027-28. Domestic rock prices have remained elevated in China due to strong demand. The government has expressed its aim for food security on several occasions, with fertilizer and animal feed production accounting for 73% of China's rock consumption.

Higher phosphate prices have also driven greater domestic phosphate production in China in 2024.

China's January-November DAP/MAP production increased 11% year on year to roughly 27.94 million t/a (tonnes product) from 25.09 million t/a, according to government figures. January-November MAP production rose 15% year on year to 13.92 million t/a, while DAP output was up 8% at 14.02 million t/a. By comparison, China's full-year 2023 DAP/MAP production reached roughly 27.5 million t/a, itself a 9% increase from 25.3 million t/a in 2022.

Export restrictions

Domestic capacity rationalisation led to spikes in Chinese phosphate prices, which the government began to control via export restrictions. These became particularly acute during the covid-19 pandemic. Hubei province, where the outbreak began and was initially at its worst, is the heartland of the Chinese phosphate industry, with 28% of production capacity. Closures dropped the fertilizer industry utilisation rate by 30-40% during 2Q 2020. At the same time, demand held up relatively well, falling only 2.5% in 2020 compared to 2019, and China's ministry of agriculture mandated an increase in grain planting in 2021, including requiring rice farmers to plant two seasons of the crop, to ensure sufficient food supply.

The upshot was that China introduced a series of export restrictions on phosphates in order to keep domestic markets supplied and ease prices to farmers. In effect exporters have only been granted licenses to export for 6 months of the year over the past few years. Total Chinese exports of finished phosphates (MAP+DAP+TSP) fell from an average of 10 million t/a P_2O_5 in 2019-21 to 6.5 million t/a P_2O_5 in 2022, recovering

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somewhat to 7.9 million t/a P_2O_5 in 2023.

Last year, export restrictions were tight for the first quarter of 2024, and there were virtually no exports from January-March, when restrictions were eased again until October, when they were tightened again; restrictions have tended to follow this pattern, with almost no exports in Q1 and Q4, before loosening in Q2 and Q3, and very high availability at those times.

No new DAP/MAP export business from China has been reported in the past few weeks, as the country suspended phosphate export inspections and customs clearance from the start of December 2024 until further notice. The current market consensus expectation is that the suspension will, as previously, continue through 2025 Q1 to guarantee domestic supply and stabilise domestic prices for the 2025 spring application season. DAP/MAP producers who still have some remaining export quota allocation will likely exercise self-discipline by not applying for any fresh export inspections. Producers also hope that previously-signed contracts will be executed on time, though there is currently no guarantee this will be possible.

Overall Chinese DAP/MAP/TSP exports are expected to have been 6.9 million t/a P_2O_5 for 2024, and will stabilise at a total figure of 7.0-7.1 million t/a for the next few years (see Figure 1)

India

Chinese exports to India – one of the largest importers of phosphate – have dropped because of tensions over the two countries' disputed border along the Himalayan mountains. Frictions over the border led to clashes between Chinese and Indian troops in 2020-21, and tensions continued into 2022-23. There have recently been signs of an easing as China and India agreed in October 2024 to resume joint patrols, but the Chinese government has placed pressure on Chinese fertilizer companies to reduce exports to India. DAP exports in 2024 Q1–Q3 dropped to 622,000 tonnes, a 71% year on year decrease, further tightening Indian availability. India in turn has moved towards greater imports of triple superphosphate (TSP) to make up for the shortfall.

There are no signs of a quick resolution to this issue, and exports between China and India will probably continue to be supressed into 2025. With lower DAP exports, this could see China switch a little more towards MAP for its overseas sales in 2025. Overall, CRU expects full-year Chinese DAP exports to fall from 4.2 million t/a in 2024 to 4.0 million t/a in 2025, while full-year MAP exports rise from 1.8 million t/a to 2.1 million t/a, barring a political resolution to the issues and a resumption of DAP exports.

Phosphoric acid

The other wrinkle in the Chinese export picture at present is an increase in merchant grade phosphoric acid (MGA) exports. Exports began around 2021 and have increased year on year. In 2024, Chinese MGA exports were expected to have reached 230,000 t/a P_2O_5, possibly as a way of Chinese phosphate producers circumventing restrictions on exports of processed phosphates. Chinese MGA exports were mostly destined for Bangladesh and Pakistan.

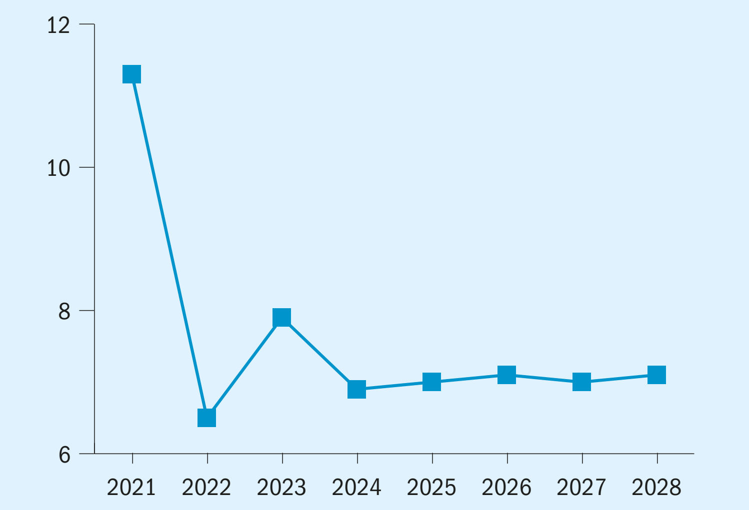
Looking forward

Chinese fertilizer consumption continues to be on a long term slowly declining trend as farmers move to more efficient use of nutrient. The current Chinese MAP/DAP capacity rationalisation is also drawing to a close, and there is some new capacity to come onstream over the next few years. However, the new government directive to prioritise domestic food security and fertilizer means that China's seasonal phosphate export restrictions are likely to continue on an annual basis, keeping exports to around 7 million t/a P_2O_5 of processed phosphates, with a possible small boost due to phosphoric acid exports.

The global phosphate market has enjoyed a run of higher prices of late, much of it due to Chinese export restrictions which have taken up to one third of Chinese MAP/DAP exports off the market. However, new capacity is continuing to come onstream in Morocco and Saudi Arabia, and this will alleviate prices in the longer term.

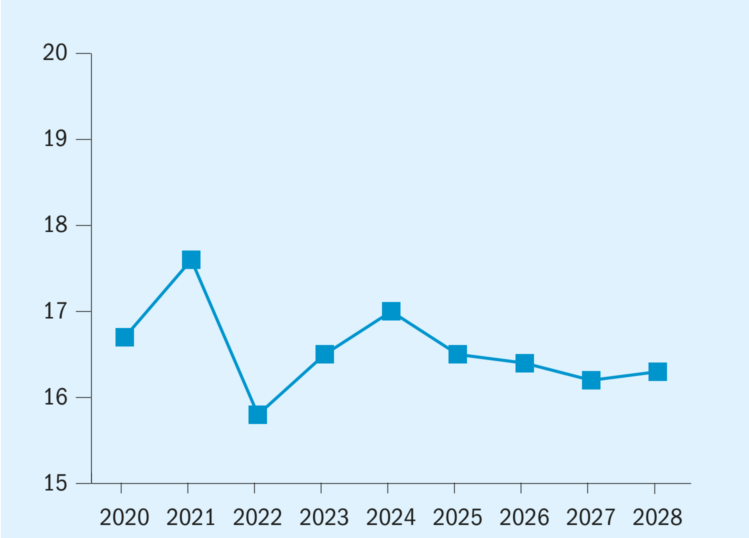
The impact on sulphur markets is likely to be a gradual decline in Chinese imports. Overall Chinese phosphoric acid production, as show in Figure 2, has declined slightly due to the overall reduction in phosphate output, and is forecast to stagnate over the next few years. Set against increased domestic production of sulphur from refineries and sour gas processing, the implication is a continuing fall in Chinese sulphur imports, from an estimated 9.7 million t/a in 2024 to around 6.2 million t/a by 2028. ■

Fig. 1: **Chinese finished phosphate exports (MAP, DAP and TSP), million t/a P_2O_5**



Source: CRU

Fig. 2: **Chinese phosphoric acid production, million t/a P_2O_5**



Source: CRU

Sulphur in central Asia

The Caspian Sea region is home to extensive sour gas reserves which produce large volumes of sulphur. Exports are difficult, but the Kazakh uranium industry is consuming an increasing amount.

The Caspian Sea region is one of the key supply centres for the world sulphur industry, mostly based on sour gas processing in the north Caspian region, but in the wider central Asian area there is also gas processing in Turkmenistan, Uzbekistan, and potentially also Iran. Oil and gas exploitation in the region has a long history, dating back to the 1920s when the first oil wells were drilled around Baku in what was then the Soviet Union, and sour gas processing likewise dates back almost 60 years to the opening of the Orenburg gas processing plant in southern Russia.

Total sulphur production in the CIS as a whole is about 11.7 million t/a, or around 17% of global sulphur production, most of it coming from central Asia, and last year sulphur exports from the region jumped to 7.0 million t/a due to extensive stock drawdowns, representing 20% of all traded sulphur.

Domestic consumption in the region is relatively low, with Russia's phosphate industry representing most of the region's sulphur consumption, and likewise Kazakhstan's highly significant uranium mining industry is consuming increasing volumes of sulphur. But sulphur exports from the region must often trace a long and tortuous route to reach a port, making logistics challenging and favouring acid gas reinjection in many projects.

Russia

Most of the sulphur in Russia comes from two large Soviet-era sour gas processing facilities operated by state gas major Gazprom via two subsidiaries, Gazprom dobycha Orenburg and Gazprom dobycha Astrakhan. Orenburg is a large oil and gas processing complex which processes gas from local oil and gas fields as well as very sour (up to 13% H_2S) gas from the Karachaganak gas field which lies across the border in Kazakhstan. Sulphur output at Orenburg was around 1 million t/a (1.07 million t/a in 2021), but this dropped to 0.89 million t/a in 2022 and 0.88 million t/a in 2023, and the full year figure for 2024 is expected to have declined further to around 0.84 million t/a.

The Astrakhan facility processes gas from the Krasnoyarsky gas and condensate field, where gas is highly sour; up to 31% H2S. This means that Orenburg actually processes more gas, the Astrakhan gas plant is the largest producer of sulphur in Russia. In its heyday output was around 4.5 million t/a, but more recently output has declined, running at 3.34 million t/a in 2021, 3.56 million t/a in 2022, and 3.30 million t/a in 2023. Full year figures for 2024 are anticipated to be around 3.25 million t/a.

These two hubs between them represent about 80% of Russia's sulphur production. The rest mainly comes from oil refineries. Total Russian sulphur production has been in long term decline, and fell from 6.3 million t/a in 2020 to an estimated 5.2 million t/a in 2024. But exports have been dropping faster still. Prior to covid they ran at around 4-5 million t/a, both via rail and barge eastwards to China as well as westwards to the Baltic Sea and Black Sea ports. Exports dropped from 3.3 million t/a in 2020 to 1.8 million tonnes in 2021, and down to 1.0 million t/a in 2022 and 2023. Some stock reduction in 2024 means that Russian sulphur exports are expected to be slightly up, at around 1.06 million tonnes, but thereafter exports are forecast to decline further. A combination of sanctions, stock building and rising domestic demand may reduce Russian sulphur exports to only 500-600,000 t/a over the next few years. Demand has mainly come from increased phosphate production, itself down to rapidly increasing domestic phosphate demand as agriculture expands, meaning that Russian phosphate exports are actually stagnant even as production grows. Russia is currently near its phosphoric acid production capacity.

Kazakhstan

While Kazakhstan's gas originally mainly fed the Orenburg gas plant as mentioned above, in the 1980s and 90s, the discovery of large onshore and offshore oil and gas fields in and around the Caspian Sea led to major domestic developments there, at Karachaganak, Tengiz, and finally Kashagan.

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PHOTO: KAZMUNAIGAZ

The Kashagan gas processing plant, Kazakhstan

The onshore Karachaganak field, near the Russian border, began producing oil in 1984, and currently represents around 30% of Kazakhstan's gas production, via associated gas from the oil wells. It is operated by the Karachaganak Petroleum Operating (KPO) consortium, with partnership from ChevronTexaco (18%), Agip and BG (29.25% each), Lukoil (13.5%) and KazMunaiGaz (10%). About 50% of the gas produced is reinjected to maintain pressure or used as fuel gas. Gas from Karachaganak is piped across the border to the Orenburg gas plant in Russia for processing and sulphur from the gas thus forms part of Russia's output.

Tengiz was developed in the 1990s and 2000s, by the Tengizchevroil (TCO) joint venture, formed between ChevronTexaco and the Republic of Kazakhstan, with the current shareholding being Chevron 50%, ExxonMobil 25%, KazMunaiGaz 20%, and Lukoil 5%. Tengiz is the largest sulphur generating enterprise in Kazakhstan, and produced 2.7 million t/a of sulphur in 2021, 2.65 million t/a in 2022, and 2.4 million t/a in 2023. The completion of the Wellhead Management Project in 2024 has lifted output slightly, and full year production is expected to be 2.65 million tonnes in 2024. Tengiz also has a Future Growth Project which will further lift oil output, and which is due for completion in 2025, but it will reinject all of the additional associated gas to maintain reservoir pressure.

TCO has had a running battle with the Kazakh government over sulphur storage. In the 2000s most of the sulphur was poured to block, but complains over fugitive dust led to the stockpile – which reached 9 million tonnes in 2006 - gradually being melted down and sold off.

The other major project in Kazakhstan is the huge offshore Kashagan oil and condensate field in the north Caspian Sea, run by the North Caspian Operating Company (NCOC), which includes ExxonMobil, Eni, Shell, Total and KazMunaiGas (KMG), each with a 16.8% stake, as well as Japan's Inpex with 7.56%, and the China National Petroleum Corp (CNPC). Kashagan has been a large and complex development, with technical factors complicating the project including high concentrations of H_2S in the oil and associated gas (ca 17%). Corrosion caused by H_2S meeting water in the pipelines led to it being shut down for repairs until 2016. About half of the associated sour gas is reinjected into the wells to maintain pressure, but the rest is processed onshore at the Bolashak gas sweetening plant. Kashagan produced 1.34 million t/a

Table 1: **Sulphur production, consumption and exports, CIS countries, 2024 (million t/a)**

	Production	Consumption	Exports	Implied stock build
Azerbaijan	0.0	0.0	0.0	0.0
Belarus	0.2	0.2	0.0	0.0
Kazakhstan	4.3	0.6	4.9	-1.2
Russia	5.2	4.2	1.1	-0.1
Turkmenistan	1.5	0.1	1.0	+0.4
Uzbekistan	0.6	0.3	0.1	+0.1
Total	**11.7**	**5.5**	**7.0**	**-0.8**

Source: CRU

of sulphur in 2021, 1.0 million t/a in 2022, and 1.36 million t/a of sulphur in 2023. Output for 2024 is expected to be around 1.4 million t/a.

Similar to the situation in Russia, the Tengiz and Kashagan sour gas plants collectively represent more than 90% of overall Kazakh sulphur production, which was 4.0 million t/a of sulphur in 2023, and an estimated 4.3 million t/a in 2024. The Kazakh government has been encouraging domestic use of the sulphur, via the country's large uranium mining industry. The uranium is extracted via sulphuric acid leaching, and the relatively high pH of the rocks means that large volumes of acid are needed. In 2023 uranium mining consumed 210,000 tonnes of sulphur. Phosphate processing represented another 160,000 t/a. Overall consumption runs at about 600,000 t/a, leaving a surplus of 3.7 million t/a of sulphur, meaning that Kazakh exports have overtaken Russia's to become the largest source in the region.

Strict regulations on storage of sulphur means that almost all of this is exported, and recently the producers have also been running down stockpiles, leading to a spike in Kazakh sulphur exports in 2024 even after reaching a historical high in 2023. Kazakhstan sulphur exports totalled 4.02 million t/a for the year to Oct 2024, up 35% year on year. Morocco has been the main destination, accounting for 73% of total sales, followed by other African countries (12%). The export surge has been driven by a stock drawdown. Kazakhstan started a stock drawdown programme in 2023 with crushed lump sulphur sales. This volume flow has increased in 2024 which, along with a rise in production, has pushed exports to record levels. It is estimated that an additional 1.2 million tonnes of stockpiled sulphur has been sold during 2024. The sale of inventory is expected to end in 2025, allowing exports to fall back to typical levels of around 3.5 million t/a from 2026 onwards. Exports are mainly via rail across Russia to the port of Ust-Luga near St Petersburg.

Turkmenistan

Turkmenistan, south of Kazakhstan, also borders the Caspian Sea. It is a relatively modest holder of oil reserves, and produces only around 220,000 bbl/d, mostly for domestic use. However, it is the world's fourth largest holder of natural gas reserves, after Russia, Iran and Qatar. With relatively low levels of gas demand, development of natural gas production for export has been seen as a way of monetising those reserves, but disputes with Russia over pipeline access slowed development in the 1990s and 2000s. Gas production has been increasing rapidly hover the past two decades, however, on the back of Chinese investment.

About half of Turkmenistan's gas comes from a series of fields that make up the Galkynysh reservoir, including South Yolotan, Osman, Minara and Yashlar. Production from the field began in 2013, and amounts to around 30 bcm per year, with a significant (about 6%) content of H_2S. The Galkynysh (formerly South Yolotan) gas processing plant has the capacity to produce 1.8 million t/a of sulphur. Production in 2022 and 2023 was about 1.2 million t/a, but this increased last year to about 1.54 million t/a, representing essentially all of Turkmenistan's sulphur output. Further expansions are expected to take sulphur production to 2.1 million t/a by 2028.

Around 120,000 t/a of sulphur are consumed in Turkmenistan for industrial uses, but again most of the sulphur must be stored or exported. Turkmen exports of sulphur currently run at around 1.0 million t/a, but are expected to rise towards 2 million t/a over the remainder of the decade.

Uzbekistan

Uzbekistan, south and east of Kazakhstan, is a relatively minor oil and gas player. Its oil reserves are comparable to Turkmenistan, but its gas reserves are much smaller. They are however, sour, and so processing of gas and condensate from the Kandym, Kuvachi-Alat, Akkum, Parsanal, Khoji and West Khoji is processed at the Kandym sour gas plant in Uzbekistan, which began operations in April 2018. Uzbekistan produces about 550,000 t/a of sulphur, and exports around 300,000 t/a.

Export issues

Sulphur exports from central Asia are problematic because of the immense distances involved. The port of Ust-Luga on Russia's Baltic cost is 2,300 km from Orenburg, and further still (3,000 km) from Tengiz. River and canal travel is impossible during winter as waterways freeze over, so much of the sulphur must travel by rail, taking weeks and placing a major logistical burden upon exports. This has encouraged the use of gas reinjection in region for acid gases, though these place their own burden in terms of cost of acid-resistant piping and the potential for leaks which can shut down processing facilities for months. For this reason, sulphur prices need to be high enough to justify exports rather than stockpiling (although Kazakhstan has its own issues with sulphur stockpiles and a government that has tried to monetise them via lawsuits against producers).

Sulphur prices are presently on their way up again after a relatively low period during 2022-24, and this has tempted additional volumes of sulphur onto the market from central Asia. Sulphur supply from the CIS region is expected to have increased in 2024 for the first time since 2019, mainly due to increased utilisation at existing facilities in Kazakhstan and Turkmenistan and stock drawdowns in Russia and Kazakhstan. From 2026, exports from the CIS region are expected to rebound as global demand will encourage these volumes to enter the market, with Turkmenistan leading trade growth due to expansions at its sour gas processing facilities. ■

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The rapid growth of nickel sulphate

Nickel sulphate is an intermediate step in the production of materials for batteries, and is seeing rapid demand growth as the auto industry moves towards electric power trains.

PHOTO: HUAYUE

Huayue New Energy Technology's HPAL plant, Sulawesi, Indonesia.

The sixth most abundant element on earth, nickel is a key raw material for many applications, but has historically mainly been used in the production of stainless steel, as well as various alloys, other steels and plating applications. But its use in various battery chemistries have propelled it into the limelight in recent years. Nickel metal hydride (NiMH) batteries have long been the preferred power train for hybrid electric vehicles. Two of the most commonly used types of batteries, nickel cobalt aluminium (NCA) and nickel manganese cobalt (NMC) use 80% and 60-90% nickel respectively. Most lithium ion batteries also now rely on nickel lithium nickel manganese cobalt oxide (Li-NMC). The nickel in these batteries is present in the form of nickel sulphate hexahydrate crystals, NiSO4.(H2O)6, often a vivid turquoise colour, as shown on our front cover. While there are non-nickel battery technologies which also have wide uptake, such as lithium iron phosphate (LFP), nickel is likely to be present in about 50% of batteries used in vehicles and stationary power applications by 2030, and the battery share of the nickel market will rise from around 16% in 2022 to 28% by 2030.

Conversion processes

Nickel ores broadly group into two types; laterites (ca 60%), which are oxides found close to the surface, mostly in tropical areas, and sulphides (ca 40%), which are generally deeper and often in remote areas. Laterites can usually be recovered by open cast mining, which makes them cheaper to extract, but they are generally lower grade (~1.4% Ni compared to 2.8% for sulphides). Laterites include saprolites, which are higher in magnesium, and limonites, which are higher in iron. The high cost of underground mining compared to open cast means that laterites have become the preferred source of nickel, especially for new projects, and they represent 70% of nickel production.

Historically, laterites have generally been heat treated, at lower temperatures to produce lower grade (4-15% Ni) 'nickel pig iron' (NPI), or at higher temperatures to produce higher grade (20-40% Ni) ferronickel, both of which are used in steelmaking – NPI generally for lower grade steels. Sulphide ores, meanwhile, are processed using a traditional flotation, smelting and refining processing route. The concentrate generated by flotation is smelted to form a mixed nickel-iron sulphide known as a matte, which contains 30-60% Ni. The matte is passed through a rotating converter which converts the iron to an oxide and uses a silica flux to remove it, leaving a nickel sulphide matte. Final conversion

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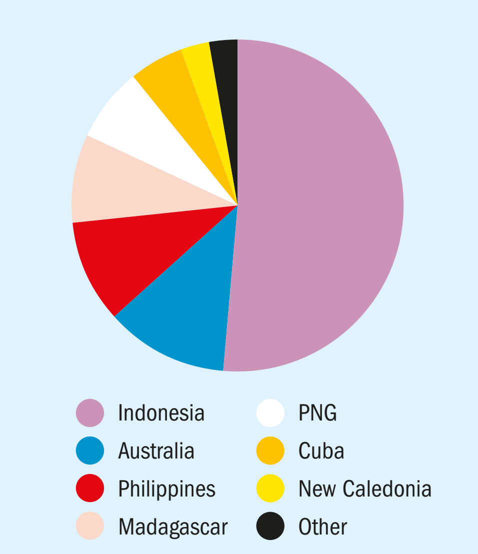
Fig. 1: **Sulphuric acid consumption for nickel production, 2024**



Source: CRU **Total: 15.1 million t/a**

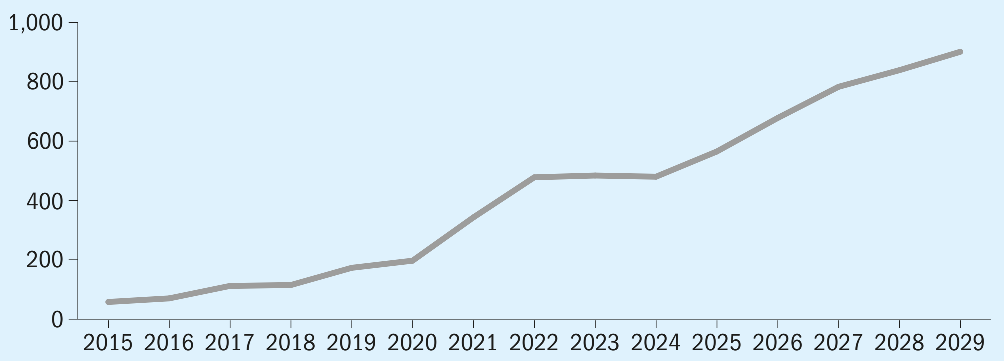
uses leaching or electrorefining to produce high purity end products such as nickel cathode, briquettes or nickel sulphate, depending on the finishing process used. Nickel sulphide ores can also be treated using a biological leach process, leading to a mixed sulphide precipitate.

A growing (ca 25%) proportion of nickel is also recovered from other nickel products, including spent batteries, generally via a pyrometallurgical process, with stainless steel the final destination. But growing demands for higher grade ('Class 1') nickel for battery use have required the development of bridging technologies from laterite to high grade nickel products. The most prominent of these is high pressure acid leaching (HPAL), which uses sulphuric acid at high temperatures and pressures to convert limonite and similar ores to a mixed hydroxide precipitate (MHP) or mixed sulphide precipitate (MSP), which then require a further refining step using sulphuric acid to produce nickel sulphate and/or ammonium sulphate. An alternative is heap leaching, which occurs at atmospheric pressure, but which takes more acid and much longer time to extract the nickel. Nickel pig iron can also be smelted to produce a nickel matte, followed by solvent extraction and purification to produce nickel sulphate, though this is an energy intensive process. Other processes for conversion are under development, including oxygen side blowing (OSBF) to produce matte from laterite ore at a lower operating cost compared to the NPI to matte conversion via rotary kiln electric furnace (RKEF). Atmospheric leaching processes to sulphate conversion include direct nickel (DNi) and pressure oxidation (POX). DNi permits leaching of all laterite ore types, while POX uses concentrate beneficiated from sulphide ores as the feedstock for the POX autoclave.

Production

The complexity of these processing options means that manufacturers must balance various factors, from cost of recovery of ores, energy and labour costs, and even carbon intensity of production – pyrometallurgical processes are needless to say that most carbon intensive. Producing battery materials for lower carbon electric vehicles via a high carbon intensity extraction process would seem to defeat the object. At present, HPAL seems to have a clear advantage in terms of production of nickel sulphate, and has become the dominant technology for the current wave of nickel capacity, most of it based in Indonesia. Indonesia's policy regarding low-grade nickel ore exports, commencing with a ban in 2014, a relaxation of the policy in 2017, followed by a return to the original ban in 2020, has incentivised the development of domestic refining capacities, bolstered by investments from Chinese companies. Since the ban in 2014, Indonesia's refined nickel output has increased from just 24,000 t/a to around 1.4 million t/a, with several new projects under development. The Chinese producers have focused on MHP production, seeing it as the most cost effective material to be transported to China for processing. Figure 1 shows just how dominant Indonesia has become in acid leaching, with more than half of all production in 2024.

Fig. 2: **Nickel consumption for batteries, '000 t/a**



Source: CRU

Overcapacity

The rush to build new HPAL capacity has had its own effect upon the market, with a glut of nickel on the market at present, and prices at low levels; the LME nickel price has traded at around $16-17,000/t during the second half of 2024. There has been an oversupply of nickel sulphate and nickel battery precursors as a result of overproduction of NMC and NCA from 2021 to 2023, which resulted in significant stock building, and these stocks have been drawn down during 2024, during which time actual demand for nickel sulphate has been relatively flat, and it has been Chinese stainless steel demand which is carrying the nickel market at present, rising by 6.5% in 2024 and forecast to rise by 5% in 2025. Higher net exports of stainless have supported the rise in Chinese stainless production, although over the medium term (to 2029), global stainless production is forecast to rise by a CAGR of 3.8% with China remaining the key driver. Meanwhile, in spite of flat demand in 2024, in the medium term, nickel sulphate demand from the battery sector will rise at a CAGR of 12%. By 2029, it is projected that global nickel sulphate demand will reach 1.1 million t/a. Outside of China, CRU forecasts that production will more than double by 2029. This will mainly be supported by capacity ramp-up and new capacity additions in Indonesia and South Korea. But the market will remain oversupplied going into 2025, as oversupply will likely increase further as production growth will more than offset the recovery in consumption. This surplus will likely persist through 2029, keeping nickel sulphate prices in China slightly lower than LME cash prices out to 2029. Nevertheless, Indonesian HPAL producers remain towards the bottom of the industry cost curve, and the surplus is unlikely to affect them too badly. ■

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SULPHUR index 2024

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PHOTO: PPL

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Bulgaria	Aurubis awards contract for flash smelter rebuild	Mar/Apr	12
Canada	First Phosphate closes second tranche of financing	Jan/Feb	13
	First Phosphate produces first phosphoric acid	Mar/Apr	12
	Pilot plant for production of merchant phosphoric acid	May/Jun	14
	Worley alliance on lithium battery materials	Jul/Aug	12
Chile	Codelco and SQM to cooperate on lithium project	Jan/Feb	13
	Codelco and SQM to partner on Atacama	Mar/Apr	14
	Commissioning begins of copper project	Jan/Feb	13
	Copper output down at Codelco	Jul/Aug	14
China	Metso to supply technology for battery grade nickel	May/Jun	12
	Zijin acid output up in 2023	Jan/Feb	15
Egypt	US investor considering new phosphoric acid plant	Sep/Oct	12
EU	Anti-dumping investigation on titanium dioxide	Jan/Feb	14
Finland	Metso expands solvent extraction range	May/Jun	14
	Metso launches high efficiency scrubber optimiser	Jan/Feb	12
	Metso technology for off gas quenching	Jul/Aug	14
Germany	BASF collaboration on lithium ion batteries	Jan/Feb	14
	New pilot plant to develop gas cleaning technologies	May/Jun	14
Ghana	New refinery includes acid alkylation unit	Mar/Apr	14
India	Copper smelter to start up in March	Jan/Feb	14
	Coromandel begins work on new sulphuric acid plant	Jul/Aug	12
	Coromandel to build new sulphuric acid plants	Mar/Apr	13
	Coromandel to restart sulphuric, phosphoric acid plants	Sep/Oct	13
	Haldia refinery completes WSA plant	Jul/Aug	12
	HURL concludes agreement on SSP distribution	Jul/Aug	14
	Mangalore and Paradeep to merge	Sep/Oct	14
	Metso delivers scrubbers for SO_2 emissions reduction	Nov/Dec	13
	Start-up for new copper smelter	May/Jun	14
Indonesia	Antam to build new HPAL plant next year	May/Jun	15
	Asiamet reports progress on nickel project	Jan/Feb	12
	Copper smelter expansion inaugurated	Jan/Feb	12
	Freeport official opens new copper smelter	Sep/Oct	14
	Harita reports rising HPAL outout	Sep/Oct	14
	HPAL project moving forward	Jan/Feb	12
	Nickel Industries signs contract with Glencore	Jan/Feb	12
Iraq	Bids to be invited for phosphate project	Mar/Apr	13
Jordan	New phosphoric acid tank for JIFCO	Mar/Apr	12
Kazakhstan	Acid shortage impacting uranium production	Mar/Apr	12
	Agreement for copper smelter project	Jul/Aug	13
	EuroChem signs agreement for phosphate expansion	Jul/Aug	13
	New uranium processing project	May/Jun	14
Mauritania	India seeking phosphate supply deal	Mar/Apr	14
Morocco	OCP Group to boost fertilizer production	Nov/Dec	12
	OCP joint venture on green fertilizer production	May/Jun	12
	OCP selects Chemetics acid technology	Sep/Oct	12
	US raises duty on Moroccan phosphates	Jul/Aug	14
Namibia	Sinomine buys Tsumeb smelter	May/Jun	12
New Zealand	Ravensdown to stop making superphosphate	Sep/Oct	13
Russia	Agreement on new phosphate plant	Sep/Oct	12
	PhosAgro acid output up 5%	May/Jun	14
	PhosAgro increased acid production in 2023	Mar/Apr	13
Saudi Arabia	Acid imports down 50% in Q1	Jul/Aug	13
	Lithium plant will use alkaline leach	Mar/Apr	13
	Ma’aden develops phosphogypsum recycling process	Jan/Feb	15
	Ma’aden to buy out Mosaic share of phosphate JV	Jul/Aug	13
Senegal	Coromandel increases stake in BMCC	Nov/Dec	13
Serbia	Elixir to decarbonise phosphate production	Jul/Aug	13
Sweden	Iron ore miner outlines phosphate market re-entry	Nov/Dec	13
	New duplex tube for acid environments	May/Jun	12
UK	CRU launches new Battery Tech and Cost Service	Jul/Aug	13
US	Asarco to restart copper smelter	Jul/Aug	13
	Electronic grade phosphoric acid plant for Texas	Sep/Oct	12
	Hurricanes affect phosphate production	Nov/Dec	12
	Metso builds new training centre	Jan/Feb	13
	More efficient lithium extraction	May/Jun	15
	New alkylation complex	Jul/Aug	13
	OCP says phosphate tariffs may be withdrawn	Nov/Dec	12
	Veolia sells its acid regeneration business	Sep/Oct	12
Uzbekistan	Alamyk places new smelter order	May/Jun	12
World	Electric vehicle policy updates	Jan/Feb	14
	Report warns of gap in copper supply chain	Sep/Oct	14
Zambia	Cash injection for Mopani	Jan/Feb	14
	Contract for copper project	Nov/Dec	13

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A novel catalyst for sulphur dioxide oxidation

This study introduces a new platinum-promoted honeycomb catalyst for sulphur dioxide (SO_2) oxidation, designed to enhance energy efficiency and reduce emissions in sulphuric acid production. Compared to conventional vanadium oxide based catalysts, the platinum-based catalyst demonstrates higher catalytic activity, lower ignition temperature, and significantly reduced toxicity.

J. Hofer, A. Sigg, M. Felsberger, P. Piantino, L. Dobrosi, W. Kaltner, H.-G. Reinbacher, M. Dielacher (P&P Industries)

Sulphuric acid (H_2SO_4) is the world's most important industrial chemical, with applications in a wide range of sectors, including fertiliser production, petroleum refining, wastewater treatment and chemical synthesis. The primary method of producing sulphuric acid is the contact process, a highly efficient process that uses catalysts to convert sulphur dioxide (SO_2) to sulphur trioxide (SO_2), which is then absorbed in diluted sulphuric acid to produce strong sulphuric acid or oleum. This catalytic conversion process has largely replaced older methods due to its higher yield, efficiency and environmental benefits.

PHOTO: P&P

Fig. 1: Platinum-promoted honeycomb catalyst

The contact process consists of three main stages: SO_2 generation, catalytic oxidation and absorption. In the first stage, sulphur or sulphur containing compounds are burned or spent acid is thermally decomposed to produce SO_2 gas. The second stage, the heart of the plant, is where the catalytic action takes place, converting sulphur dioxide into sulphur trioxide through a reversible reaction facilitated by various catalysts. These catalysts play a crucial role by lowering the activation energy and allowing the reaction to take place at moderate temperatures and high yields, maximising the conversion efficiency. Finally, the sulphur trioxide is absorbed in diluted sulphuric acid to form strong sulphuric acid.

The use of highly efficient catalysts in the production of sulphuric acid offers several advantages, such as increased reaction rates and energy efficiency, ultimately reducing production costs and emissions. As a result, catalytic processes in sulphuric acid production are critical to meeting the high demand for this versatile acid while minimising the environmental impacts associated with large-scale chemical production.

State of the art catalysts are based on vanadium pentoxide (V_2O_5) on Kieselguhr extrudates which, in addition to their negative environmental impact based on their classification as toxic, environmentally harmful and hazardous, have practical limitations in operation due to limited catalyst activity and durability.

P&P Industries' platinum-promoted honeycomb catalysts (see Fig. 1) are designed to take both material durability and catalyst activity to new levels, enabling higher conversion and increased plant capacity while reducing capex and opex.

Catalyst development

The new platinum-promoted honeycomb catalyst, which was invented by P&P is highly cost efficient, due to effective employment of platinum as an active phase in combination with a tailor-made washcoat on a sturdy and resilient ceramic support. The recipe as well as the manufacturing process are patented and proprietary.

Methodology

Catalyst characterisation

The catalyst samples were manufactured in accordance with the P&P wash coating process. The material properties of PPH (platinum-promoted honeycomb) catalysts were analysed using a scanning electron microscope with energy-dispersive X-ray spectroscopy. The operational properties of the materials are withdrawn from the operational experience of P&P sulphuric acid plants and laboratory test results.

The catalyst activity was evaluated on a

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Table 1: **Inlet gas composition and volume flows in 1st hurdle**

Component	SO_2	O_2	N_2	Sum
Vol-%	13.0	12.0	75.0	100.0
Nm³/h	9,522	8,789	54,935	73,247

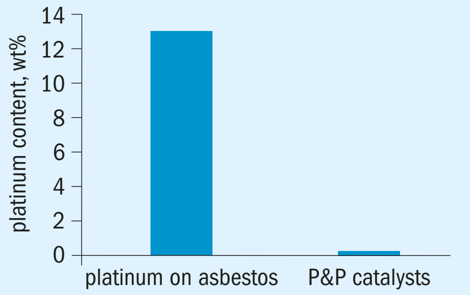
Source: P&P

Table 2: **Hurdle inlet temperature specification for PPH and vanadium pentoxide catalysts**

Component	Vanadium pentoxide	PPH
Inlet temperature hurdle 1, °C	420	350
Inlet temperature hurdle 2, °C	420	350
Inlet temperature hurdle 3, °C	420	350
Inlet temperature hurdle 4, °C	360	350

Source: P&P

Fig. 2: **Comparison of platinum content in historic and PPH catalysts (indicative values)**



Source: P&P

test rig at the P&P Technology Center, which was equipped with a gas mixing station, a temperature control module and online gas analysis. The gas concentration, volumetric flows and temperatures were selected as representative of those encountered in industrial applications.

Test case

A production plant with a capacity of 1,000 tonnes of H_2SO_4 per day was used as a test case. The design of the catalytic reaction and the corresponding converter were investigated. The feed streams were defined as shown in Table 1 and Table 2. Conversion calculations were performed according to the Sulphuric Acid Manufacture Analysis, Control and Optimization Book (Second Edition, 2013), supported by P&P's own knowledge of real catalyst performance in industrial operation and laboratory test results.

Test results

Material characterisation

Historically, platinum-based catalysts for the oxidation of SO_2 have contained a wasteful amount of precious metal immobilised on a support, for example, asbestos. Improved manufacturing techniques have enhanced metal dispersion and surface accessibility through increased porosity, resulting in a dramatic reduction of over 100 times the amount of platinum used, as shown in Fig. 2. Furthermore, the porosity of the washcoat was tailored to highly effective ignition behaviour.

The main criticism, beneath the cost, of the use of noble metal supported catalysts is their susceptibility to catalyst poisoning. However, state-of-the-art gas cleaning techniques such as hot gas filters, scrubbers and (wet) electrostatic precipitators have largely eliminated catalyst poisoning, making PPH catalysts an alternative to state-of-the-art Vanadium pentoxide catalysts.

In addition to significantly reduced precious metal consumption, innovative manufacturing techniques, such as the P&P wash coating process, enable vastly improved material properties, as summarised in Table 3. Firstly, the honeycomb shape of the PPH catalyst, compared to the extruded vanadium pentoxide, greatly reduces the pressure drop (see Fig. 3), allowing either reduced main blower power consumption or increased flow rates, thereby increasing overall plant efficiency. Second, PPH catalysts exhibit increased mechanical stability, which has a positive impact on catalyst lifetime due to increased hardness and largely avoided attrition losses, eliminating the need for periodic catalyst screening. However, increased mechanical stability comes at the cost of higher bulk density and therefore higher specific gravity. This obvious disadvantage is completely overcome by the increased catalyst activity resulting in reduced catalyst volume, as discussed in the following section.

Analysis of the surface morphology by SEM-EDX reveals a highly porous gas exchange layer obtained by the P&P wash coating process, which is decorated with fine platinum particles.

The geometric surface area of the honeycomb ceramic monolith itself, which is already higher than the geometric area of bulk catalyst extrudates (see Table 3), is further increased to reach a very high

Table 3: **Comparison of material properties of PPH and vanadium pentoxide catalysts**

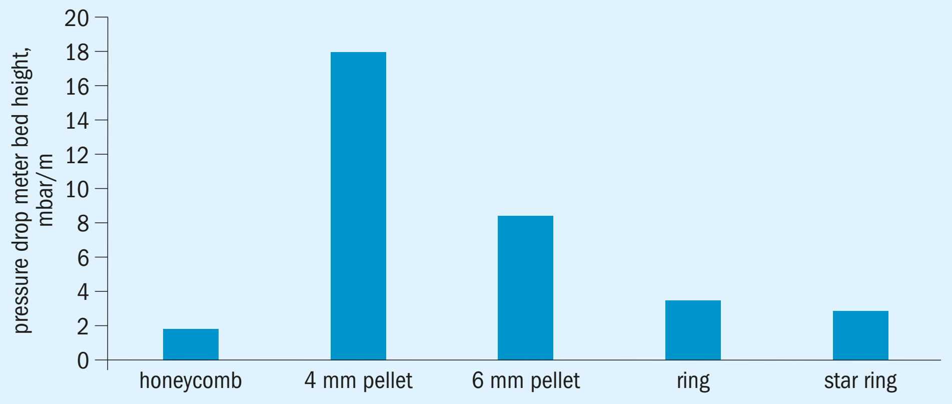
	V_2O_5 bulk catalyst	P&P's platinum based catalysts
Pressure drop, mbar*	7-46	1.7-2
Surface area, m²/m³	1-2 x10⁶	5 x10⁶
Screening	5-20% of volume lost per year (worst case assumption)	None
Bulk density, kg/m³	450	800
Toxicity	Carcinogenic, acidic, etc.	None, dust protection
Service life, years	5-10	≈ 10
Hardness	Cutting: 70-11 0N	Vickers: ≈ 25 GPa Mohs: 9
Attrition, %	1-2	< 0.05

Source: P&P

BET (Brunauer- Emmett-Teller) surface of the monoliths.

The analysis also shows a high dispersion of platinum on the accessible surface of the porous layer, which explains the greatly reduced platinum requirement. Furthermore, by applying a gas exchange layer, the amount of inaccessible active material is reduced, allowing the precious metal to remain sustainable. This is a big advantage against so called fully extruded precious metal catalysts. Due to the relatively low thickness of the gas exchange layer, diffusion lengths within the catalysts are reduced, resulting in improved conversion characteristics.

Fig. 3: **Comparison of pressure drop for PPH catalysts and various shapes of vanadium pentoxide catalysts (indicative values)**



Source: P&P

Catalytic performance of PPH

In the P&P Technology Center, the catalytic performance of the previously discussed PPH catalyst was evaluated in comparison to state-of-the-art vanadium pentoxide-based catalysts (obtained by P&P clients for detailed analysis). To this end, a comprehensive testing of the operational window of each individual catalyst sample was conducted, varying temperature but fixing gas velocity and gas composition. Fixed conditions were selected according to the actual process design of P&P. For each catalyst system, two qualities were tested at identical space velocities.

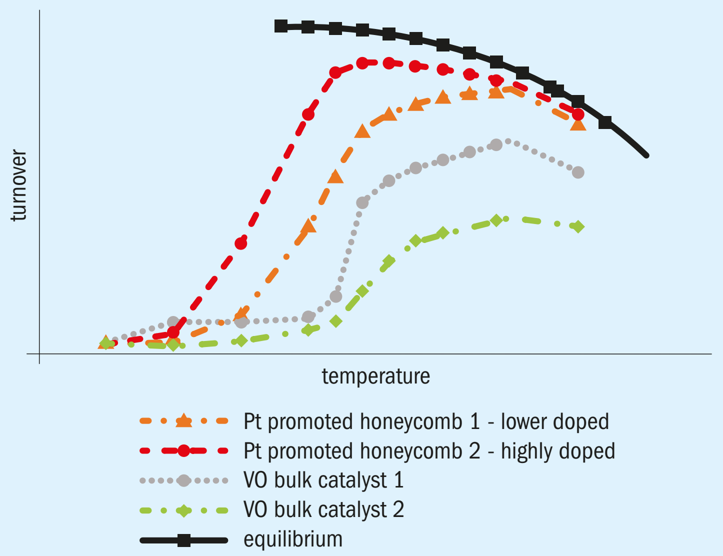
A comparative analysis of the turnover results is presented in Fig. 4. It is evident that PPH catalysts exhibit a remarkably reduced ignition temperature, thereby enabling their operation at considerably lower hurdle inlet temperatures. This offers two significant advantages. Firstly, the potential for higher SO_2 conversion prior to reaching thermodynamic equilibrium, and secondly, the possibility of high heat recovery rates.

The experimental data indicate that, as the temperature increases, the ignition occurs relatively rapidly and approaches the thermodynamic equilibrium for the PPH catalysts. In contrast, vanadium-based catalysts display a comparatively slower ignition rate at elevated temperatures. This phenomenon may be explained by the shorter diffusion lengths observed within the gas exchange layer, the increased surface area, and the superior catalytic activity exhibited by the highly dispersed platinum particles.

The elevated specific activity of the PPH catalyst is reflected in the enhanced space-time yields (STY, converted moles of SO_2 per time interval and catalyst volume), as illustrated in Fig. 5. Only an increase in the amount of applied catalyst could offset the lower space-time yield (STY) of vanadium pentoxide catalysts. Therefore, more vanadium pentoxide based catalyst is necessary to reach the same conversion goal in comparison to platinum based catalysts.

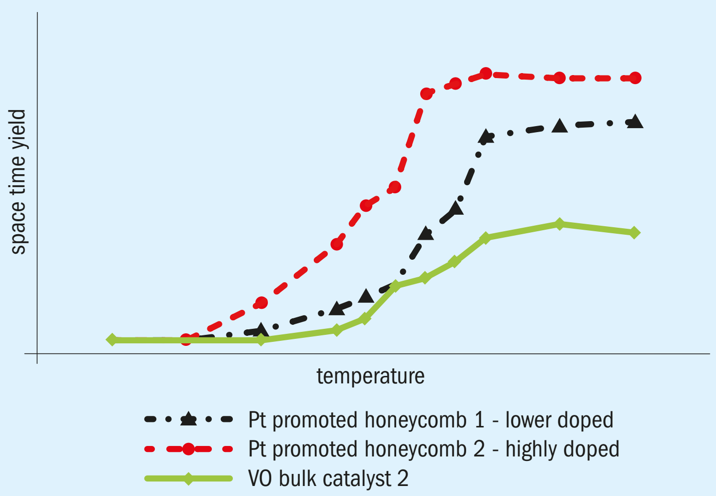
From the kinetic and thermodynamic analysis presented, it can be concluded, that an up to three-fold reduction in catalyst volume replacing vanadium pentoxide catalyst with P&Ps PPH catalysts for the conditions tested is possible. This challenges the previously held assumption that the increased bulk density would be

Fig. 4: **Comparison of conversion for PPH and vanadium pentoxide based catalysts as a function of temperature. Selected gas concentrations were representative of P&P sulphuric acid plants (indicative values)**



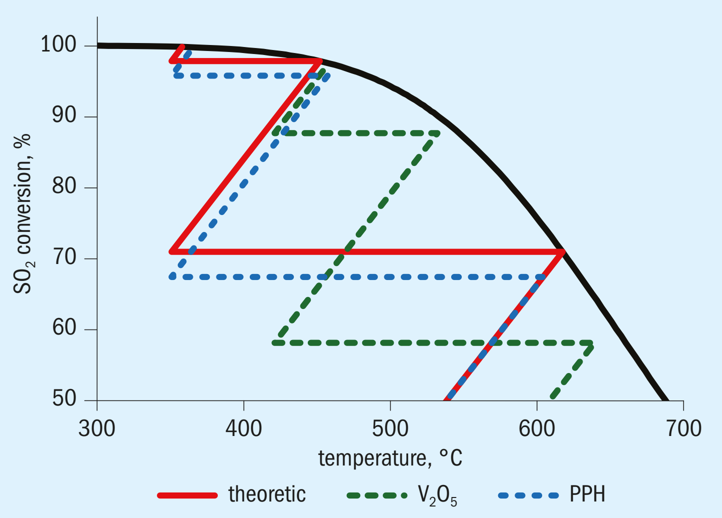
Source: P&P

Fig. 5: **Comparison of the space-time yield for PPH and vanadium pentoxide-based catalysts as a function of temperature. Selected gas concentrations were representative for P&P sulphuric acid plants (indicative values)**



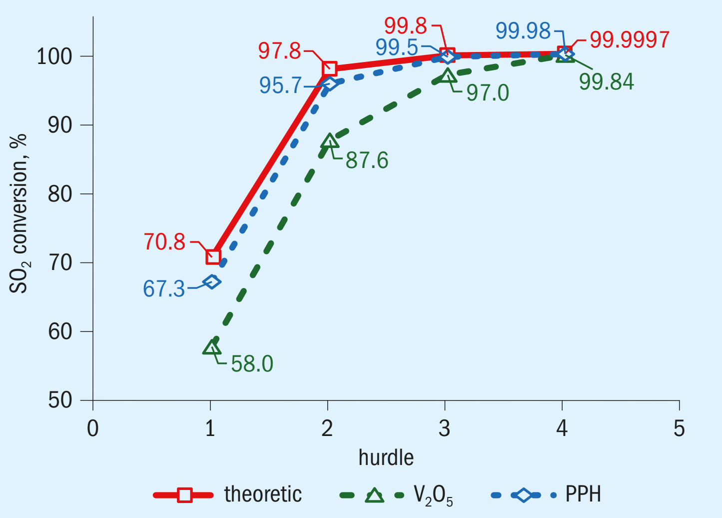
Source: P&P

Fig. 6: **Comparison of heat-up paths for PPH catalyst and vanadium pentoxide catalyst for hurdles 1 - 3. "Theoretic" refers to conversion reaching thermodynamic equilibrium**



Source: P&P

Fig. 7: **Comparison of achievable SO_2 conversion for PPH catalyst and vanadium pentoxide catalyst in the 1,000 t/d test case**



Source: P&P

a disadvantage, for the necessary catalyst volume is much lower with PPH catalysts.

Impacts on process reactor design

In accordance with the experimental catalyst assessment conducted at the P&P Technology Center, a representative reaction and reactor design for a 1,000 t/d test case has been developed. The initial reaction conditions are presented in Table 1 and Table 2. In the case of the vanadium pentoxide catalyst, the inlet temperature for hurdles 1-3 was fixed at 420°C, while the inlet temperature for hurdle 4 was reduced to 360°C, both in accordance with the specifications for standard and caesium-promoted vanadium pentoxide catalysts that are commonly used in this field, respectively. For PPH catalysts, inlet temperatures of 350°C for hurdles 1-4 were chosen in agreement with analysed experimental data. Calculations for the theoretic conversion (SO_2 conversion fully reaches the thermodynamic equilibrium) was performed with identic settings as for PPH catalysts. Overall, the process is designed in a three-plus-one configuration, with acid making through absorption occurring between catalyst hurdles 3 and 4.

The results of the thermodynamic and kinetic assessment of the heat-up paths are presented in Fig. 6. In accordance with thermodynamic expectations, a reduced inlet temperature indicates the potential for enhanced SO_2 conversion, thereby highlighting the significance of low ignition temperatures, as demonstrated by the PPH catalyst. Consequently, the overall SO_2 turnover prior to intermediary acid making is estimated to be 2.5% higher for the PPH catalyst than for vanadium pentoxide-based catalysts, as illustrated in Fig. 7. Despite the ability of caesium-promoted vanadium pentoxide catalysts to significantly reduce the inlet temperature at hurdle 4, the total SO_2 turnover across all four hurdles remains below the levels achieved with PPH catalysts investigated in this study.

From the shown data it is obvious, that lowered gas inlet temperatures to especially the first hurdles boost the total conversion to a level which cannot be compensated by reducing inlet temperature of the last hurdle due to application of specialised and costly caesium-promoted vanadium pentoxide catalysts solely.

In consideration of the kinetic and thermodynamic aspects, a prospective example reactor configuration was designed. The corresponding results are presented in Fig. 8. The inlet and outlet gas streams are based on the results of the kinetic and thermodynamic calculations performed on the PPH catalyst. The total demand for the PPH catalyst in order to achieve the four specified hurdles is about 65 m³. In comparison, the use of 200 to 220 m³ of vanadium pentoxide catalysts would be required to achieve the same conversion, reflecting the superior performance of the PPH catalysts. Prior to the initial hurdle, the installation of a protective layer of inert packing, designed to filter residual dust from the inlet gas stream, could be considered, contingent on the specifications of the inlet gas in the design case. The indicated pressure drop for the dust guard is analogous to that anticipated for vanadium pentoxide catalysts per hurdle and is consistent with the data presented in Fig. 3.

The presented reactor setup is in compliance with established standards for emission limits. The indicated 38 ppm SO_2 at the sack corresponds to 108 mg/Nm³ and 99.98% conversion. This is therefore below the limits set out in the German TA Luft (less than 400 mg/Nm³, greater than 99.9% total conversion). An analysis of the vanadium pentoxide thermodynamic data (total conversion of SO_2 = 99.84 %) may indicate the necessity for additional SO_2 removal techniques or an increase in catalyst amounts to achieve closer alignment with the thermodynamic equilibrium, in order to comply with the regulations of TA Luft. It should be noted that this emission rating is to be considered as an example of the possibilities of the order of magnitude, for the reachable emission limits and should not be understood as binding figures for every possible design case.

Transforming the hurdle volumes into steel construction reveals the possibility to reduce overall reactor size. This results in a reduction in investment costs associated with the steel construction. In the presented case study, the cost of the steel construction material can be reduced by a

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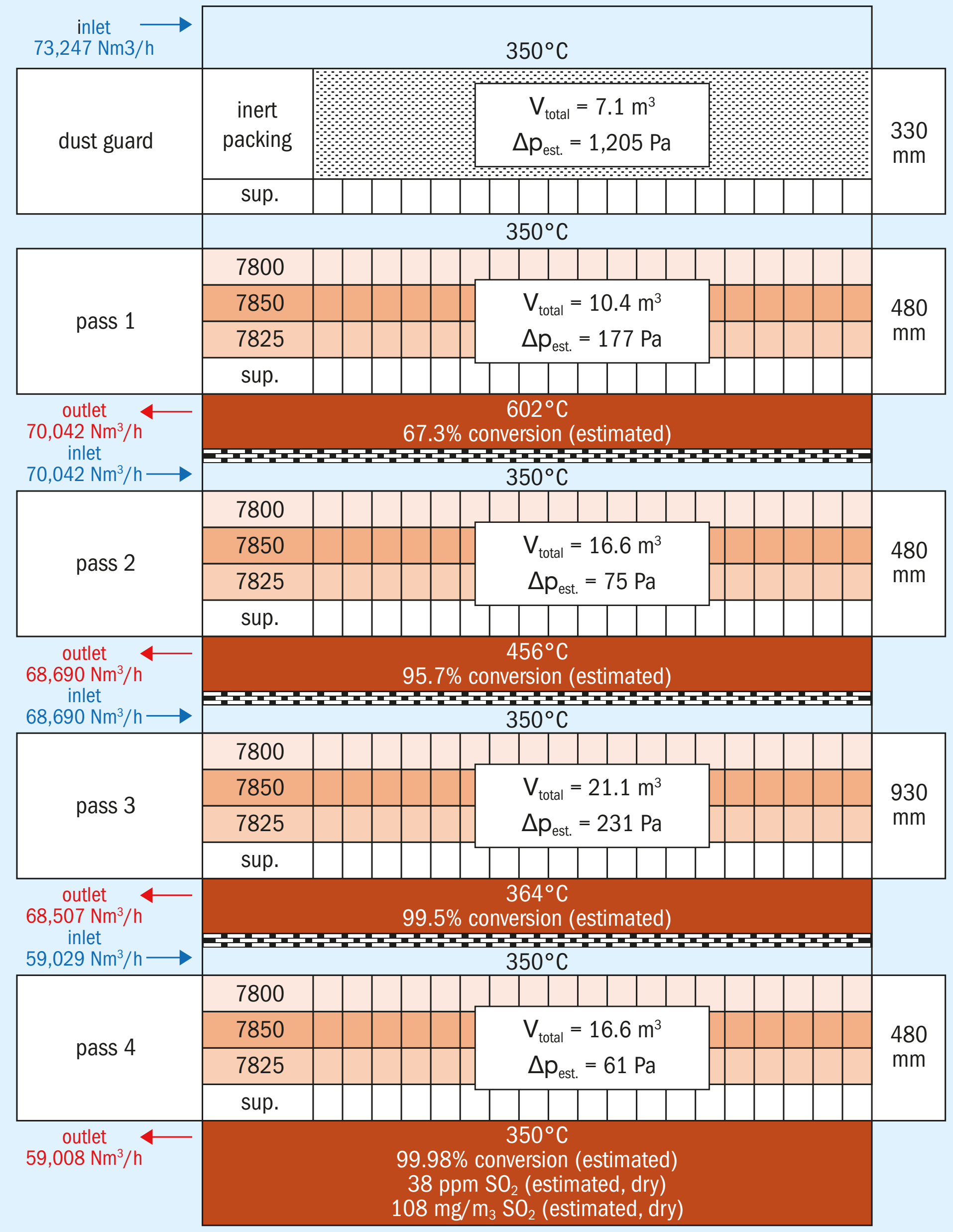
Fig. 8: **Suggested reactor design for the 1,000 t/d test case**



Source: P&P

factor of three (see Fig. 9), which correlates with the proposed threefold reduction in catalyst volume. The investment cost can be significantly reduced, contingent on the grade of steel utilised in the construction process.

The PPH catalyst exhibits not only enhanced activity but also superior durability, resulting in minimal attrition loss. In contrast to vanadium pentoxide catalysts, no screening is required. A comparison of the costs associated with the screening of vanadium pentoxide catalysts is presented in Fig. 10. While the investment cost for the catalyst is comparable between the PPH catalyst and vanadium pentoxide catalysts, the replacement of the catalyst due to attrition loss (10% loss per year assumed) results in an increase in investment cost of up to 1.5 over a ten-year period. These are only indicative values to show the possibility of the technology.

In contrast to vanadium pentoxide-based catalyst, which is classified as hazardous waste and must be disposed of accordingly, PPH catalyst can be recycled in order to recover the precious metals that have been applied. The quantity of recovery is dependent upon the quality of the applied PPH utilised in the process. After the end of life, a recycling quote of about 75 % of the platinum metal is expected.

Transition of theoretic knowledge into real world applications

The PPH catalysts are characterised by a square base area, which renders them particularly suited to rectangular reactor cross-sections. Nevertheless, as the base area is considerably smaller than the reactor diameter, the PPH catalyst can be installed in a circular reactor cross-section without any issues. The use of ceramic fibre materials ensures that bypass formation is avoided. The PPH catalyst has been installed and operated in plants designed by P&P in locations across the globe for over a decade.

The PPH catalysts are thereby not only installed in plants for manufacturing of sulphuric acid but also in the waste gas treatment applications such as carbon monoxide oxidation in metallurgical or power plants, respectively.

Especially waste gas treatment in metallurgical plants show challenging gas compositions as the removal of all potential catalyst poisons is almost impossible. However, the PPH catalyst system developed by P&P and operated by customer in the metallurgical sector provides high resilience for catalyst poisons.

As an example, a catalyst which was heavily poisoned by arsenic was tested on the Catalyst Performance Unit of P&P's Technology Center. No sufficient activity in the temperature range of 380°C to 480°C was detected. After several hours at 480°C, the arsenic could be removed by thermal evaporation.

The PPH catalyst showed excellent performance in CO oxidation with high bearing SO_2 gases in metallurgical applications. Despite the poisoning situation, Pb, HF, Hg and Cd were also present in the gas phase, the catalyst shows excellent turnover performance. While thermal oxidation with natural gas is often used, the application of PPH catalysts is advisable as high energy saving can be achieved due to low operation temperatures (of about 150 to 200°C). For gas streams containing the poisons described in the upper section, higher temperatures are recommended for in situ regeneration of the catalyst.

Expanding PPH catalysts to new dimensions of SO_2 oxidation

Although the PPH catalyst has demonstrated its resilience in the challenging gas atmospheres encountered in metallurgical processes, a common catalyst issue remains unresolved. The conversion of high-concentration SO_2 streams, which are typical for metallurgical processes involving gases, remains a challenging task. The conversion of up

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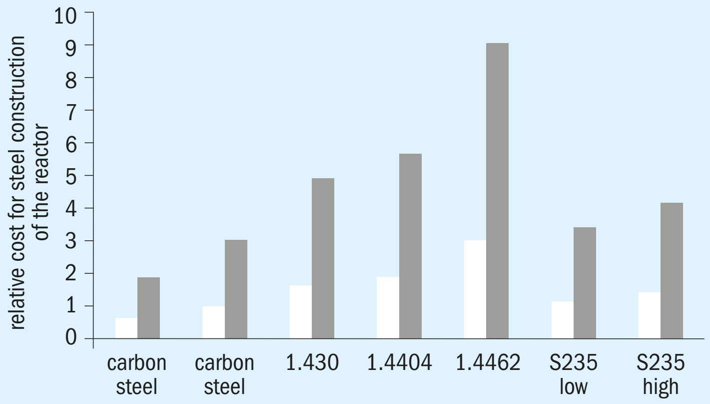
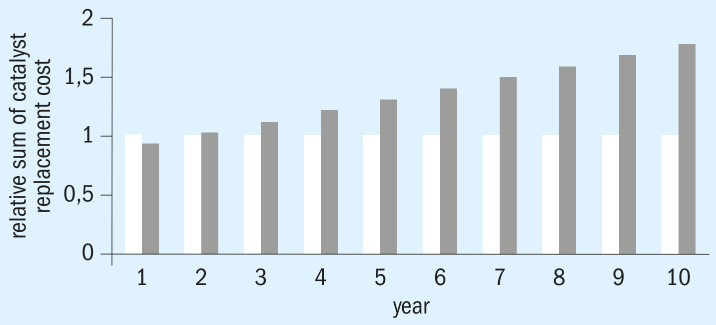
Fig. 9: **Comparison of steel construction for PPH catalyst and vanadium pentoxide catalyst (shaded bars) equipped reactor (indicative figures)**



Source: P&P

Fig. 10: **Comparison catalyst investment and replacement cost of PPH catalyst and vanadium pentoxide catalyst (shaded bars). 10% attrition loss for vanadium pentoxide was assumed (indicative figures)**



Source: P&P

to 35% SO_2 observed in these gases has been found to exceed the thermal limits of state-of-the-art vanadium catalysts, resulting in their complete destruction within a short period of time.

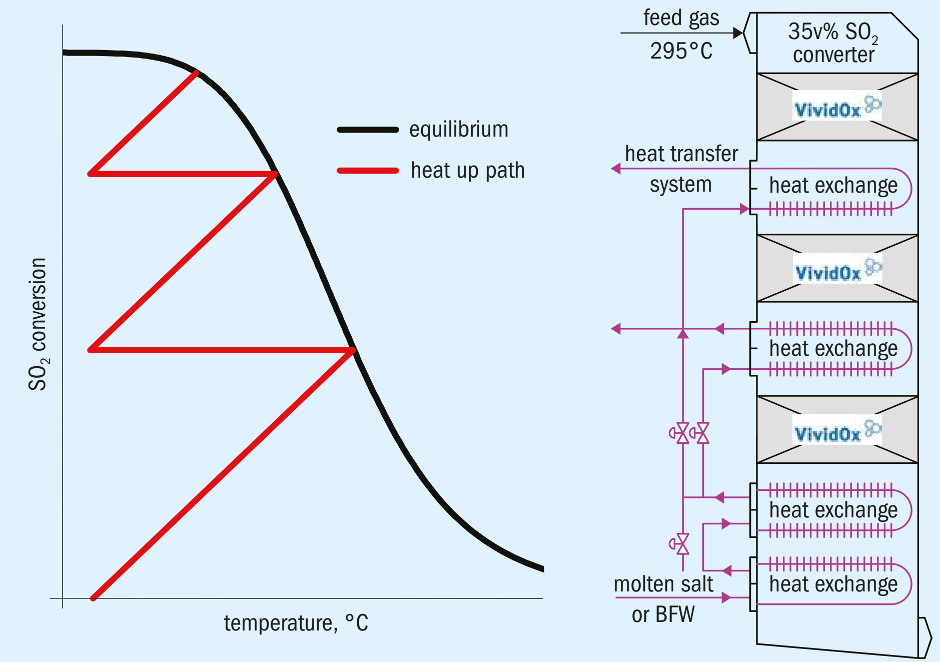
The mechanism of vanadium catalyst destruction at elevated temperatures is well documented and attributed to the collapse of the porous structure and sintering of the catalytically active species, which ultimately results in the loss of catalytic activity.

Consequently, complex and costly workarounds, such as process gas recycling or SO_2 dilution, were developed to safeguard the catalysts.

At the P&P Technology Center, a novel PPH catalyst was developed with the objective of determining its ability to handle these gas streams containing high concentrations of SO_2 without the need for workarounds, such as dilution or gas recycling. The catalyst exhibits a considerably lower ignition temperature and increased temperature resistance in comparison to current PPH catalysts. These characteristics were achieved through the development of a novel formulation of the P&P wash coating process.

The results shown in Fig. 11 were obtained by expanding recent experimental data on the novel PPH catalyst to a potential converter design for 35 vol-% SO_2 in the inlet gas. The extended operational window, which encompasses a range of temperatures from low to high, enabled the conversion of approximately 95% of the SO_2 over three hurdles in one reactor. The presented design aligns with the observed conversion yields of conventional sulphur oxidation plants but increases sulphuric acid production drastically. When coupled with the P&P heat transfer system, which employs thermal salt, the enhanced heat generation can be readily managed, and the associated costs remain within the range of standard sulphuric acid plant designs.

Fig. 11: **Experimental catalyst operation and reactor design for the oxidation of gas streams with up to 35% SO_2**



Source: P&P

P&P Industries AG employs a step-by-step approach to carefully validate and enhance catalyst performance in laboratory, demonstration, and pilot-scale settings, prior to commercial application. By understanding the challenges faced by customers, P&P can provide needed catalyst solutions that have a remarkable impact.

For this very valuable development P&P Industries is currently looking for a partnership to construct a pilot plant as a proof of concept.

Conclusion

PPH catalysts produced with P&P's proprietary technique have shown superior catalytic properties over state-of-the-art vanadium pentoxide catalysts. Catalytic activity, ignition temperature and pressure drop were lifted to a new level enabling reduced capex and opex while improving environmental footprint of the processes at the same time.

The presented technology has proven itself as a reliable product in industrial sulphuric acid manufacturing. P&P's platinum-promoted honeycomb catalysts are successfully installed in over 30 plants all over the world.

Even PPH catalysts can be applied in challenging environments such as metallurgical processes underlining the resilience against catalyst poisoning. ■

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Staying ahead of SO_2 emission limits

Due to ever stricter legislation towards lower SO_2 emissions, superior catalyst shape and composition has become ever more important. **Jochen Willersinn** of BASF SE explains how BASF's high-performance catalyst 04-116 Quattro combines the benefits of an increased surface area with a superior caesium-promoted active phase composition enabling significantly lower ignition and operating temperatures and thus reducing SO_2 emissions.

BASF has produced sulphuric acid for various industrial applications since 1866 and has been producing catalyst for the sulphuric acid process since the early 20th century. Today, BASF operates six sulphuric acid and 12 sulphonation plants with inline SO_2 oxidation units worldwide, all using BASF's in-house catalyst technology with world class plants operating at emission levels below 50 ppm SO_2. The last 20 years have brought new challenges such as tighter emission regulations and cost pressure to the sulphuric acid market. This has led BASF to be at the forefront with cutting-edge research into one of the oldest catalysts of the portfolio.

BASF works directly with customers to make sure customers achieve the best performance under the specific design and operation conditions of their reactors. This is enabled through BASF's state-of-the-art testing facility and analytics combined with more than 150 years of research and experience.

SO_2 emission regulation

Nearly all chemical and industrial processes result in a certain amount of by-products or waste components, which are harmful for our environment. The impacts are plentiful and can lead to soil contamination, eutrophication, and most importantly, to global warming. In order to reduce their negative effects on the environment, the emission of these harmful components is regulated, and measures are taken by companies to reduce their emissions. Sulphur dioxide (SO_2) and sulphur trioxide (SO_3) also fall under these regulations. Starting from the first ratification of the Helsinki Protocol in 1985, the emission limits were further decreased, and other protocols were implemented to decrease the amount of SOx emitted through various sources (e.g. automotive, electricity generation, and industrial processes) namely the Oslo Protocol in 1994 and the Gothenburg Protocol in 1999, which was further amended in 2012. Since SO_2 is not just poisonous, but also a major contributor to acid rain when it is released to the atmosphere, the emission limits for SO_2 for sulphuric acid plants became ever stricter over the past decades. The graph in Fig. 1 displays the development for average SO_2 emission limits for sulphuric acid producing units in Germany, which follow the regulations provided by the European Union and the German Federal Government.

As displayed in Fig. 1, there has been a significant decrease in emission limits for the most common sulphuric acid producing technologies over the past 25 years in Germany. Furthermore, a new LVIC-BREF (best available techniques reference document for the manufacture of large volume inorganic chemicals) for the European Union is under discussion which will most likely result in a further decrease in SO_2 emission limits in the near future. These emission limit reductions for SO_2 resulted in a lot of changes in the industry: The use of scrubbers to remove excess SO_2 for single contact units, double contact units with five catalyst beds, and the implementation of caesium-promoted catalysts that are active at lower temperatures to maximise the conversion of SO_2 to SO_3. Among others, these changes made a major contribution to the reduction of SO_2 emissions whilst also maximising the sulphuric acid output of these units. However, as stricter emission regulations are already on the horizon, more powerful tools need to be implemented in the future to be able to comply with the regulations.

New extruded shapes

An elegant way to accomplish this is with the use of even more powerful catalysts, which enable higher conversion rates. BASF's approach to achieve this is through the improvement of catalyst shape geometry.

In 2016 BASF launched the Quattro shape geometry for its sulphuric acid catalyst family. This outstanding catalyst shape geometry combines a 30% increased surface area with significantly increased catalyst strength whilst maintaining the pressure drop of Star Ring catalysts.

Since the launch of 04-115 Quattro in 2016, many additional customers are benefiting from realised performance improvements, such as higher capacity, lower catalyst loading volume, or significant conversion increase. A major gamechanger in emission reduction is BASFs high performance catalyst 04-116 Quattro. This catalyst combines the geometrical benefits of the Quattro family with a superior active mass composition and enables significant reduction in emissions.

04-115 versus 04-116

For caesium-promoted catalysts, there are two different application fields. The first application field is as an ignition layer for the first pass. This is mostly necessary

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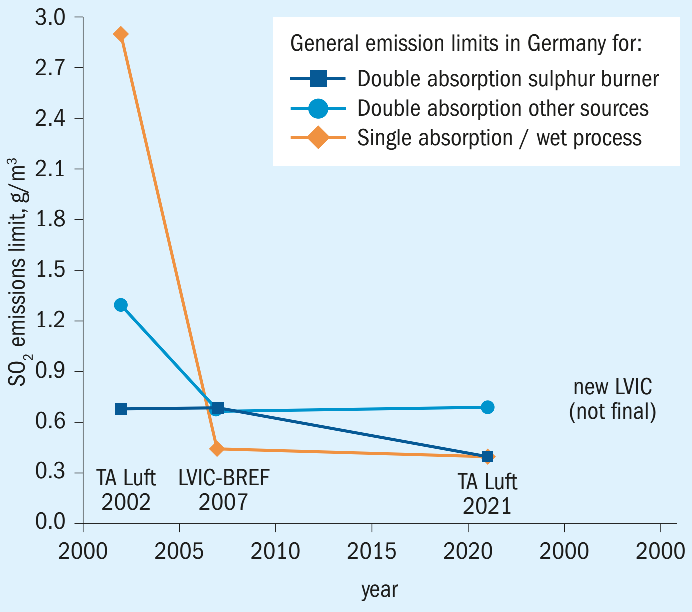
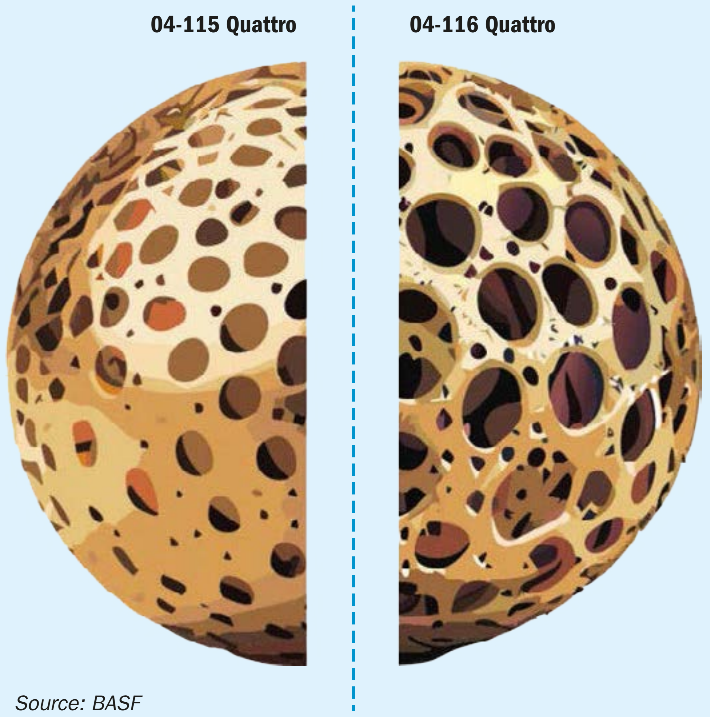
Fig. 1: **Historic view on SO_2 emission limits in Germany over the past 25 years. Special regulations for existing units with active permissions are not reflected here.**



Source: BASF

Fig. 2: **Schematic comparison of the carrier material composition of 04-115 Quattro and 04-116 Quattro displaying a different pore structure.**



Source: BASF

in metallurgical plants, where the inlet temperature to the first bed can fluctuate and is in most cases around 400°C. The second field of application is for emission reduction after the intermediate absorption step as described above. As both fields have a different set of requirements, such as different upper operating temperatures, or mass transfer properties, it is not favourable to use one single catalyst to do both jobs, as a lot of potential remains unused. Hence, BASF developed two different caesium-promoted catalysts in its portfolio, namely 04-115 as the catalyst dedicated to operating in bed 1 ignition layers and in single absorption units, i.e. situations with high SO_2 and SO_3 concentrations where the conversion is mostly equilibrium controlled. 04-116 was developed as the high-performance low temperature catalyst for applications after the intermediate absorption, where a high mass transfer rate is key to maximise the conversion.

These catalysts have a different amount of caesium in their composition, which is regulating the melting point of the active phase and therefore the activity at low temperatures. But that is only a small part of what distinguishes these catalysts. The choice of the carrier material composition (Fig. 2) is a crucial step for the desired application field of a catalyst.

As displayed in the schematic in Fig. 2, the key difference between 04-115 and 04-116 is the pore structure and pore size distribution of those catalysts. The carrier material of 04-115 is specifically designed to operate under conditions where the oxidation reaction of SO_2 to SO_3 is equilibrium controlled meaning high temperatures and high SO_2 and SO_3 concentrations. Here, the stability of the catalyst is crucial, to withstand the extremes it is experiencing and an increase in porosity has no apparent benefit, as the reaction is not mass transfer limited. The opposite is the case for the intended application field of 04-116. Here mass transfer limitation is the key issue, which needs to be overcome by a superior pore size structure to enable a fast diffusion of all reactants in and out of the active phase.

Surpassing state-of-the-art performance

When applying the fundamental concepts of a change in shape geometry from Star Ring to Quattro, 04-116 displays not just the same benefits as seen with the other catalysts, such as a higher mechanical strength, lower attrition and a higher geometric surface area. The activity increase surpasses the expected boost originating from the higher geometric surface area. This is a result of a synergistic effect between the pore structure of the O-116 carrier material and the Quattro shape geometry surpassing the activity standard catalysts by far. When comparing the kinetic rates of 04-115 Quattro and 04-116 Quattro, 04-116 Quattro has a significantly higher activity between 20 and 40% at temperatures below

Table 1: **Comparison of ignition temperatures and operating ranges of 04-115 and 04-116 Star Ring and Quattro.**

	04-115		**04-116**	
Shape	Star Ring	Quattro	Star Ring	Quattro
Rel. geometric surface area, %	100	130	100	130
Ignition temperature, °C*	340	330	330	320
Operating range, °C *	390-630	375-630	380-600	365-600

Source: BASF **Depending on gas composition.*

405°C. This is significantly higher than is the case for the Star Ring geometries and can only be explained by a synergistic effect, since the base composition of the catalyst is not changed and only a change in the shape geometry was conducted.

Furthermore, the activity of the catalyst is increased to such an extent that the ignition temperature of the Quattro catalyst is 10°C below the one of Star Ring, Moreover, this results in a lower operating limit temperature for 04-116 Quattro, which at 365°C is 15°C below 04-116 Star Ring catalyst (see table 1).

The superior activity and the low ignition and operating temperature of 04-116 Quattro enable sulphuric acid producers to further decrease their SO_2 emissions without the need to conduct significant capex investments. The catalyst is capable to oxidise more SO_2 due to its increased geometrical surface area enabling a higher conversion with the same amount of catalyst, which was employed before. 04-116 Quattro is significantly outperforming 04-115 Quattro, which displays a comparative activity and operating range to the old 04-116 Star Ring. The significantly lower ignition temperature and improved operating range enable entirely new potentials for emission reduction in sulphuric acid plants.

04-116 Quattro reference

The target of this project for the client was to reduce the start-up SO_2 emissions of the converter after hot and cold shutdowns. The client operates a zinc smelter in Europe and has an annual SO_2 emission contingent. This means that there is a total amount of SO_2 per year, which the client is allowed to emit.

Especially after a cold shutdown, the initial emission level during start-up is quite high until the catalyst in each converter bed reaches the operating temperature. Therefore, it is of key interest to reduce these SO_2 emissions upon start-up and avoid exhausting the emission contingent.

The converter is a double absorption unit with an intermediate absorption step after the 2nd stage and a nominal capacity of 1,080 t/d with a target conversion of 99.90%. The average gas composition is as follows:

- Nominal volume flow: 129,000 Nm³/h
- Feed source: metallurgical
- SO_2: 7.8 vol-%
- O2: 9.9 vol-%
- Nitrogen: balance

Fig. 3: **Schematic view on converter loading and inlet temperatures before catalyst changeout.**

Bed	Catalyst loading before changeout	Inlet temperature, °C
1	04-110 Star Ring 11x4mm	420
2	04-111 Star Ring 11x4mm	440
3	04-111 Ring 10x5mm	425
4	04-111 Ring 10x5mm	410

Source: BASF

As shown in Fig. 3, the converter was loaded with Star Ring- and Ring-shaped catalyst only, with the latter being phased out in the meantime. Additionally, this converter setup was not utilising any caesium-promoted catalysts in the original setup but was solely running on pure vanadium catalysts. Since a catalyst changeout was scheduled in late-2022, BASF conducted BOSS100 measurements in early 2022 to assess the current performance of the converter and give indications about potential catalyst changeouts.

As visible from Table 2, the performance measurement on 31 January 2022 displayed that bed 1 is due for a changeout. This was expected, as the catalyst was installed more than two years prior to the measurement and the catalyst activity had decrease to the expected extent, where a changeout is required. Additionally, bed 3 performance is below average and displays signs of catalyst aging. The measured SO_2 conversion of the bed was only 66%, which is below expectations. Beds 2 and 4 were still able to regain the loss of conversion of their preceding passes, but the target conversion of 99.90% was not reached during the period when the BOSS100 measurement was conducted. Therefore, it was decided to exchange the first pass as scheduled and additionally change out pass 3 to fully regain the converter performance. Due to the need of the client to reduce the SO_2 emissions on start-ups, it was decided to install an ignition layer in the third stage after the intermediate absorption step. BASF proposed to employ the newly launched 04-116 Quattro catalyst to fully harness the benefit of this catalyst technology as ignition layer.

In total, 30% of the total bed volume was changed to 04-116 Quattro. This should ensure good start-up behaviour

Table 2: **SO_2 conversion determined via BOSS100 measurements on 31.01.2022**

	Bed 1	Bed 2	Bed 3	Bed 4
Gas flow in, Nm³/h *	130351	127735	117347	116985
SO_2 measured in, vol-%**	7.19	3.22	0.50	0.15
SO_2 measured out, vol-%**	3.15	0.49	0.17	0.008
Cumulative conversion, %	57.09	91.89	99.79	99.89

Source: BASF

**Gas flow for beds 2, 3, and 4 was calculated based on the inlet gas flow provided by client. **SO_2 measurements underly certain fluctuations in the gas flow leading to deviations in the SO_2 concentrations.*

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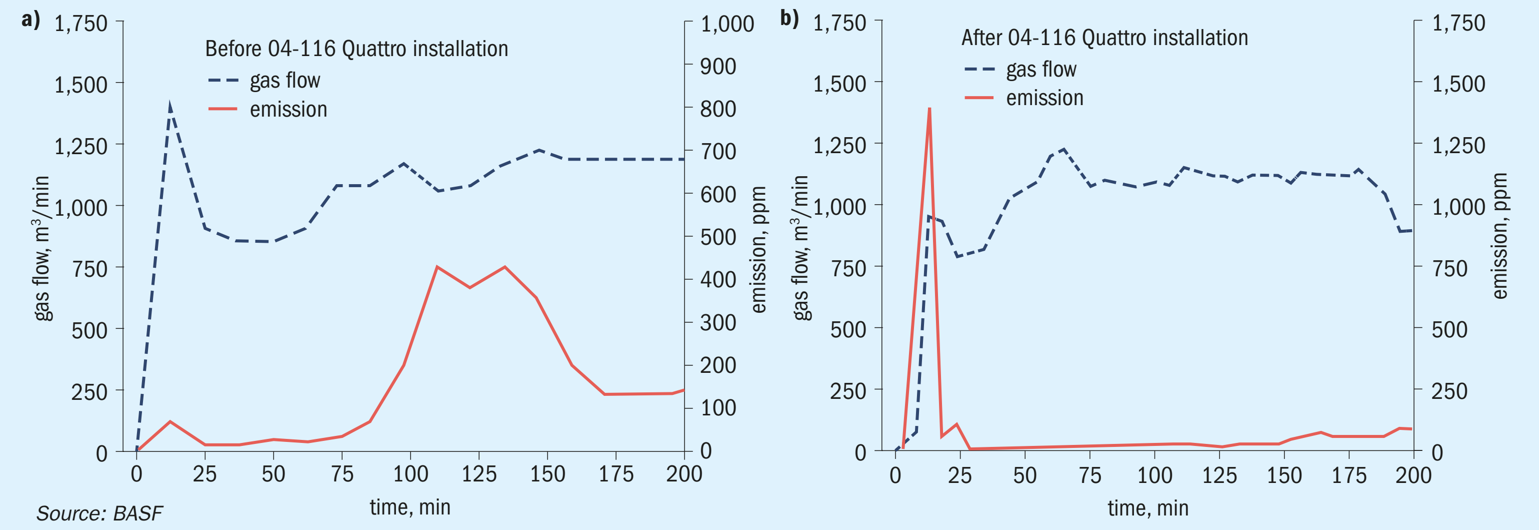
Fig. 4: **Gas flow and stack SO$_2$ emissions of the start-up after a cold shutdown**
a) Before the catalyst exchange in bed 3 **b)After catalyst exchange**



Source: BASF

of beds 3 and 4 following the intermediate absorption stage, and thus result in a decreased SO$_2$ emission upon start-ups. The remainder of the bed was equipped with 04-111 Star Ring catalyst. Beds 2 and 4 were not touched during the shutdown and the inlet temperatures for each bed remained the same as before.

Approximately a year after the catalyst exchange, a second BOSS100 measurement was conducted to verify the conversion increase predicted from the simulations.

As shown in Table 3, the catalyst exchange in bed 1 resulted in the expected performance increase of the respective bed. In addition, the catalyst exchange in bed 3 resulted in a significant performance increase of the bed from 66% to 96.9% of the incoming SO$_2$ converted to SO$_3$. This exceptional increase of 46% of conversion also strongly contributes to the total conversion increase to 99.93%, which strongly exceeds the targeted conversion of 99.90%. This result displays the power of caesium-promoted catalysts as well as the Quattro shape geometry achieving significantly higher SO$_2$ turnovers even with only 30% of the catalyst bed being equipped with this technology. However, the main reason for the exchange was to improve the start-up behaviour of the converter and thus reduce the SO$_2$ emissions during startup.

Start-up behaviour improvements using 04-116 Quattro

To demonstrate how an ignition layer after the intermediate absorption stage can contribute to a significant reduction in SO$_2$ emissions, two start-up cases were investigated. The first investigated cold start-up in May 2022 from the period before the catalyst changeout was conducted. The second investigated case was in May 2023 after the new catalyst was installed (Fig. 4).

As displayed in the graph in Fig. 4a, a short emission peak of 67 ppm was detected directly after the gas flow to the converter was started. The flow then decreased for approx. 40 minutes before increasing again to 1,880 Nm³/min. During that increase, the SO$_2$ emission detected at the stack increased to around 422 ppm for an hour, before settling down to 133 ppm and stabilising. The total duration of the startup emission peak was two hours, with an emission of 91.4 kg SO$_2$ measured at the stack of the converter. The observed trend with a timeframe, where the emissions are significantly above the average, can be regarded as normal. The converter beds are not fully at operating temperature resulting in decreased activity. Only when all beds are fully thermally equilibrated do the SO$_2$ emissions drop significantly.

Subsequently in May 2023, a comparative cold start-up was investigated. Here, the 04-116 Quattro ignition layer was already installed, and the results are displayed in Fig. 4b. As shown in the graph, there is one very sharp emission peak visible upon start of the gas flow. The peak exceeds 12,000 ppm for approximately a minute to immediately reduce to 25 ppm. The entire emission peak upon this start-up lasted for only 33 minutes, before the emission measured at the stack stabilised to values between 20 and 25 ppm. To better compare the two start-ups, a comparison of the first 180 minutes of the start-up timeframe was conducted. As displayed in Table 4, the emission of SO$_2$ for this period was 17.08 kg, which is only 18% of the emissions observed during the startup investigated a year before.

This outstanding result displays the high potential of 04-116 Quattro catalysts as an ignition layer. Under ideal conditions this catalyst can significantly decrease the SO$_2$ emissions upon start-up and thus

Table 3: **SO$_2$ conversion determined via BOSS100 measurements on the 27.09.2023**

	Bed 1	Bed 2	Bed 3	Bed 4
Gas flow in, Nm³/h *	121,200	118,488	108,754	108,425
SO$_2$ measured in, vol-%**	7.37	2.83	0.55	0.017
SO$_2$ measured out, vol-%**	2.89	0.59	0.017	0.006
Cumulative conversion, %	62.08	92.29	99.80	99.93

Source: BASF

**Gas flow for beds 2, 3, and 4 was calculated based on the inlet gas flow provided by client. **SO$_2$ Measurements underly certain fluctuations in the gas flow leading to deviations in the SO$_2$ concentrations.*

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Table 4: **Comparison of stack emissions during start-ups in May 2022 and May 2023**

	Duration (min)	SO_2 stack emission (kg)*
May 2022	180	94.70
May 2023	180	17.08
Difference, abs	-	77.66
Difference, %	-	82

**Emissions calculated from the corresponding ppm values measured at the stack over the startup period.*

Source: BASF

contribute to a decreased risk of exceeding the SO_2 emission contingent for the client.

However, this can only be achieved when the entire converter is at least pre-heated close to operating conditions, before the process gas is directed to the converter. Without the preceding converter beds being operational, an ignition layer after the intermediate absorption step can reduce the stack emissions upon cold start-ups, but it cannot compensate for a significantly reduced conversion in the first passes. Therefore, standard start-up procedures, such as sufficient pre-heating of the converter still need to be followed to achieve the desired effects of an emission reduction. As always, operational excellence and diligent personnel training are key to a sustainable operation of sulphuric acid units and staying ahead of today's and tomorrow's SO_2 limits.

Conclusion and next steps

With the launch of 04-116 Quattro, BASF has completed the Quattro product family offering the most powerful catalyst technology to date. However, the Quattro technology is not the end of what BASF can offer as new catalyst technology to supports clients in achieving their production and emission targets. BASFs X3D® catalyst technology based on 3D-printing marks further step change in catalyst technology.

As shown in Table 5, X3D® technology enables an even higher potential to reduce start-up emissions with the lower ignition temperature and operating range, as well as the higher surface area. Due to the low pressure drop increase, this catalyst can be added as ignition layer on top of existing beds without the threat of losing capacity due to increased pressure drop and can significantly contribute to increased conversion during continuous operations and especially during start-ups. ■

Table 5: **Comparison Comparison of 04-116 Quattro with 04-115 X3D®**

	04-116 Quattro	04-115 X3D®
Packing density, kg/m³	450	400-420
Rel. geometric surface area, %*	130	150-160
Rel. pressure drop, %*	100	35±10
Ignition temperature, °C**	320	310
Operating range, °C**	365-600	350-630

**Geometric surface area and pressure drop values are given relative to Star Ring catalysts, which are regarded as 100%. **Depending on gas composition.*

Source: BASF

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PHOTO: SGS SULPHUR EXPERTS

Optimising European SRU incinerators

The 2030 greenhouse gas emission reduction goals in the European Union are driving oil and gas producers to reduce CO_2 emissions wherever possible. This extends to even the incinerator attached to a sulphur recovery unit (SRU). In this article Sulphur Experts review the role of the incinerator, how the three most common European TGUs each affect the demand on the incinerator itself, and the potential reduction in CO_2 emissions for a generic facility of each type.

Leah Goettler, Peter Seville, Jan Kiebert (SGS Sulphur Experts)

The sulphur recovery unit (SRU) often gets left out of money-making conversations. Its entire purpose is to minimise SO_2 emissions, which is a noble cause, but rarely a profitable one. Optimisations in this part of the process have historically been focused on avoiding fines for emissions violations, improving reliability, or adjusting throughput in response to market or feedstock changes.

At the very end of the SRU lies the humble incinerator. A simple design for a simple purpose: to take the leftover sulphur-containing compounds and burn them all to SO_2. While often forgotten or ignored, it is still possible to optimise this part of the process and Sulphur Experts have encouraged operators around the world to do so for decades. There are several benefits, including using less fuel and therefore reducing operating costs. Some refiners in Europe burn city or natural gas in the incinerator and the cost of natural gas has increased over the last few years, from approximately €15 per MWh between 2016 and 2020 to now approximately €35 per MWh. But many refineries can use the fuel gas produced on-site in the incinerator and so this change may not affect all operators' wallets. Nonetheless, reducing fuel use can sometimes eliminate unnecessary SO_2 emissions from H_2S or mercaptans that may be left in the refinery fuel gas.

Optimisation also means reduced NOx and SO_3 emissions, which means less smog formation and "acid rain", associated with airborne sulphur compounds. Very importantly, it also means emitting less CO_2. And while this has been an excellent marketing slogan for several decades, there are now very real (and financial) reasons to care about CO_2 emissions reductions. The European Commission released The European Green Deal back in 2019. The goal is a climate-neutral Europe by 2050, with an original interim 2030 target of reducing CO_2 emissions by 55% compared to 2005 levels; this has recently been updated to a 62% reduction target for 2030. In order to achieve this, each tonne of CO_2 or CO_2-equivalent must be accounted for with an "allowance". Certain industries receive a number of free allowances each year, but that number of allowances will decrease over time to encourage companies to maintain or increase their efforts. If more allowances are needed, they can be bought on the European Energy Exchange, and likewise, unused allowances can be sold there. SRU incinerators could offer low-hanging fruit to help operators make the most of this new CO_2 commodity trading.

Unlike their North American counterparts, European SRU incinerators have a greater variety of incoming contaminants to deal with due to the greater number of non-amine-based tail gas units (TGUs). Add on additional regulations for various airborne pollutants, and a larger number of catalytic incinerators in service, and optimisation becomes a more complex process.

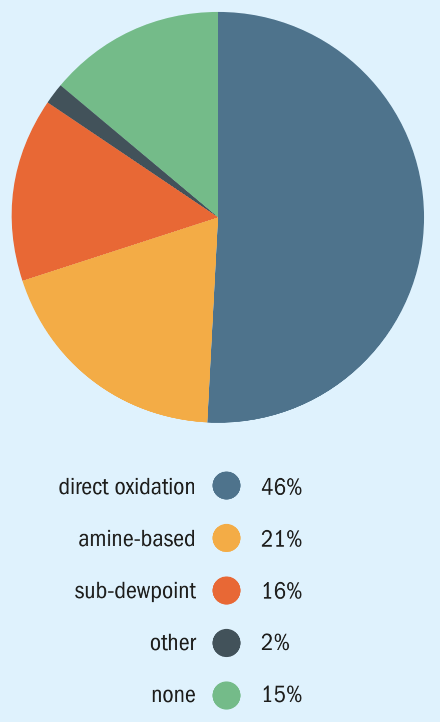
The typical European SRU incinerator

Before optimisation can start, it is important to fully understand what the typical European incinerator system looks like. This includes the feed gases, the technology used to oxidise the contaminants, and its typical operating conditions.

Incinerator inlet

The type of TGU attached to the SRU directly affects the composition of the incinerator inlet gas. Based on the Sulphur Experts test database from 2015 to 2023 (see Fig. 1), there are three main types of TGU operating in the European region: direct oxidation, amine-based, and sub-dewpoint. It was also commonly found that some refineries had no TGU of any type, usually in countries with less stringent emissions limits, or from earlier

Fig. 1: **Types of European TGUs, based on Sulphur Experts testing from 2015 to 2023**



Source: SGS Sulphur Experts

Table 1: **Generalised incinerator inlet contaminants based on TGU type**

Contaminant	**Direct oxidation**	**Amine-based**	**Sub-dewpoint**	**No TGU**
H_2	1%–3%	2%–7%	~3%	~3%
CO	0.1–1.5%	< 0.1%	0.1–1.5%	0.1–1.5%
H_2S	50–400 ppmv	~200 ppmv	< 0.1%	~0.5%
COS	30–200 ppmv	0–20 ppm	30–150 ppmv	30–150 ppmv
CS_2	0–30 ppmv	0 ppmv	0–100 ppmv	0–100 ppmv
Benzene / hydrocarbons	typically 0 ppmv	typically 0 ppmv	typically 0 ppmv	typically 0 ppmv
Elemental sulphur	> 0 ppmv	> 0 ppmv	> 0 ppmv	>> 0 ppmv

Source: SGS Sulphur Experts

tests. There are also a small number of facilities that have comparatively rare systems (for example, LO-CAT® or Sulferox) – these are outliers and beyond the scope of this paper.

As the main goal of the incinerator is to ensure complete combustion of the contaminants in the SRU tail gas, it will not affect chemical compounds such as water, carbon dioxide, sulphur dioxide, and nitrogen. Table 1 shows the typical concentrations of combustible inlet contaminants depending on the TGU type. These values are generalised from Sulphur Experts testing data from 2021 to 2023, and are based on air-only operation in the modified-Claus unit reaction furnace. Oxygen enrichment of the combustion air would concentrate these species since there is much less nitrogen in the process.

The most popular TGU process is direct oxidation. The technology uses a chelated iron catalyst to react H_2S directly with oxygen to form elemental sulphur. Poor selectivity resulting from suboptimal reaction conditions or poor catalyst health can result in the formation of SO_2 in the catalyst. Some variations use special catalysts that may also react with COS. This technology does not affect any other components in the Claus tail gas.

The next most prevalent type is an amine-based system, wherein all non-H_2S sulphur components are converted to H_2S with a hydrogenation catalyst. Most of the CO is also converted to H_2 via the gas-water shift reaction. The process gas is then cooled, sent through a quench tower to remove excess process water, and finally sent through a low-pressure amine absorber. The overhead gas is sent to the incinerator. A regenerator strips out the H_2S from the amine and the H_2S-rich gas is recycled to the front of the SRU. Given the various reactions that occur over the hydrogenation bed and the separation of the H_2S in the absorber, the gas sent to the incinerator is much cleaner than the original Claus tail gas.

The third most popular TGU type is sub-dewpoint. There are various technologies and configurations on the market, but they are all consistent in that they use a semi-batch processing method to allow the Claus reaction to proceed further by operating below the dewpoint of elemental sulphur. At least two beds are needed such that one is tied in to the process while the other is regenerated by having the liquid sulphur boiled off. Since this TGU type is purely an extension of the modified Claus reaction, the tail gas sent to the incinerator will look exactly like a Claus tail gas, just with less H_2S and SO_2.

Hydrogen (H_2) and CO are formed in the Claus section reaction furnace due to the combustion of hydrocarbons in the reducing atmosphere. The exact concentration depends on the proportional volume of hydrocarbons in the SRU feed gases. Hotter temperatures encourage more CO formation. The amount of H_2 and CO passes through the Claus, direct-oxidation, and sub-dewpoint units unchanged, therefore, the composition of the gas leaving these processes is relatively similar. There is some variation when dealing with direct oxidation TGUs, as variations of this technology, such as the upstream process EUROCLAUS®, involve a hydrogenation and hydrolysis step that will affect the tail gas H_2, CO, COS, and CS_2 concentrations. Amine-based TGU systems depend on having an excess of hydrogen to reach thermodynamic equilibrium in the hydrogenation reactor. Therefore, the hydrogen content of the Claus section tail gas is increased either in the form of a supplemental hydrogen stream (of varying purity), or via a direct-fired reheater operated sub-stoichiometrically to produce additional H_2 and CO. The CO participates in the gas-water shift reaction to form additional hydrogen within the reactor vessel. Healthy catalyst leaves some, but relatively little, residual CO in the reactor tail gas.

The H_2S concentration in the tail gas will vary based on the number of Claus stages and the activity of each reactor. Direct oxidation reactors with good activity can achieve lower tail gas H_2S concentrations than even some amine-based TGUs. COS and CS_2 are formed in the reaction furnace due to the presence of CO_2 and hydrocarbons in the feed gases, and their concentrations are also related to reaction furnace temperature. Hotter temperatures favour COS formation, while relatively cooler temperatures favour CS_2 formation. Roughly 95% of these species are typically hydrolysed in the first Claus reactor, which is intentionally operated hot (300-320°C) for this purpose. Subsequent Claus reactors and sub-dewpoint TGUs have no effect on COS and CS_2. Some direct oxidation technologies, when the catalyst has aged, can form some COS. As stated previously, COS

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47 48 49 50 51 52

and CS_2 are hydrolysed over the amine-based TGUs hydrogenation catalyst bed. Residuals are very low, with COS being less than 20 ppmv typically and CS_2 being present only in severely deactivated beds.

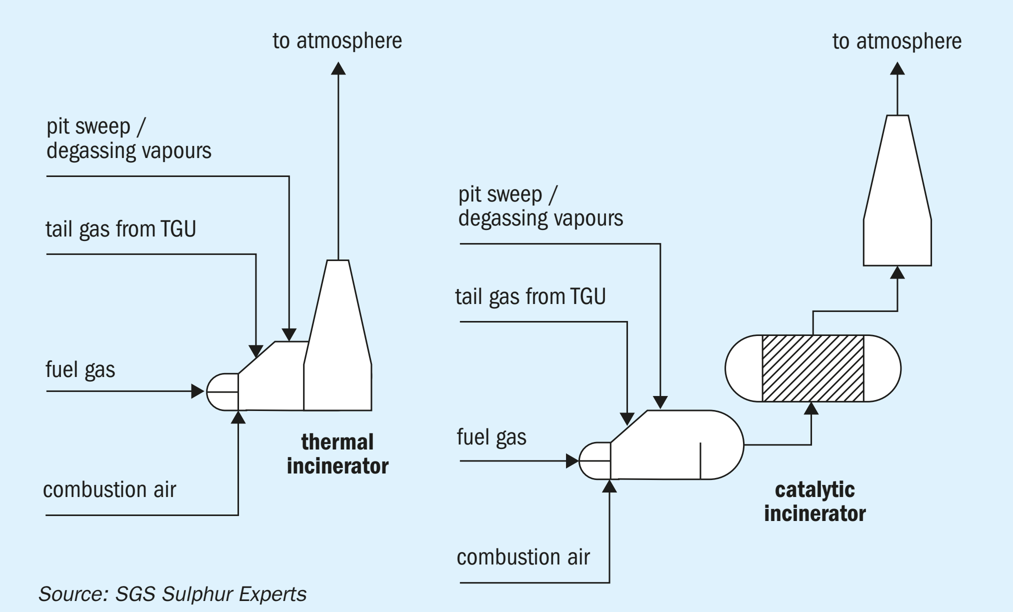
Hydrocarbons, including straight-chain and the infamous BTEX (benzene, toluene, ethylbenzene, and xylene), are rarely found in the tail gases regardless of the type of TGU system. If they are present, it is typically due to: an upstream direct-fired reheater operated with poor burn stoichiometry or burner damage; a contaminated supplemental hydrogen stream; or hydrocarbons caught in the amine loop from previous contamination.

Finally, elemental sulphur also needs to be considered as a process contaminant to the incinerator. Even if entrained liquid sulphur droplets are not present, most process tail gases will always have some residual sulphur vapour, which is a function of the H_2S concentration in the total feed and the outlet temperature of the system's final condenser. The tail gas from sub-dewpoint systems will naturally contain much less sulphur vapour than Claus and direct oxidation processes. Only the amine-based TGUs are elemental sulphur free. Unfortunately, most incinerators must also process a separate sulphur pit sweep or degassing stream which always introduces some elemental sulphur (and more H_2S) to the incinerator regardless of the type of TGU.

Types of incinerators

There are two main types of incinerator: thermal, and catalytic (Fig. 2). Thermal oxidisers use one or more burners within a refractory-lined chamber, and rely simply on adequate time, temperature, and mixing to achieve adequate combustion of the inlet contaminants. Catalytic incinerators also use a burner, but then pass the gas through a catalyst bed which increases the oxidation reaction rate. This allows those reactions to occur at colder temperatures than needed in thermal incinerators. Thermal incinerators are typically operated at temperatures between 650°C and 1,100°C. In a catalytic incinerator, the inlet temperature to the bed will be between 150°C to 475°C. Based on Sulphur Experts' database, roughly 28% of European SRU incinerators are catalytic while the remainder are thermal oxidisers. Europe has many more catalytic incinerators in service than North America.

Fig. 2: **Schematic of thermal versus catalytic incinerators**



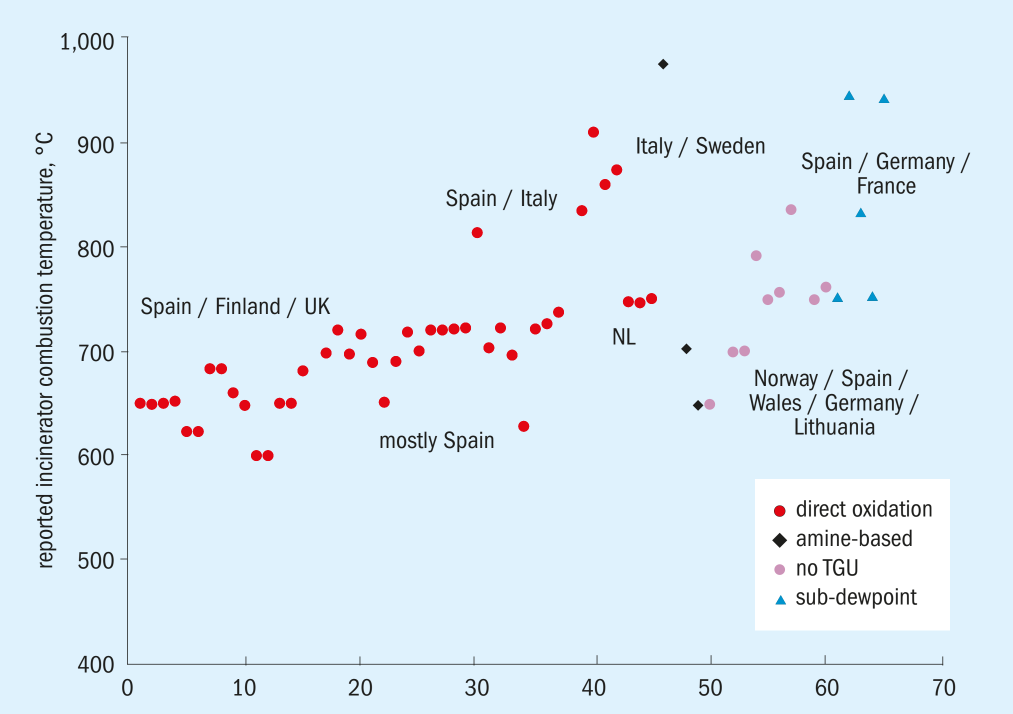
Source: SGS Sulphur Experts

Catalytic incinerators are generally more efficient than thermal devices in terms of plot space and operating cost. In SRUs, they are only truly effective in destroying H_2S. The standard catalyst used in catalytic incinerators is, unfortunately, very poor at burning COS, CS_2, H_2, or CO. There are specialised catalyst blends that would be able to burn these species, but they are designed for different units and have yet to be implemented in SRU systems. Catalytic incinerators may be a good choice for amine-based processes since they have less of these contaminants. In addition, most configurations require that the process feed gas have a low heating value (to control the temperature increase across the catalyst) and a low particulate content (to avoid fouling the catalyst).

Thermal incinerator operation

There are two major operating factors that affect combustion efficiency: combustion temperature and oxygen concentration. Residence time and turbulence/mixing are more reliant on good design and construction. Therefore it is assumed that the incinerator burners have sufficient throughput to ensure the correct gas velocity through the nozzles and good mixing.

Fig. 3: **Reported thermal incinerator combustion temperature (°C)**



Source: SGS Sulphur Experts

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Combustion temperature

Fig. 3 shows a compilation of European thermal incinerator combustion chamber temperatures as recorded by Sulphur Experts since 2015. Only tests which included analytical measurements of the stack gas are included. The data have been filtered to remove duplicate testing of the same incinerator, although several refineries employ two or more incinerators to process the SRU tail gas, in which case, all incinerators are listed. Duplicate testing of incinerators over several years has also been removed, and the most recent test always presented. Generally speaking, a facility will commit to one type of incinerator if multiple are required; likewise, an operator in a certain region may generally prefer one type of incinerator over the other. The same mentality is applied to temperature and excess oxygen targets. This is why several tests have comparably similar combustion temperatures. Data points are coloured according to the TGU system upstream. The most common countries for the data point regions are also listed for interest. As can be seen, the operating temperatures vary from 600°C all the way to almost 1,000°C. The average reported combustion temperatures for different groups of TGUs are:

- direct oxidation = 734°C
- amine based = 775°C
- no TGTU = 743°C
- sub-dewpoint = 843°C

The European averages are all significantly hotter than their USA counterparts, which run on average at about 700°C. Sulphur Experts have no universal target for combustion temperature, as the goal is simply complete (or at least adequate) combustion. Operators target whichever temperature allows them to comply with their local emissions limits. The European Union has limits and targets for airborne contaminants in the categories of:

- SO_2 (and associated sulphur oxides and reduced sulphur compounds such as H_2S and mercaptans);
- fine particulate matter ($PM_{2.5}$), meaning particles with aerodynamic diameters less than or equal to 2.5 µm;
- nitrous oxides (NOx);
- ammonia (NH_3); and,
- non-methane volatile organic compounds (NMVOCs), meaning all non-methane organic compounds capable of forming photochemical oxidants via reaction with NOx in sunlight.

Table 2: **Auto-ignition temperature in air of SRU incinerator inlet gas contaminants**

Contaminant	(°C)	(°F)
H_2S	232	450
COS	200	392
CS_2	102	216
Elemental sulphur	248-261	478-502
H_2	570	1058
Benzene	555	1031
CO	**620**	**1148**

Source: SGS Sulphur Experts

The Directive 2008/50/EC of the European Parliament consolidated as of 2015 details the emission thresholds for other additional contaminants including lead, benzene, and carbon monoxide, among others. Each country, or even region, may of course impose its own stricter limit. Several of these regulated compounds do not exist in SRUs, so only the relevant ones will be discussed. Table 2 lists the main contaminants found in the SRU tail gas along with their auto-ignition temperatures in air. While these should not be used as exact operating temperature targets, the table shows which contaminants are the most difficult to combust and the minimum temperatures required to do so.

NOx and SO_3 are mainly formed inside the incinerator, especially when run too hot and with too much air. As stated previously, benzene would generally only appear in the feed to the incinerator if it was in the fuel gas, but typically this is not an issue.

Regulations surrounding CO emissions are due to its role as an ozone precursor, similar to nitrogen oxides. CO contributes to the formation of tropospheric (ground level) ozone which can negatively affect human health and also indirectly contributes to climate change. It's important to note that CO limits were typically written for fired equipment in power plants, boilers, heaters, and catalytic cracking. Their aim was to avoid CO formation in the burner itself, not necessarily to fully combust incoming CO. Although the individual country regulations for CO differ, many of them are based on the 2015 "Best Available Techniques (BAT) Reference Document for the Refining of Mineral Oil and Gas Industrial Emissions". This documents states the following:

- CO emissions from partial combustion processes range from 20 to 42 mg/Nm³ at 3% O_2;
- the BAT-associated emissions levels for CO to air from a combustion unit are less than or equal to a monthly average of 100 mg/Nm³;
- "In the case of conventional firings, a CO concentration below 50 mg/Nm³ [43 ppmv] is achievable at temperatures above 800°C, at sufficient air delivery and sufficient retention times".

Generally speaking, most European countries adhere to the CO maximum emission limit of 100 mg/Nm³ at 3% O_2, if not less. Since CO is the hottest temperature hurdle for good combustion, this may explain why European incinerators run hot compared to many of their North American counterparts, where most locations do not have as strict limits, when they have them at all.

Another complicating factor is that European refineries often have a waste heat recovery system on the waste gas. This produces steam which is useful elsewhere in the unit or refinery and encourages operators to run the incinerator at temperatures hotter than necessary. It also limits the range of temperatures that can be targeted. For comparison, North American incinerators generally do not have a waste heat recovery system. As this limitation is facility-dependent, it will not be discussed in this article. However, consideration should always be given to downstream equipment and utility requirements when optimising the incinerator.

Excess oxygen

Excess oxygen (O_2) is a metric used to ensure the right amount of air is provided to completely oxidise the species of interest. Many facilities put an oxygen analyser on the outlet of the incinerator to monitor this parameter. This may be a passive analyser or it may be connected to the combustion air control scheme. From an efficiency perspective the ideal excess oxygen target is between 2 and 5 mol-%. Operation with less than 2% may not completely burn the target species, especially if the fuel gas composition is

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unstable, if there is a shift in load to the incinerator such as a change from low-to high-sulphur crude, or during the moment of instability such as when the TGU is bypassed. Operating with more than 5% excess O_2 also does not significantly improve combustion efficiency. Rather, it has a number of disadvantages that include increased risk of sulphur trioxide (SO_3) formation and the associated corrosion and plume visibility and an increased risk of nitrogen oxide (NOx) formation. Furthermore, adding more air than necessary increases the amount of mass that needs to be heated to the target temperature – this wastes fuel, which may have cost implications, depending on its source and value.

The measured excess oxygen concentrations for the same tests as shown in Fig. 3 are provided in Fig. 4. The same filtering parameters have been applied as were used for the combustion temperature data.

As can be seen, most of the tested incinerators use a target excess oxygen range of 2 to 5%. None of the tested sub-dewpoint TGUs had O_2 values more than 5%, for example. Of those which operated with more than 5% excess O_2, the averages are as follows:

- direct oxidation = 8.5%
- no TGTU = 7.7%
- amine-based = 8.5%
- sub-dewpoint = 4.0%

Optimised European thermal incinerator

To standardise the optimisation process, the Aspentech HYSYS® Sulsim package was used to simulate a theoretical 100 t/d 3-stage Claus unit, operating at a 2-to-1 H_2S/SO_2 tail gas ratio with a final condenser outlet temperature of 135°C. This section was then simulated after attaching the four different TGU systems using good KPIs and with incinerators using the average temperature and excess oxygen concentrations found in the historical data.

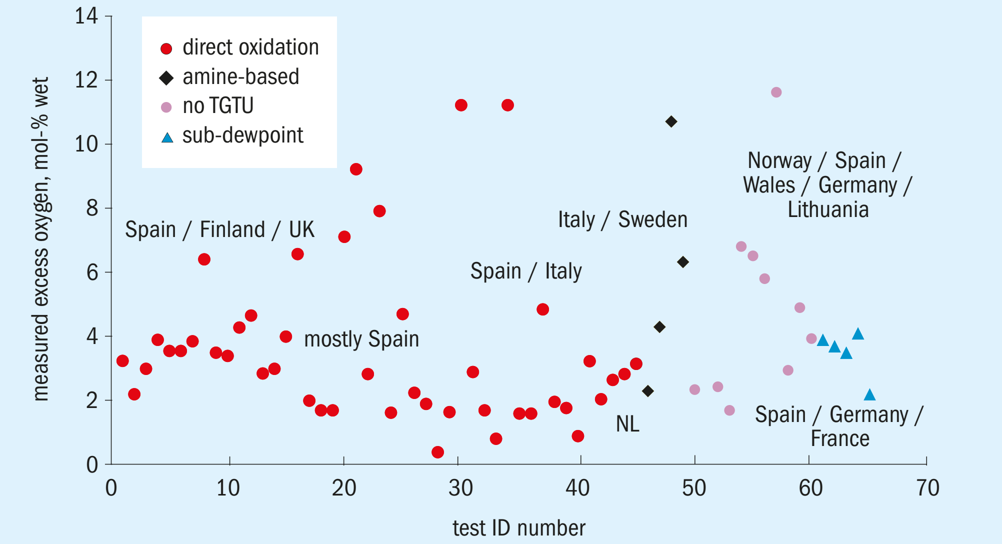
Temperature optimisation

As mentioned earlier, European incinerators typically run hot due to their CO emissions regulations. But as CO is regulated mainly due to concerns of human health, and not because it is a greenhouse gas, it is not possible to optimise temperature on the basis of CO_2 equivalence.

Many facilities operate their incinerators hotter than 800°C to adequately combust CO. But Sulphur Experts' testing data from 48 historical European tests on thermal incinerators shows that the 100 mg/Nm³ (about 80 ppmv) BAT limit can be achieved at temperatures as cool as 625°C (Fig. 5). A more consistent and conservative target appears to be around 725°C. This is anywhere from 9C° to 118C° less than the average reported operating temperature, depending on TGU type. To operate colder successfully therefore requires either less inlet CO or better mixing efficiency.

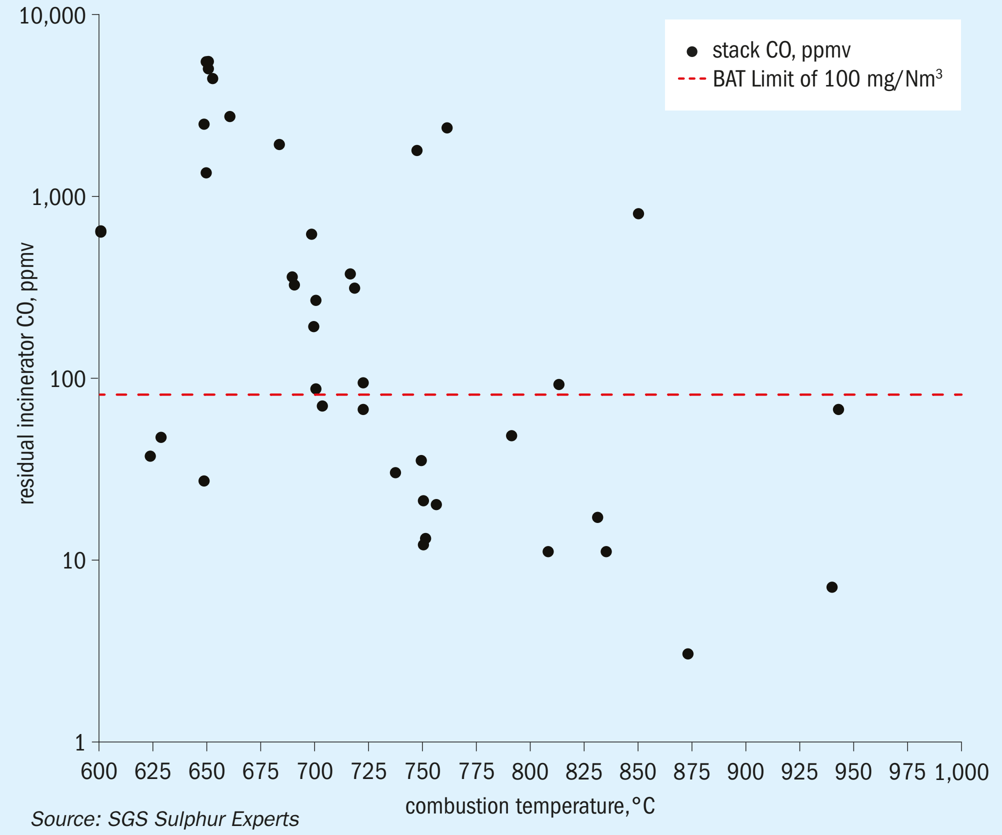
The amount of CO coming into the incinerator is mainly a function of CO_2 and hydrocarbon content in the feed gases to the SRU and the operating temperature of the Claus reaction furnace. These parameters are generally out of the control of the operator. The feed gas composition is dependent on upstream operations and crude type.

Fig. 4: **Measured thermal incinerator excess oxygen (mol-%, wet)**



Source: SGS Sulphur Experts

Fig. 5: **Measured CO concentration leaving thermal incinerators**



Source: SGS Sulphur Experts

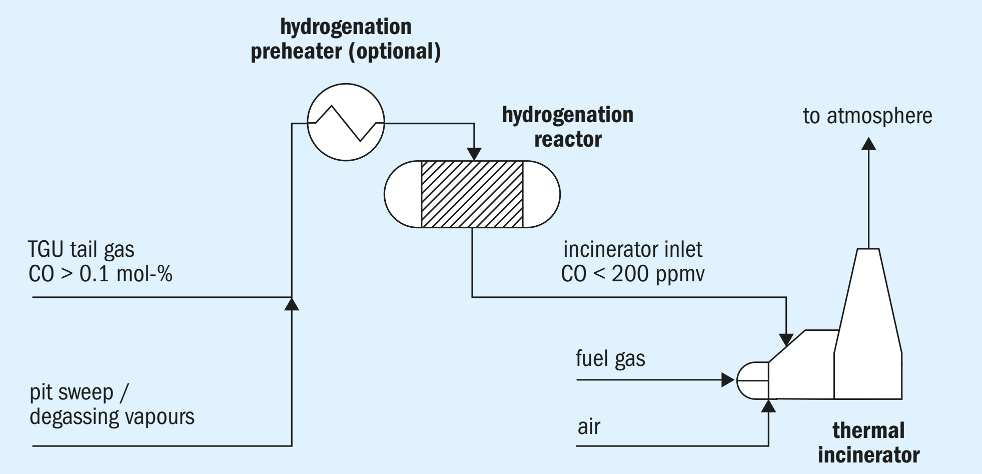
The reaction furnace temperature is set to ensure thorough destruction of contaminants (BTEX and NH_3) ahead of the Claus reactors. All TGU systems have similar tail gas CO concentrations, except for the amine-based one which takes advantage of the gas-water shift reaction in the hydrogenation bed to remove nearly all of the CO from the tail gas stream by changing it into H_2.

To take advantage of this reaction in non-amine-based TGU systems, a hydrogenation reactor could be placed just upstream of the incinerator (Fig. 6). This would convert a significant portion of the CO to hydrogen and most of the SO_2 into a combustible H_2S when it enters the incinerator. Data show that a healthy hydrogenation catalyst will reduce the CO concentration from approximately 1.0 mol-% down to 200 ppmv or less. In the incinerator, this means significantly less natural gas is required to meet the BAT CO emissions limit. Unlike with a traditional amine-based TGU, the other components such as the cooler, quench tower, and amine system are not required in this design. The normal concerns of SO_2 breakthrough in a standard amine TGU would also not be relevant. However, this option requires significant capital investment, some additional operating expense, and also requires more plot space. Overall the total capital cost of such a project would be in the seven figure range. This may become a more attractive option when CO_2 allowance prices increase in the future or if the CO emissions target tightens.

If the inlet CO concentration cannot be reduced in such a manner, perhaps a more cost-friendly approach to dealing with it is to improve the incinerator's CO destruction efficiency. Increasing the velocity of the inlet gas will enhance the mixing between the hot gas leaving the burner and the tail gas. Traditionally, the tail gas enters the incinerator through a single nozzle located downstream of the flame. Increasing the velocity means splitting the tail gas into multiple smaller-diameter nozzles. These could be oriented either radially or laterally (Fig. 7). This design can be relatively easily retrofitted to existing equipment with some additional piping and changes to the incinerator refractory. As all SRU operators know, good temperature management of the tail gas line is needed to prevent elemental sulphur from condensing and solidifying in cold spots to prevent plugging and underdeposit corrosion.

Either one or both of these changes (reducing the inlet CO, and maximising CO destruction efficiency) may be the key to achieving the BAT limit with a combustion temperature of only 725°C. Effects of optimisation were modelled using the direct oxidation and sub-dewpoint TGUs as these had the coolest and hottest combustion chamber temperatures,

Fig. 6: **Tail gas hydrogenation before the incinerator**



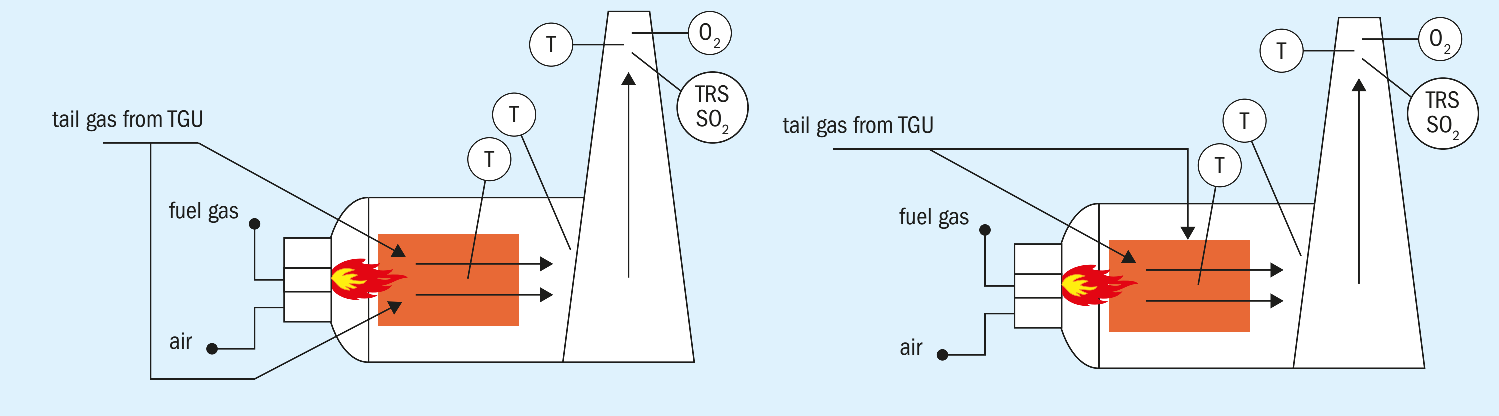
Source: SGS Sulphur Experts

Table 3: **Optimisation of combustion chamber temperatures**

TGU type	Direct oxidation	Sub-dewpoint
Average reported combustion temperature, °C	734	843
Optimised temperature, °C	725	725
Reduction in natural use, Nm^3/h	26	150
Natural gas cost savings, €/year	81,000	464,000
Reduction in CO_2 emissions, tonnes/year	485	2629
Estimated annual cost for allowances, €/year	31,042	168,230
Annual equivalent no. of vehicles cars/year	105	571

Source: SGS Sulphur Experts

Fig. 7: **Examples of staged tail gas inlet configurations**



Source: SGS Sulphur Experts

respectively. The summary is provided in Table 3. The median price for one CO_2 allowance on the European Energy Exchange has been around €64 per tonne of CO_2 or CO_2-equivalent for the majority of 2024. At this price, the CO_2 allowance savings alone could be between €31,000 and €168,000 per year, depending on the original starting temperature and the size of the SRU. Based on the five-year historical average cost of European natural gas futures, natural gas savings could be between €81,000 and €464,000 per year. This configuration revamp may be best for those operators using purchased natural gas, or considered as a plan to implement when CO_2 allowance prices increase.

Table 4: **Optimisation of excess oxygen concentration**

TGU type	**No TGU, or sub-dewpoint**	**Direct oxidation**	**Amine-based**
Typical excess O_2, mol-%	7.7	8.5	8.5
Optimised excess O_2, mol-%		3.0	
Reduction in natural gas use, Nm^3/h	328	435	408
Natural gas cost savings, €/year	1.02 million	1.35 million	1.27 million
Reduction in CO_2 emissions, tonnes/year	5,931	7,802	7,208
Estimated cost for allowances, €/year	379,575	499,359	461,328
Annual equivalent no. of vehicles, cars/year	1,289	1,696	1,567

Source: SGS Sulphur Experts

Oxygen optimisation

By far the easiest and most accessible optimisation for any incinerator is to manage the excess oxygen in the waste gas – this directly affects the amount of fuel needed and the consequent CO_2 production for any temperature operating target. Correctly controlling the combustion requires that an oxygen analyser be installed on the stack or incinerator outlet, ideally where the temperature is cooler. Incinerator burners typically use a chamber temperature measurement to control the fuel supply and combustion air is provided on a stoichiometric ratio basis, or managed manually. The new oxygen analyser can be passive but the most benefit will come from an on-line feedback control system that acts directly on the combustion air supply.

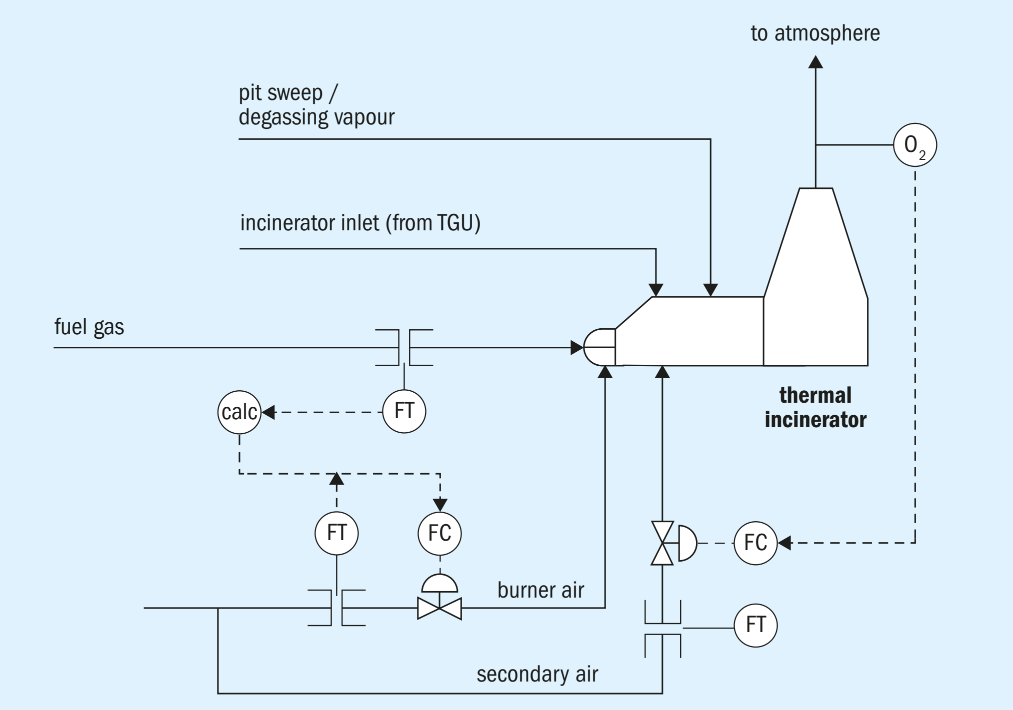
Table 4 shows the results of the oxygen optimisation on incinerators in various TGU types burning natural gas. The sub-dewpoint systems were not included as all historical data showed oxygen concentrations were less than 5%. It is assumed that these systems would respond similarly to plants without a TGU.

The results show that this simple optimisation can result in a reduction of approximately 390 Nm^3/h of natural gas for a 100 t/d European SRU. This directly translates to savings of approximately €1.2 million per year based on current natural gas futures prices. This will not be realised for those refineries using their own fuel gas. Regardless of the fuel source, this simple optimisation will reduce CO_2 emissions by approximately 7,000 tonnes per year. At the current median price of CO_2 allowances at €64 per tonne, this translates to potential savings of around €450,000 per year. Alternatively, unused allowances can be sold on the market to generate a true profit. Against the typical cost of purchasing and installing a stack oxygen analyser, the payback period would be very short.

To put this simple change into a more social context, it is the equivalent of removing around 1,500 passenger vehicles from the road every year. Other benefits of this optimisation include less risk of exceeding SO_3 or NOx emissions limits, less chance of corrosion in the piping, stack, and instrumentation, and a reduced risk of visible plumes which may affect the operator's reputation in the community. This latter benefit is quite valuable given how close many European operators are located to municipal centres.

There are many types of oxygen analysers on the market specifically designed to handle the high temperature and other conditions that exist in the SRU incinerator yet requires some care in choosing a technology. For example, zirconia-based oxygen sensors do an excellent job but may give inaccurate readings if there are residual combustibles in the stack. Tunable laser diode technologies would work well in such a service (for example, in catalytic incinerators which do not handle hydrocarbons well), but would have a significantly higher capital cost.

Fig. 8: **Example of staged air with control system**



Source: SGS Sulphur Experts

As stated, oxygen analysers are best employed as part of the control scheme of the incinerator. The oxygen measurement should be used to control the combustion air flow rate to the burner. However, this scheme may also run into operational challenges if the control action causes the flame to destabilise. The more desirable arrangement would have a staged-air system (Fig. 8) where the fuel gas enters the burner box with the first portion of air needed for 100% combustion of the fuel. This air flow rate is solely dependent on the fuel gas flow rate and a known air-to-fuel gas ratio. The amount of fuel gas delivered is usually determined by a temperature measurement in the incinerator. The secondary air stream enters downstream of the flame. This flow rate is controlled by a feedback loop using the new stack oxygen analyser. This setup allows the flame to remain stable while still allowing fine control over the excess oxygen. It also helps to maximise the flame temperature (resulting in better combustion) and avoids equipment damage caused by flame impingement on the burner or misdirection. Finally, it is standard industry practice that loss of flame in the incinerator should trip the SRU immediately or within a period of at most 30 minutes. Ensuring flame stability helps to maximise runtime even during transient operation periods.

Summary

European SRU incinerators typically operate hotter and with more combustion air than required. Optimisation of these two parameters will allow operators to reduce their fuel consumption while simultaneously reducing CO_2, NOx, and SO_3 emissions. The financial benefits are two-fold: direct savings on operating costs from less natural gas usage; and the ability to either reduce the purchase of, or even sell CO_2 allowances back to, the European Energy Exchange. The potential savings given in this article are for a theoretical SRU with 100 t/d of inlet sulphur.

Incinerator operating temperature optimisation is complicated by the amount of CO entering the incinerator since it is a regulated species. This affects the large number of non-amine based tail gas technologies in service in Europe, the prevalence of catalytic incinerators which do not reduce CO, and stringent CO emissions regulations based on a well-meaning but misguided understanding of the role of the SRU incinerator. Reducing the amount of CO leaving the incinerator may be possible by retrofitting incinerators with, for example, staged tail gas inlet nozzles to improve mixing and therefore CO destruction efficiency, or by installing an upstream hydrogenation reactor to convert most of the incoming CO to H_2. The incinerator can then be run cooler but this comes with the associated capital and operating costs. Regardless of the chosen route, by minimising the operating temperature it is estimated that fuel use can be cut by between 3 and 24%, correlating to annual savings of up to €464,000 for natural gas. Correspondingly, the estimated reduction in CO_2 emissions can be up to 2,600 tonnes per year, roughly valued at €168,000 per year, regardless of the fuel source. These optimisations may best be left for future planning should CO_2 allowance prices increase or if CO emission targets become stricter.

Incinerator excess oxygen optimisation is a very accessible tool available to every operator and offers the quickest reward. Simply controlling the excess oxygen alone to 3% can save up to €1.3 million per year in fuel use, and up to €500,000 per year from reductions in CO_2 emissions. This is the same as taking 1,500 passenger vehicles off the road every year. These numbers mean adding the necessary instrumentation and control scheme will pay out very quickly. There are also other possible optimisations around the incinerator that will improve system reliability and minimise unit trips. It is hoped that these potential savings will encourage SRU operators to explore this relatively simple process:

- determine the precise local emission limits for your incinerator;
- determine the concentrations of the controlled species in the SRU incinerator feed gases;
- model and then field test to determine the lowest combination of excess oxygen and incinerator temperature which will achieve the required emission;
- evaluate necessary permit changes or discuss options with permitting authorities;
- change the incinerator operation. ■

Acknowledgements

The authors would like to acknowledge the many individual European SRU sites that have shared their permits and their understanding of the permitting process with Sulphur Experts over the years. Regional regulations were also collected with the help of the SGS network, and technical information about operation of oxygen analysers is courtesy of Novatech. The authors would like to give thanks for their contributions as well. The authors would also like to acknowledge the historical incinerator studies and incinerator model development conducted by past Sulphur Experts colleagues starting as far back as the 1970s; their work is the basis for much of the modelling presented in this article and has been responsible for significant fuel gas savings and CO_2 reductions for over 40 years.

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Decarbonisation in the sulphuric acid industry

New concepts focused on the transfer and combination of existing sulphur and sulphuric acid technologies to support decarbonisation of the sulphuric acid industry are being investigated. In this article three research projects are discussed: sulphur dioxide depolarised electrolysis for green regeneration of spent acid, use of renewable heat and catalyst to the splitting process from sulphuric acid to SO_2 for reduction of fossil fuel consumption, and sulphur as an energy vector.

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Martin Kuerten, Jonas Michels (GRILLO Chemicals GmbH)

Industry is seeking new concepts and ideas to reduce the use of fossil energy sources in favour of renewable energy like green electricity and solar energy. The sulphuric acid industry has the possibility to contribute to this goal with new technology approaches. Grillo Chemicals, a sizable player in the European fresh and spent acid market, together with the research centre Deutsches Zentrum für Luft- und Raumfahrt (DLR), and other research institutes are part of an international consortium working on different research projects. The projects focus on the transfer and combination of existing technologies with new ideas, applying innovative concepts to established sulphur and sulphuric acid technologies. The main objective of this article is to present these approaches and broaden the outlook for possible synergies and new opportunities. While the approaches discussed are R&D projects, there are already very promising results for steps towards commercial implementation.

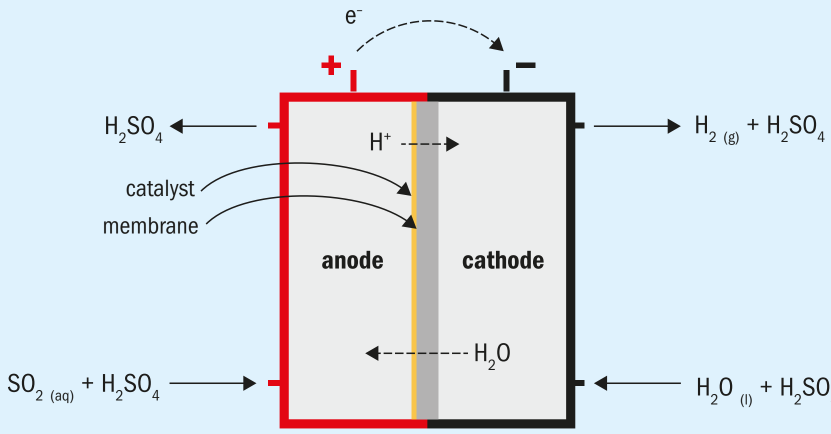
Sulphur dioxide depolarised electrolysis

Research project EU-HySelect[1] for green regeneration of spent acid focuses on the implementation of sulphur dioxide depolarised electrolysis (SDE) in a sulphuric acid recycling plant. SDE is a modified water electrolysis concept producing hydrogen and sulphuric acid out of SO_2 and water. In this electrolysis, sulphur dioxide and water form sulphurous acid, which is used to depolarise the anode. Sulphuric acid is produced yielding two protons and two electrons, which pass through the electrolyte separator and are conducted via an external circuit respectively, towards the cathode, where they are recombined forming hydrogen. This requires electrical power with a theoretical cell potential of only 0.17 V corresponding to about 14% of conventional water electrolysis exhibiting a theoretical voltage of 1.23 V[2].

Fig. 1 shows a schematic representation of sulphur dioxide depolarised electrolysis.

The sulphur dioxide depolarised electrolyser has the potential to significantly reduce the amount of electrical power required compared to conventional water

Fig. 1: **Schematic representation of sulphur dioxide depolarised electrolysis**



Source: Grillo

Table 1: **Reactions in sulphur dioxide depolarised electrolysis**

	Reaction	Temperature (°C)	Theoretical potential (V)
Electrolysis	$SO_2 + 2H_2O \rightarrow H_2SO_4 + H_2$	50	0.17
Anode	$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H^+ + 2e^-$		
Cathode	$2H^+ + 2e^- \rightarrow H_2$		

Source: Grillo

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electrolysis and offers promising effects for hydrogen production, especially in an industrial context. So far, reported experimental SDE electrolysers are cloned from water PEM stacks, consisting of two electrodes and a proton exchange membrane, which allows H^+ ions to pass through, similarly to PEM fuel cells. The electrode active layers are usually made of carbon-supported platinum catalysts. In this configuration, reasonable potentials (0.7 to 0.9 V) might be obtained at current densities 0.2 to 0.4 A/cm² at 60-80°C, however SO_2 carryover through the PEM membrane leads to its reduction to elemental sulphur (Pt catalyses this reaction) and parasitic losses, reducing SDE performance in terms of hydrogen produced. This decreases the reliability of the process as frequent cleaning of the system is required and formed sulphur needs to be properly disposed of.

Current efforts are aimed at tackling engineering challenges in terms of SO_2 carryover, corrosion resistance and industrial scale-up of the process. These efforts focus on the development of catalysts, membranes and membrane electrode assemblies (MEAs), without the use of critical materials (Pt or Pd), such as Au, and a significant decrease of SO_2 crossover, as is the case for polybenzimidazole (PBI) membranes. The experimental SDE setups developed in DLR are designed to guide the jump from the lab-scale SDE unit to a 30 to 40 kW_{el} pilot unit electrolyser, which is planned for installation in the premises of Grillo.

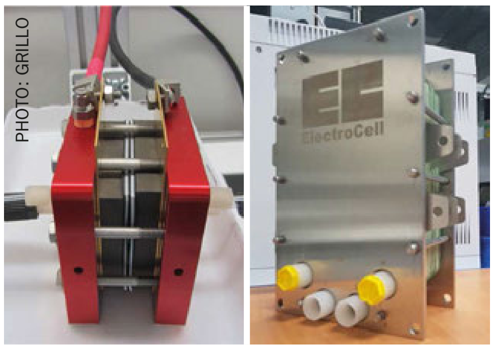

Fig. 2: Cell[3] and stack[4] for SDE in the experimental setup at DLR

Fig. 2 shows the cell and stack for SDE in the experimental setup at DLR and Fig. 3 is a block flow diagrams of the SDE experimental setup at DLR.

Produced hydrogen can easily be used for thermal processes, i.e. the combustion of spent sulphuric acid in recycling processes as in Fig. 4. Numerous possible implementations in other industrial processes exist, where SO_2 is a waste stream that cannot be directly converted to sulphuric acid, for example, applications within sulphuric acid production with a sulphur burner, in the non-ferrous metal industry and in fertilizer production.

Sulphuric acid splitting

Another research focus towards a circular economy is the improvement of the splitting process from sulphuric acid to SO_2. The use of catalysts to lower the required temperature of the splitting reaction and the use of renewable heat in the thermal process for reduction of fossil fuels consumption are promising options. Renewable heat can be supplied to the process via concentrating solar technologies (e.g., heliostat field and solar tower) or via options for renewable heat storage (latent heat or chemical energy storage).

Catalytic sulphuric acid splitting

Sulphuric acid splitting (SAS) is the sum of the thermal dissociation of sulphuric acid (H_2SO_4) first to water (steam) and sulphur trioxide (SO_3) and the subsequent catalytic dissociation of SO_3 to sulphur dioxide (SO_2) and oxygen (O_2). These two reactions, sulphuric acid decomposition (SAD) and sulphur trioxide splitting (STS), are performed experimentally in combination: concentrated sulphuric acid from a reservoir is vaporised and driven first through a medium-temperature zone where its stoichiometric dissociation into steam and SO_3 takes place; the vapour mixture is then passed through the catalytic reactor at higher temperatures where the STS reaction is performed.

With respect to catalytic materials for SO_3 splitting, if expensive PGM-based catalysts are to be avoided, the next best possible solution is single or mixed oxides of abundant transition metals[5,6,7]. Indeed, many studies, have demonstrated that certain metal oxide compositions can ensure catalytic activity quite close to that of Pt/Al_2O_3 benchmark catalysts[8,9]. Such state-of-the-art oxide catalytic phases with, in principle, long-term stability (≥500 h) as well as limited deactivation (2-7%) as

Fig. 3: **Block flow diagram of the SDE experimental setup at DLR**

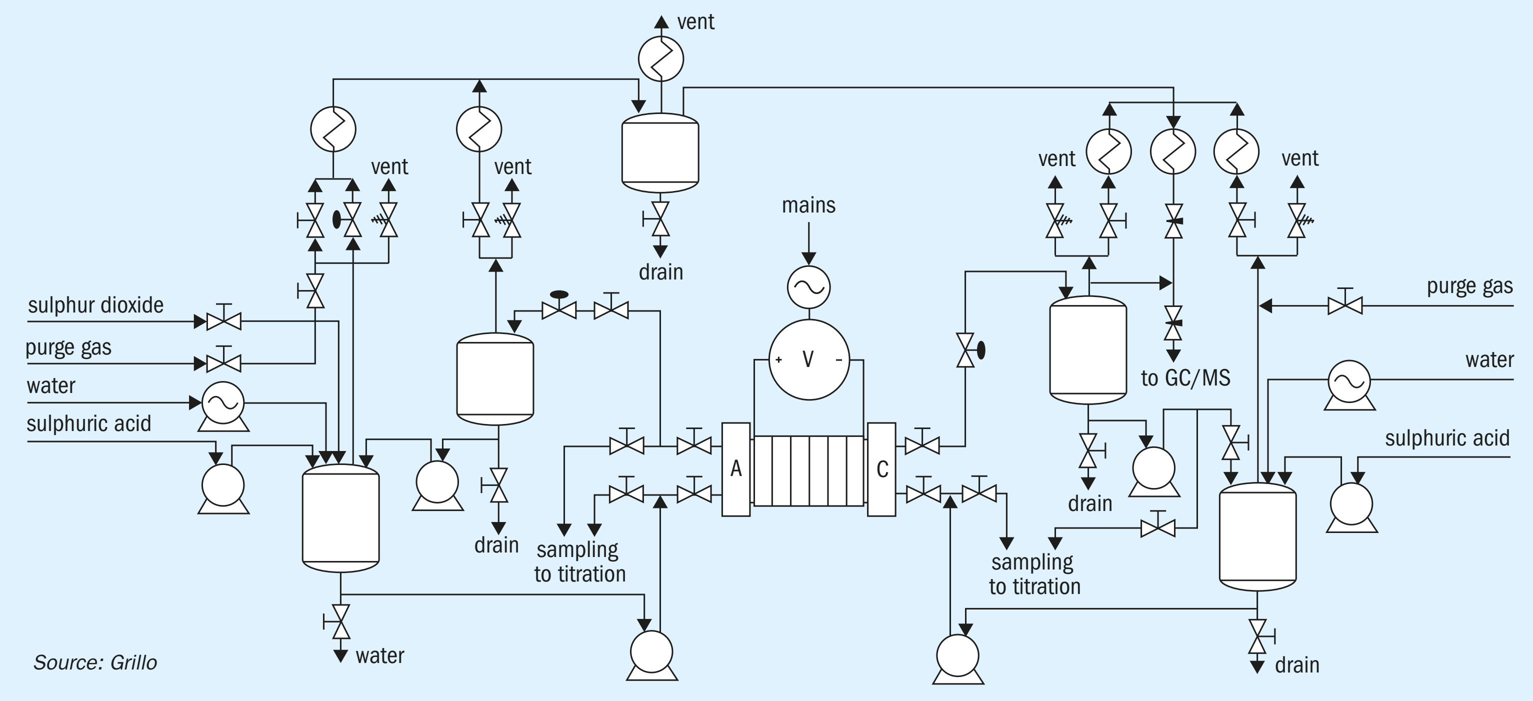

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Fig. 4: **Application of the SDE in Grillo's spent sulphuric acid recycling plant in Duisburg**

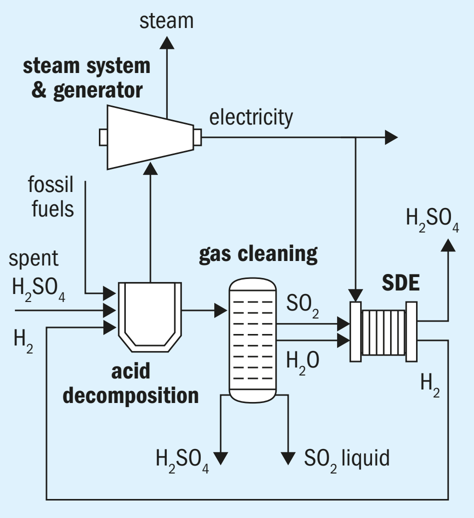

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Table 2: **Sulphuric acid splitting reactions**

	Reaction	Temperature (°C)	ΔH° (kJ/mol)
Sulphuric acid splitting – SAS	$H_2SO_{4(g)} \rightarrow SO_{2(g)} + H_2O_{(g)} + ½\ O_{2(g)}$		
Sulphuric acid dissociation – SAD	$H_2SO_{4(g)} \rightarrow H_2O_{\ (g)} + SO_{3(g)}$	450-500	+98
	or equivalent:		
	$H_2SO_{4(g)} \rightarrow H_2O_{\ (g)} + SO_{3(lg)}$		+134
Sulphur trioxide splitting – STS	$SO_{3(g)} \rightarrow SO_{2\ (g)} + ½\ O_2$	650-950	+99

Source: Grillo

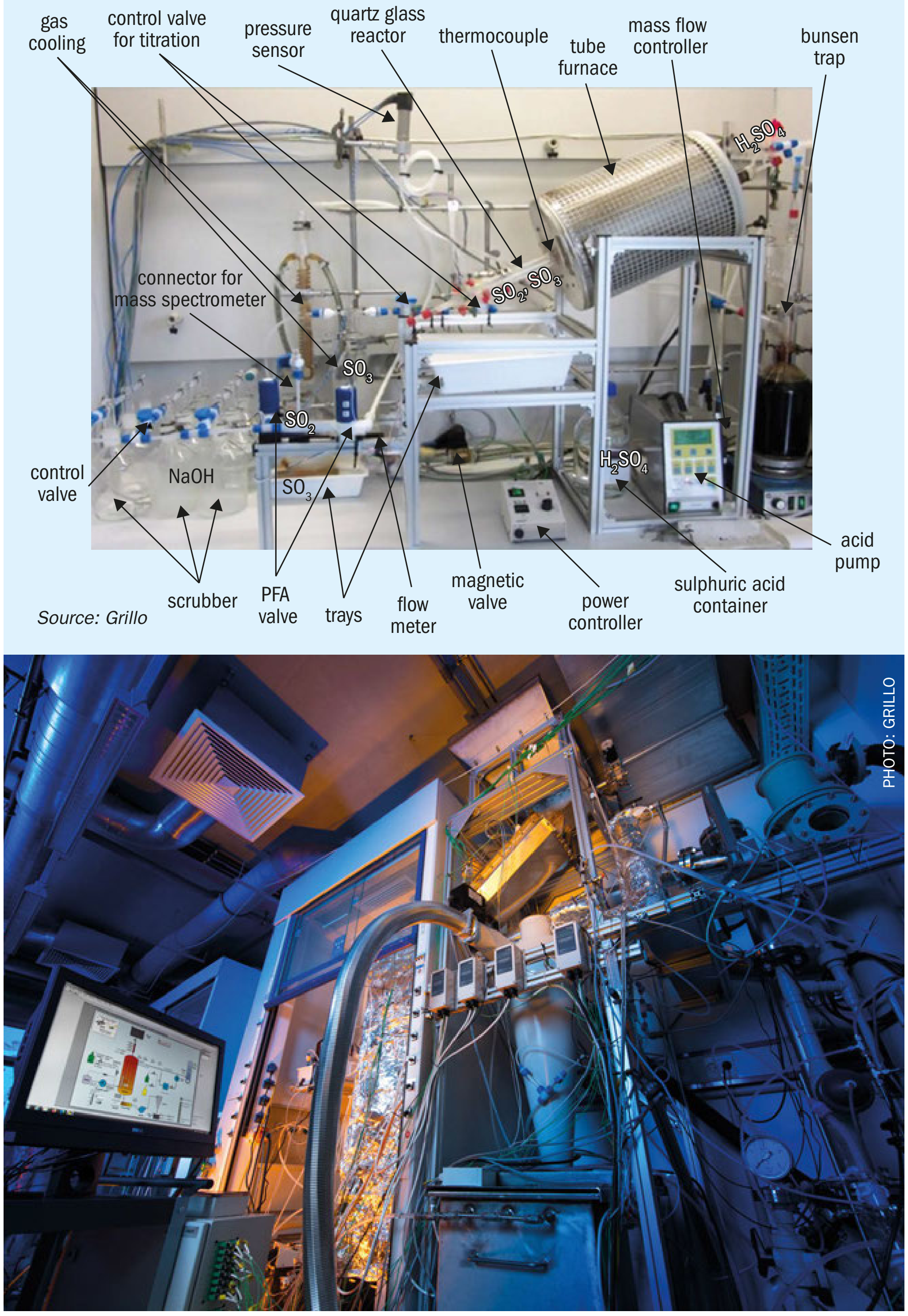
evaluated by lab-and pilot scale reactors (Fig. 5) include principally iron oxide (Fe_2O_3) or CuO-based compositions[10,11,12]. These oxides require temperatures of 800-900°C at 1 atm to achieve conversions close to equilibrium. Formation of stable sulphates is a common problem for both oxides and noble metals supported on oxides. Deactivation of metal oxides due to sulphate formation becomes more significant at lower reaction temperatures. Metal vanadate-based catalytic formulations suitable for lower temperature SO_3 splitting catalysis, i.e. ≤ 650°C have been proposed, specifically, Cu-V based catalysts[13] and (partially) molten phase vanadates[14].

These metal oxide compositions for low and high temperature catalytic sulphuric acid splitting are tuned, both compositionally and morphologically via suitable synthesis methods, and shaped into appropriate structures such as pellets, monoliths or foams consisting either directly of the metal oxide or coated on appropriate supporting materials (Fig. 6).

Sulphuric acid splitting with renewable heat

The high-temperature endothermic reaction of the catalytic sulphuric acid splitting can be driven with renewable heat in so-called allothermal reactors (Fig.7). This term was first coined by the nuclear energy research community to exploit the high temperature (in the range of 900°C) of the helium gas stream from nuclear very high temperature reactors (VHTRs)[19]. In an allothermal SAS reactor,

Fig. 5: **DLR lab-scale reactor[15] for catalytic sulphuric acid splitting (top) and pilot-scale[16,17] reactor (bottom)**



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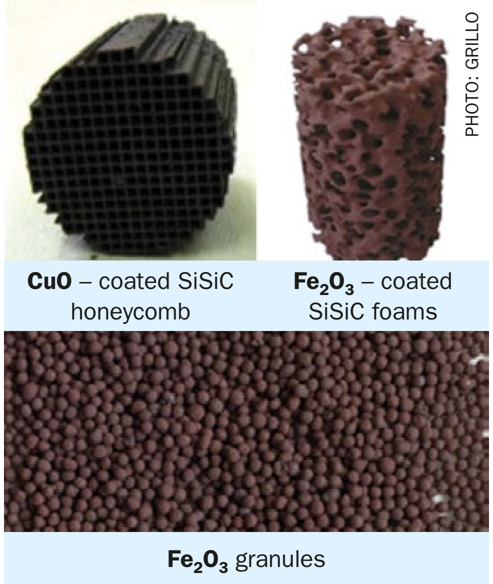
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CuO – coated SiSiC honeycomb

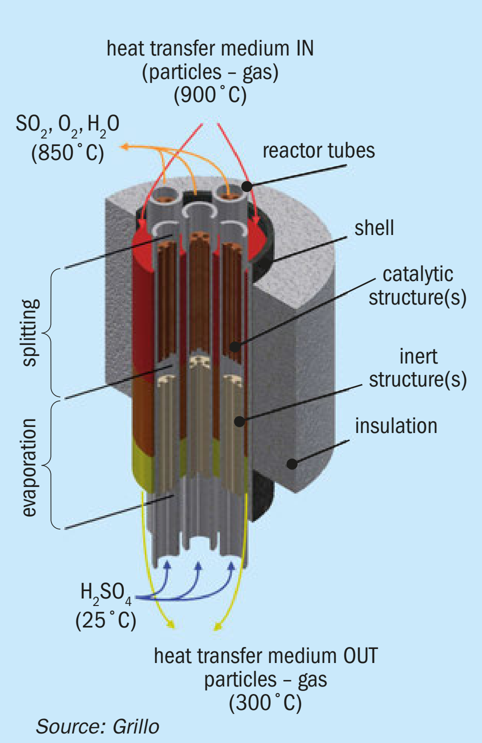
Fe_2O_3 – coated SiSiC foams

Fe_2O_3 granules

Fig. 6: Metal oxide structures[11,15,18] employed for catalytic sulphuric acid splitting in DLR

a heat transfer fluid (HTF), is heated and then is fed to the reactor featuring a shell-and-tube heat exchanger design. The HTF flows downwards on the shell side supplying the necessary heat for the STS reaction in the upper part of the reactor and for the SAD reaction in the lower part. On the tube side, rising sulphuric acid vapours come into contact with a non-moving catalytic bed containing the catalyst in various structured forms like granules, pellets, honeycombs or foams[15,20], as already presented in Fig. 6.

Fig. 7: **Concept sketch of a catalytic sulphuric acid splitting reactor powered by renewable heat[21]**



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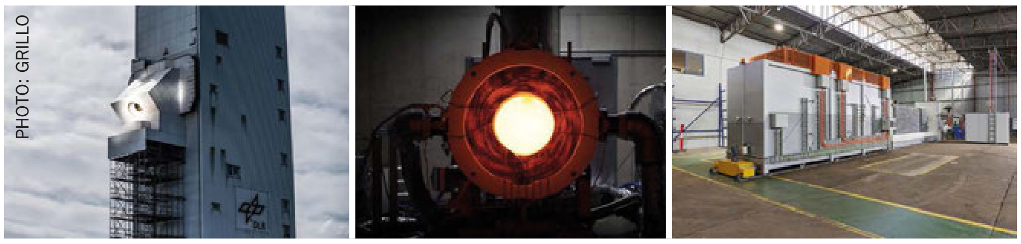
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Fig. 8: High temperature industrial renewable heat possibilities for catalytic sulphuric acid splitting, left: CentRec® solar receiver at the DLR solar tower in Juelich[27], middle: Synhelion solar receiver[28], right: SiBox® module for latent heat thermal energy storage[29].

Obviously, for such an operation, the HTF should be heated via renewable heat to a temperature exceeding the temperature required for STS (850 to 900°C). This can be accomplished with different approaches in a sustainable way. Concentrating solar technology (CST) systems come into play as a means to supply high-temperature renewable heat as the necessary energy source for the performance of this endothermic step, specifically CST tower plants[2,22,23]. Two such solar receivers for towers developed recently, capable of reaching the required temperature for SAS (and above) with a very promising commericalisation potential are shown in Fig. 8. The first is a centrifugal receiver developed by DLR utilising ceramic (bauxite) particles that reached a temperature of 950°C[24,25]. The second, developed by the company Synhelion, is based on direct absorption of thermal radiation by a gaseous HTF, similar to the well-known greenhouse gas effect[26] that can reach temperatures in the range of 1,500°C. In the former, particles can be used to sensibly store solar heat in a hot storage system (tank); the latter is also coupled to a porous solid thermal energy storage (TES) system. Thus, both can be employed also off-sun to thermally drive the SAS reaction in cases of either diurnal solar radiation interruption or overnight, guaranteeing SO_2 production. Alternatively, a third non-solar option for driving the SAS reaction with renewable heat (Fig. 8 right) could be by using latent heat, stored by a technology such as SiBox provided by company 1414°. In this case the latent heat storage module is charged with low-cost renewable energy when prices are low and stores it as heat in a silicon storage media. It can then consistently provide high-temperature air up to 900°C to the downstream SAS process.

The hybrid sulphur cycle

An interesting approach is the combination of the above-mentioned steps, the SDE with the catalytic splitting of sulphuric acid in (allothermal) reactors driven by renewable (e.g. solar) heat. The combination of both steps in a single process is called the hybrid sulphur (HyS) cycle, as presented in Fig. 9, originally proposed in 1975[23] and developed by Westinghouse Electric corporation. The process is called hybrid because of the combination of the thermal decomposition of sulphuric acid with the electrochemical oxidation of SO_2 with water (electrolysis) to yield hydrogen and re-generate sulphuric acid which is completely recycled in the process.

The HyS cycle is one of the most promising water-splitting (WS) thermochemical cycles (TCs) which combined with concentrating solar technologies (CST) has an inherently much higher theoretical efficiency potential than e.g., photocatalysis. Thermochemical water splitting cycles are a series of consecutive chemical reactions, their net sum being the splitting of H_2O to H_2 and O_2. DLR and GRILLO are investigating the experimental demonstration of the HyS cycle within the EU-funded project HySelect, with planned operation of the demo plant in 2026. A schematic of the proposed plant is shown in Fig. 10.

Sulphur as an energy vector

A further project, albeit with a lower technology maturity, opens up opportunities for sulphur as an energy vector in order to overcome the disadvantages of hydrogen. Instead of storing hydrogen it is possible to convert the produced SO_2 from sulphuric acid splitting with a downstream disproportionation reaction into elemental sulphur and sulphuric acid (Fig. 11). The renewable heat stored in the form of elemental sulphur is simple to store and to transport and ready to be used as an industrial energy carrier, dispatchable and on-demand when the energy is needed. DLR is investigating this so-called solid sulphur (SoSu) cycle with an international consortium in the EU-funded project Sulphurreal[31]. The project sets forth an innovative approach for thermochemical direct storage of concentrated solar irradiation harvested energy to solid elemental sulphur, a very energy-rich chemical to be used both as a chemical energy vector and seasonal storage medium for solar thermal energy as well as a renewable carbon-free source for power or high temperature heat generation. The concept is a combination of three major process steps, namely the decomposition of H_2SO_4 (as described in the previous sections), SO_2 disproportionation and elemental sulphur combustion, as originally proposed by General Atomics[31].

The solid sulphur cycle is a combination of the same sulphuric acid splitting reaction, followed by the disproportionation of SO_2 into elemental sulphur (S) and H_2SO_4. Elemental sulphur can then be combusted in air on demand to produce high-temperature heat and SO_2. The SO_2 from combustion can be converted back into H_2SO_4 to close the cycle via industrially established processes. The reactions of the SoSu cycle are summarised in Table 3.

The valuable outcome of this SoSu cycle is not a chemical product, but the high-quality sulphur-combustion heat at temperatures in excess of 1,200°C, suitable for combustion in gas turbines and hence allowing efficient combined cycle power generation. The SoSu cycle is also flexible enough to be operated on demand as an "open cycle", employing/providing material feedstocks (H_2SO_4, S, SO_2) in combination with sulphuric acid production or with desulphurisation of flue gas or natural gas. Solid S and H_2SO_4 can be stored economically and indefinitely using existing industrial technologies already used in the sulphuric acid industry under ambient conditions. Exploiting the very high energy density of solid S and its very low cost, this cycle is particularly suited (but not limited) to concentrating solar power plants with high-density energy storage.

Outlook

Three approaches have been presented (sulphur dioxide depolarised electrolysis, catalytic sulphuric acid splitting, sulphur as an energy vector) that are being actively pursued as viable add-on or supplementary technologies to existing industrial operations. These approaches carry great promise for a meaningful next step in decarbonisation of the industry by using sulphuric acid technology. ■

Table 3: **Reactions in the solid sulphur storage and power generation cycle**

	Reaction	**Temperature (°C)**	**ΔHo (kJ/mol S)**
Sulphuric acid splitting	$3H_2SO_{4(aq)} \rightarrow 3SO_{2(g)} + 3H_2O_{(g)} + \frac{3}{2}O_{2(g)}$	650-950	+826
Sulphuric acid disproportionation	$3SO_{2(g)} + 2H_2O_{(l)} \rightarrow 3H_2SO_{4(aq)} + S_{(s)}$	50-200	-254
Sulphur combustion	$S_{(l)} + O_{2(g)} \rightarrow SO_{2(g)}$	500-1500	-297
Contact process	$SO_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow SO_{3(g)}$	380-635	-99
Absorption	$SO_{3(g)} + H_2O_{(g)} \rightarrow H_2SO_{4(aq)}$	55-280	-176

Source: Grillo

Fig. 9: **Basic reaction scheme of the HyS cycle, main inlets and product hydrogen**[30]

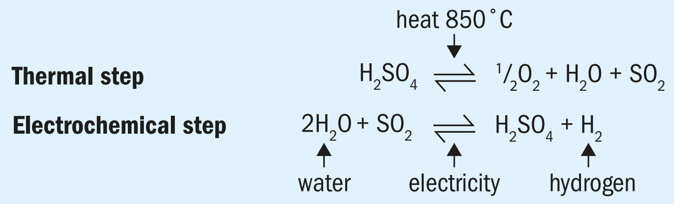

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Fig. 10: **Basic The demonstration plant planned for project EU-HySelect in DLR and GRILLO**[1]

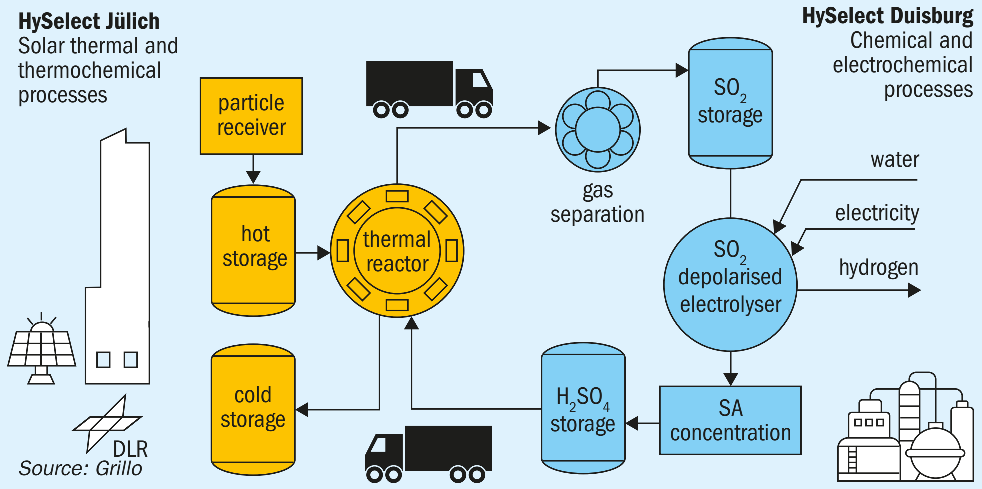

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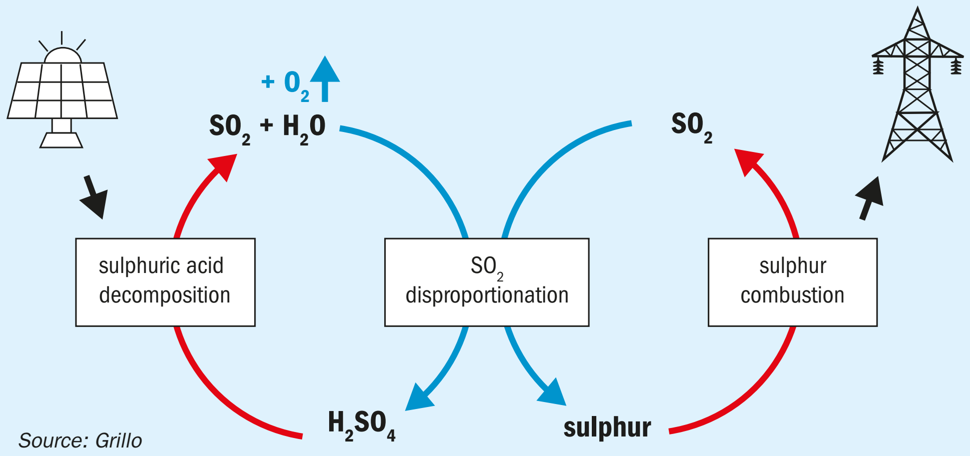
Fig. 11: **Conceptual process scheme for use of solid sulphur as a renewable fuel and for solar energy storage**[4]



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