1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27

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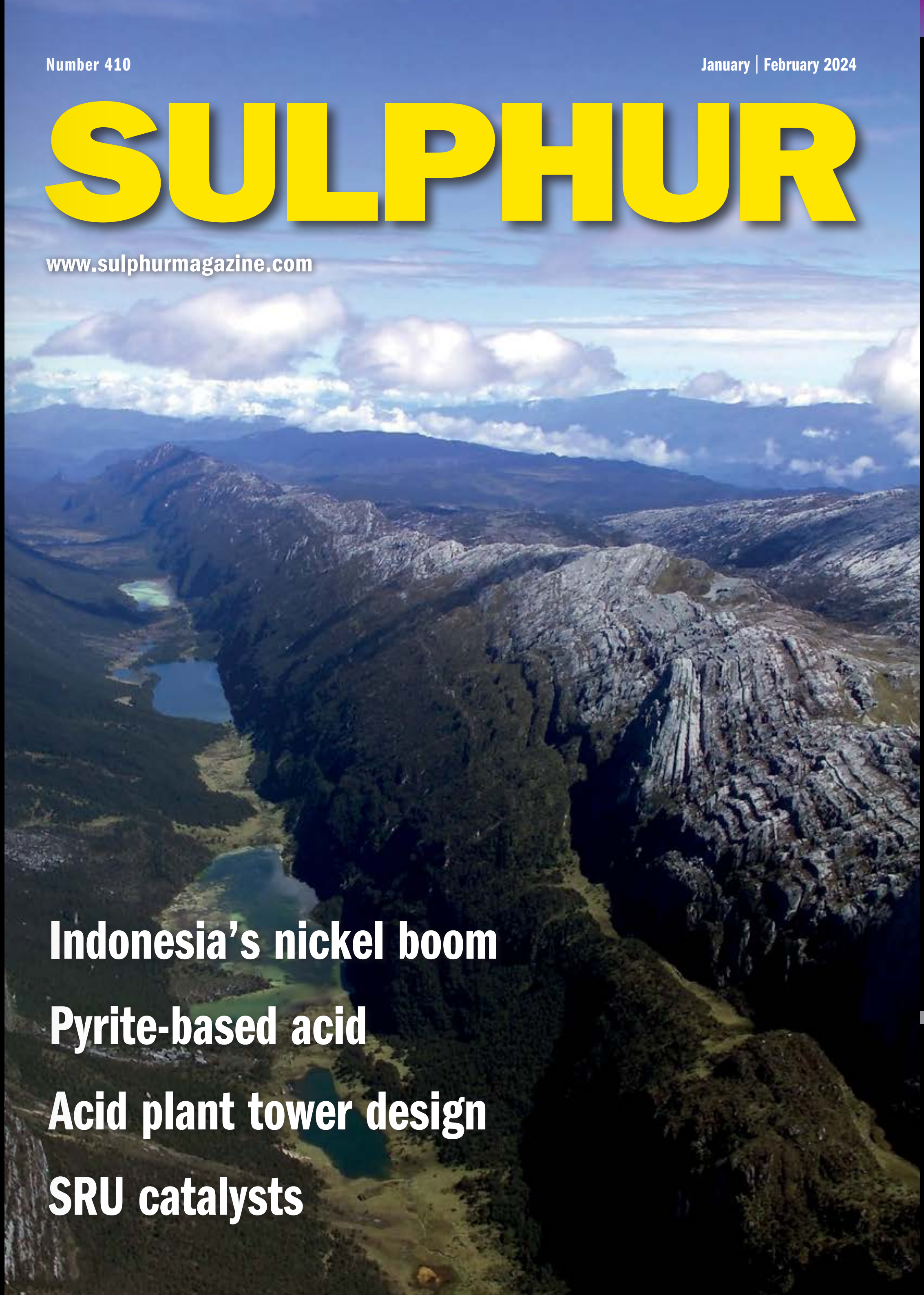

Indonesia’s nickel boom

Pyrite-based acid

Acid plant tower design

SRU catalysts

■ CONTENTS
What’s in issue 410

■ COVER FEATURE 1
Indonesia’s nickel boom

■ COVER FEATURE 2
Pyrite-based acid

■ COVER FEATURE 3
Acid plant tower design

■ COVER FEATURE 4
SRU catalysts

SULPHUR
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1
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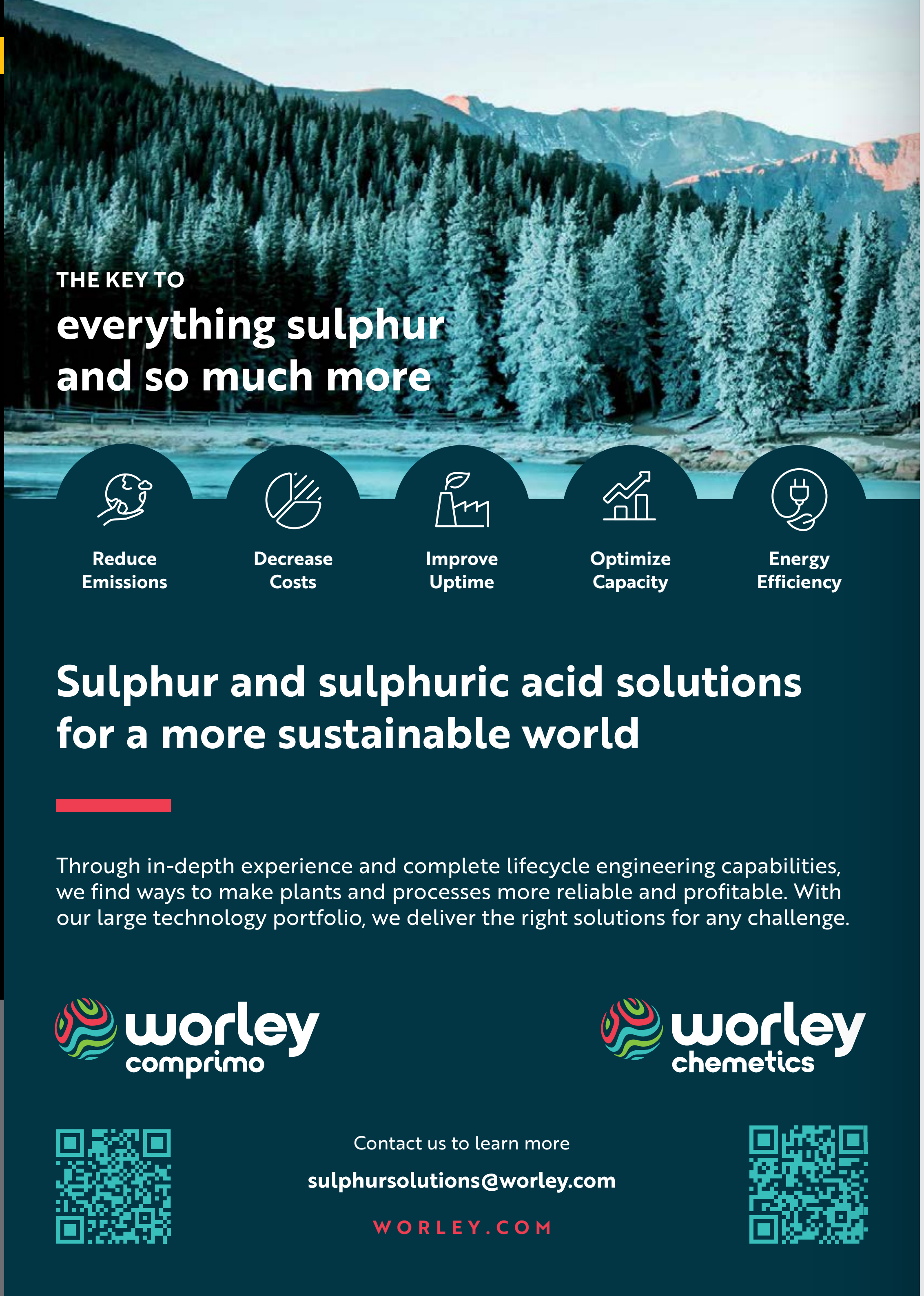
27



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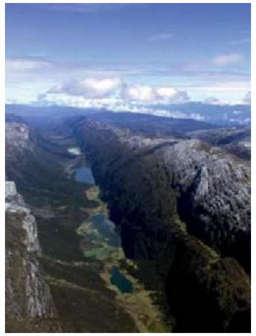

Cover: *The mountains near Grasberg mine, Indonesia. Photo: iStockPhoto*

CONTENTS

9 **Indonesia's nickel surge**
The nickel market has been through a period of unprecedented change over the past few years due to demand for batteries for electric vehicles, with Indonesia becoming a centre for production via high pressure acid leaching.

11 **The future of pyrite production**
Pyrite roasting as a source of sulphuric acid continues to be a significant, albeit minor sector of the overall acid market.

12 **Small scale sulphur recovery**
Small quantities of sulphur in a refinery or gas feed can present challenges for conventional large scale sulphur recovery techniques.

13 **Sulphur 2023 index**
A full listing of all news items and articles published in Sulphur last year.

14 **New low-density titania catalyst for improved sulphur recovery**
Axens has developed a new titania-based catalyst with increased porosity allowing customers to optimise their capex by either reducing the Claus reactor size or loading volume of TiO_2 catalyst.

16 **New impaction technology for acid plant towers**
MECS has developed a new impaction-based mist eliminator, Brink® Prime Impact™, which offers equivalent or improved efficiency at higher throughput and the same pressure drop as traditional impaction beds.

19 **Replacement of upper part of a co-current flow quench tower**
Steuler and Eco Services discuss a case study for the replacement of the upper part of a co-current flow quench tower using pre-lined workshop fabricated equipment.

20 **Back to the roots: single versus double absorption**
With increased demands to reduce SO_2 emissions and lower energy consumption, Clark Solutions highlights the advantages of single absorption sulphuric acid plants compared to double absorption plants.

22 **Cobalt-molybdenum catalyst activation in low temperature TGUs – Part 1**
Michael Huffmaster explores CoMo catalyst activation at low pressure, focusing on the impact of temperature and the composition of the sulphiding media on reaction kinetics, specifically the concentration of H_2, H_2S, and H_2O.

9

Nickel markets
Indonesia remains the driving force

19

Tower revamping
Brick lining an acid plant quench tower

REGULARS

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CRU

CONTENTS
What's in issue 410

COVER FEATURE 1
Indonesia's nickel boom

COVER FEATURE 2
Pyrite-based acid

COVER FEATURE 3
Acid plant tower design

COVER FEATURE 4
SRU catalysts

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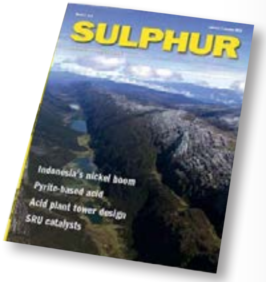
A return to the fold



We are very pleased to be able to tell you that, as of this issue, *Sulphur* magazine has a new publisher. Or rather, an old publisher, as the magazine is now once again part of the CRU Group.

Sulphur originally began life in 1953 as the *Quarterly Bulletin of the Sulphur Exploration Society*, a society formed to look for new sources of Frasch sulphur, which later became the British Sulphur Corporation. By the 1960s the magazine had become the *Journal of World Sulphur*, and finally simply Sulphur, while the British Sulphur Corporation was in turn acquired by CRU in the early 1990s. The magazine's content changed as the sulphur industry itself changed radically during those decades, moving from Frasch mined sulphur to recovered sulphur from sour oil and gas, and downstream demand for particularly phosphate fertilizer production expanded rapidly.

In 2007, CRU's Publishing division was spun off as a separate entity, BCInsight Ltd, as CRU sought to focus on its core activities of analysis, consultancy and conferences, but the new company retained the magazine staff who had been working on it for many years, and continued a close relationship with our former colleagues at CRU, liaising especially over CRU's industry conferences.

The current move back to CRU is in part a result of the changing nature of how people seek and acquire knowledge and network in a digitally saturated age. *Sulphur* will now be housed within CRU's new Communities business unit, headed by Nicola Coslett, CEO of CRU Communities, which will seek to strengthen engagement and facilitate knowledge-sharing and networking across the fertilizer and wider chemicals industries.

The move will also allow us access to CRU's Fertilizer consultancy division, with its unrivalled team of dedicated and highly experiencedanalysts, enhancing our ability to deliver even more comprehensive and insightful information to our readers. With so many new entrants into the ammonia, phosphate and fertilizer industries, the need for technical knowledge and insights has never been more important.

In the longer term, it will also allow us to make improvements to our product offerings that were beyond the resources of a small publishing company, and we hope to have more news on that in due course. But rest assured that the team writing and publishing the title remains the same as always. Myself and Lisa Connock, our Technical – and now Managing – Editor, and Marlene Vaz, our Sales Manager, will look forward to seeing you under our new guise at CRU's sulphur conferences during the year, at MEScon in Abu Dhabi on March 20-23 and of course at Sulphur + Sulphuric Acid in Barcelona in November. ■

> **"The need for technical knowledge and insights has never been more important."**

Richard Hands, Editor

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Price Trends

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Sulphur prices declined in Q4 following the increases seen during Q3, because of ample availability and limited spot demand. One contributing factor was that phosphate fertilizer producers in China, the largest importer of sulphur, have cut downstream production due to increased export restrictions. In addition, high sulphur stocks at Chinese ports and continuing high domestic sulphur production mean that domestic buyers have other options aside from international purchases.

Phosphate fertilizer price increases during H2 2023 have further improved sulphur affordability for consumers, although there is still the potential for price declines within H1. Nevertheless, affordability of sulphur relative to phosphates remains good even at forecast price levels, with affordability for metals markets also good. Q1 contract prices to North Africa were assessed at $90-100/t CFR.

Sulphur demand in Indonesia for nickel is set to increase further over the coming months following a big jump in imports since 2022, limiting the possible downside to global spot prices despite a weaker nickel market.

On the supply side, Russian exports have increased from the tightest periods that were experienced following the country's invasion of Ukraine, but prices need to remain high enough to draw exports out, particularly given logistics constraints.

Kazakhstan's Kashagan oilfield is facing government pressure to reduce its sulphur stocks, and sources indicate that it is moving crushed lump supply, adding to market length. However, Kazakh and Russian exports may be tighter for Q4 and Q1 due to the northern hemisphere winter reducing river navigation.

Availability from Vancouver has been strong due to relatively high production at sites in Canada, as well as increased remelting of solid sulphur stocks. Sources suggest that supply from Canada may be even stronger this year.

Production at refineries in other regions has been high to meet demand for refined products, particularly in the US. Although the market there has tightened from the exceptional surplus of the mid-year as the driving season has concluded, US availability still appears plentiful. US Gulf contract prices for liquid sulphur deliveries in the first quarter of 2024 were settled down $33/lt from 2023 Q4. This leaves the contract price at $69/lt FOB Tampa.

New project commissions and expansions accelerated last year, with Middle East producers adding considerable volume to the market. Much of the new capacity can access the market with low logistics costs, adding to the market surplus, though there are fewer capacity additions to come in 2024 and demand is expected to catch up with supply by next year. Meanwhile, Saudi Arabia has been selling crushed lump from stockpiles in addition to its new production. Domestic production in China is also set to continue increasing.

Overall, the recent growth in sulphur production, in addition to stock drawdown and high China inventories, is expected to limit the upwards potential for prices in the short term, and keep sulphur prices low relative to phosphates. Still, affordability continues to support raw materials purchasing and leaves room for price increases, especially if downstream production picks up as expected.

Some contracts for supply of liquid sulphur in northwest Europe in the first quarter of 2024 have now been reported settled at rollovers from 2023 Q4. The price range for Q4 was published at $103.50-123.50/t Benelux for barge/railcar, with the truckload range at $123.50-153.50/t CPT NW Europe, after settlements were reported at increases of $16.50/t from Q3. Increases in global prices over the course of Q3 meant that Europe had to follow the trend. Still, relatively weak demand within Europe due to a struggling industrial sector is expected to limit the increase. During Q4, global prices weakened, but tight availability in Europe meant that buyers were unable to achieve a decrease on Q1 contract prices. Molten sulphur availability in Europe is set to remain tight throughout the year despite weakness in the downstream caprolactam sector, as European production continues to decrease.

SULPHURIC ACID

Sulphuric acid prices are expected to decline further from their current levels, with slightly lower prices likely through 2024. The key risk remains to the downside and prices may be pushed lower if demand is weaker than expected. China, the key source of marginal seaborne acid supply, requires higher acid prices to draw out more volume, as domestic sales offer favourable pricing, although production is increasing further this year. Less Chinese exports are likely to be required in 2024, as some Asia/Pacific importers will have greater domestic availability. Smelters in Japan and South Korea have needed to commit 2024 supply and have sold on term agreements at prices from single-digit FOBs to low double digits.

Buyers in Chile are relatively well covered with contract supply, with the majority of volume agreed in the $120s/t CFR, increasing buyer resistance to high prices. Sources indicated that most of the volume on term contracts is below $130/t CFR for this year. Chilean buyers will likely be unable to source as much from Europe this year, necessitating that they pay to cover logistics costs from the Far East, limiting the downside to delivered prices.

Spot prices for acid sales into Chile were assessed stable at $130-140/t CFR in early January, though deals at the upper end of the range were increasingly unlikely, and forward offers were reported at much lower prices. The assessment is still up 59% from early August 2023, though the mid-point is down from a high of $280/t CFR in June 2022. Ocean swells in the New Year led to Chilean port closures until at least 8th January, according to sources, delaying offtake and reducing spot demand. There was some concern about potential knock-on effects reducing spot import demand over the coming weeks and months.

Market players are mostly bearish for the coming months, particularly for Asia/Pacific markets, as supply is set to climb considerably in India, Indonesia and China. The tone for Europe/Atlantic markets is a bit more positive as Brazil and the US seem to be relatively steady, Morocco's OCP is buying again, and there are some big European maintenances coming up, particularly in Q2.

India's import demand is under pressure as sulphur offers a more affordable raw material option. In addition, buyers are adding sulphur burner capacity, limiting merchant acid requirements, with additional smelter acid production also expected in India within 2024.

Indonesian imports increased steeply in 2023, but import demand there is also likely to decline as domestic production increases from both integrated sulphur burners and new smelting capacity, while sulphur will generally be more favourably priced.

In Europe, demand remains constrained, leading to ample acid availability. Industrial demand is not guaranteed to improve within the forecast period, but it is at least unlikely to weaken further, while a strong producer maintenance slate should prevent supply overhang.

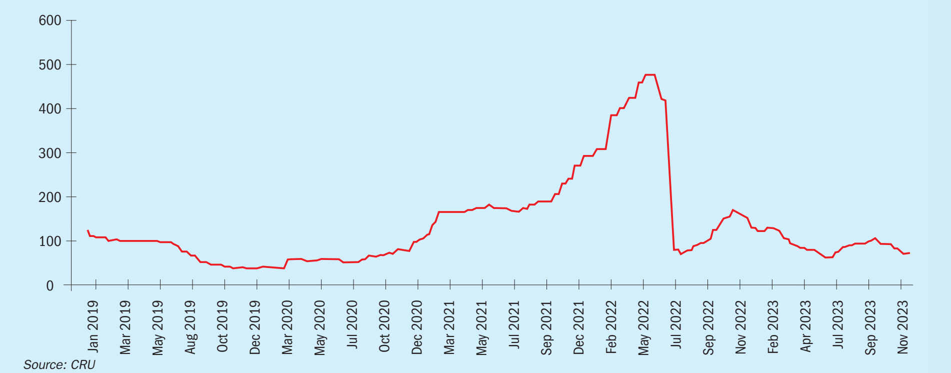
Renewed appetite from Morocco should absorb some European supply, but this will likely just replace some Chilean demand from last year. Morocco's continued demand will be a key determinant of market balance, and it is likely it's consumption will be slightly higher than last year, but still well below the highs of other recent years. Imports are also likely to be more spread through the year than in 2023, avoiding price shocks, with spot purchases likely to be more opportunistic.

Improving availability of smelter acid and sulphur in the US Gulf has been limiting merchant acid import requirements there. Though the sulphur market there may tighten slightly, it is unlikely this will push up acid demand and prices much, with sulphur prices still suggesting lower levels on acid.

Other import destinations such as Brazil have also had limited spot requirements, though downstream demand should be steady over the coming months.

Overall, acid affordability remains acceptable relative to downstream commodities, despite high freight rates keeping CFR levels high; but acid is less affordable than it has been for some time and appears very expensive compared with upstream sulphur. Buyers in need should be willing and able to pay up at current prices for spot acid cargoes, but requirements are limited, while availability is set to increase in a range of locations. ■

Fig. 1: **Sulphur Vancouver f.o.b., $/t**



Source: CRU

Price Indications

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

Cash equivalent	**August**	**September**	**October**	**November**	**December**
Sulphur, bulk ($/t)					
Adnoc monthly contract	80	103	111	98	78
China c.fr spot	113	120	128	110	103
Liquid sulphur ($/t)					
Tampa f.o.b. contract	55	55	102	100	100
NW Europe c.fr	95	95	117	139	139
Sulphuric acid ($/t)					
US Gulf spot	67	83	117	115	104

Source: various

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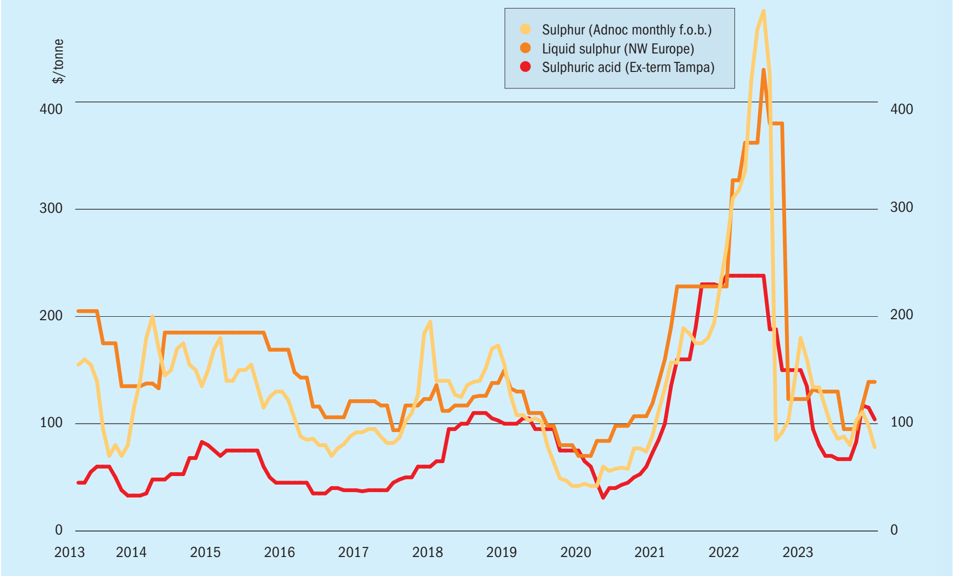
Market Outlook

Historical price trends $/tonne



Source: BCInsight

SULPHUR

- Sulphur prices are expected to increase during H1 2024, reversing the trend of recent declines, though good availability will limit the upside to price gains in the short term. However, should fertilizer production prove weaker than expected, prices may remain below expected levels.
- Chinese import demand should increase later in the forecast period if export restrictions are eased, and delivered sulphur prices to China are expected to increase over the coming six months to a high of $136/t CFR by June.
- Morocco's OCP is also expected to increase its phosphate fertilizer production further over the coming months, as the buyer has ample spare capacity and the potential for good revenues and margins.
- Sulphur demand in Indonesia for nickel is set to increase further over the coming months, limiting the possible downside to global spot prices despite a weaker nickel market.
- Overall, the recent growth in sulphur production, in addition to stock drawdown and high China inventories, is expected to limit upwards potential for prices in the short term, and keep sulphur prices low relative to phosphates. Still, affordability continues to support raw materials purchasing and leaves room for price increases, especially if downstream production picks up as expected.

SULPHURIC ACID

- Morocco remains in the market for sulphuric acid tonnages for early 2024 arrival. The sulphuric acid line up at Jorf Lasfar was estimated at a total of 330,000 tonnes scheduled for arrival during 4Q23.
- Chilean sulphuric acid demand is expected to remain firm next year, with more end users keeping some of the volumes to be supplied by the spot market in anticipation of lower f.o.b. prices in Asia. The rise in northwest European prices and the ongoing logistics issues in vessels crossing the Panama Canal will likely affect vessel arrivals into Chile and result in more acid remaining in nearby destination markets.
- European suppliers are sold out for October-November loading. Some additional European supply could become available for December loading considering the current high export prices, but it remains to be seen if European producers can manage to free up some tonnes for loading towards the end of the year.
- European acid pricing is expected to remain firm next year as heavy maintenance at key smelters – such as Aurubis' Hamburg smelter – is scheduled in the second quarter of 2024, which will tighten acid availability from Europe.
- Chinese acid pricing is expected to soften as 2024 progresses on the back of new smelter acid capacity coming online, as well as output ramp-ups from already completed projects. However, a risk to the forecast could be a strong domestic market, which may limit acid availability for the export market. ■

Sulphur Industry News

UNITED STATES

Oil production reaches record levels

US domestic oil production has surged during 2023, reaching 13.3 million bbl/d in December, a record not just for the US but for any single country's oil production. Adding in natural gas liquids and biofuels takes overall liquids production to 21.4 million bbl/d. Exports are also running at record levels, around 6 million bbl/d. This is a remarkable turnaround from 2008, when production was less then 5 million bbl/d and exports essentially zero. Furthermore, non-OPEC production is continuing to expand, with Brazil reaching 3.4 million bbl/d of oil production and 4.2 million bbl/d of liquids, and Canada producing 4.8 million bbl/d of crude and 5.7 million bbl/d of total liquids, keeping oil prices moderated in spite of OPEC+ production cuts. Global oil production is expected to reach a record level in 2024, with non-OPEC+ liquids growth projected to increase by 2.7 million bbl/d, far more than demand growth of 1.6 million bbl/d. ■

Fire at refinery sour water tank

Marathon Petroleum suffered a fire at its 593,000 bbl/d Galveston Bay refinery in Texas in mid-December. The fire was reported at a vent on a sour water tank at the plant's power unit, leading to an explosion in a second tank at the Power 2 unit. No injuries were reported and production was unaffected. The Power 2 unit provides utility water, fuel gas and steam to the refinery.

UNITED KINGDOM

Topsoe to provide flue gas technology for carbon capture project

Essar Oil UK has selected Topsoe to provide its sustainable flue-gas treatment technology, *SNOX*™, for Essar's planned £360 million ($460 million) Essar Energy Transition Industrial Carbon Capture facility. The carbon capture facility will be an integral part of Essar's Stanlow refinery in northwest England. The carbon capture facility is expected to be operational by 2028, eliminating an estimated 1 million tons of CO_2 per year – the equivalent of taking 220,000 cars off the road. The captured CO_2 will be permanently sequestered in depleted gas fields under the sea in Liverpool Bay.

Topsoe will deliver its *SNOX*™ technology for the removal of nitrogen oxides, sulphur dioxide, carbon monoxide, dust and other contaminants from the flue gas emitted in the production process. Topsoe's technology will be one of a number of integrated licensed solutions supporting Essar's plant, and will contribute to reducing their CO_2 footprint.

Deepak Maheshwari, CEO of Essar Oil UK, said: "We are ready to move into the next phase of Essar Oil UK's decarbonisation strategy. With an investment of $1.2 billion, Essar Oil UK is positioned to be the world's first low carbon refinery. The industrial carbon capture facility, combined with our upcoming hydrogen fuel switching project, will reduce the refinery's CO_2 emissions by 95%. Topsoe is a valuable partner in this endeavour. With Topsoe's *SNOX*™ technology we are getting a well proven and highly sustainable flue-gas treatment."

YEMEN

Missile strikes disrupt oil and gas transport

Over the past two months Houthi rebels in Yemen have launched a series of attacks using drones and missiles against shipping around the Gulf of Aden at the entrance to the Red Sea. Although many have missed and some have been shot down by US and other naval vessels operating in the area, several ships have been hit, including the container ships Al Jasrah and Palatium III, the Norwegian tankers Strinda and Swan Atlantic, while the vehicle carrier Galaxy Leader was boarded using a helicopter and hijacked to a Yemeni port.

The attacks have caused consternation in international shipping; around 12% of global shipping traffic passes through the narrow straits, which are only 30 km across, en route to or from the Suez Canal, including 8 million bbl/d of global oil and oil products traffic and up to 8% of global LNG shipments, mainly from Qatar to Europe. On December 18th BP suspended tanker traffic through the Red Sea, following similar decisions by container shippers Maersk and Hapag-Lloyd. Alternative routes to Europe via the Cape of Good Hope could increase shipping times by 22 days on a round-trip basis. So far the impact on spot LNG prices has been minimal due to high inventories in Europe and North Asia, and oil prices likewise remain at around $80/bbl, with high non-OPEC production (see above) causing fears of a surplus in 2024. However, freight rates for crude transport from the Middle East to Europe have gone up by 25%, with insurance war risk premiums rising from $2,000 to $10,000.

INDIA

Market launch of sulphur coated 'urea gold'

The Indian the Ministry of Chemicals and Fertilizers, Department of Fertilizers, has issued a notification to all fertilizer manufacturing companies approving the sale of sulphur-coated urea, dubbed 'urea gold' in India. The sale of sulphur coated urea had been approved in principle last year by the Cabinet Committee on Economic Affairs (CCEA). The Department of Fertilizers note approves the sale of urea gold in in 40 kg bags, with pricing set at equivalent to 45 kg bags of neem-coated urea, i.e. a maximum retail price of rupees 322.50 ($3.20). The move is part of Indian government efforts to promote sustainable and innovative agricultural practices. Sulphur-coated urea is expected to play a role in enhancing soil health, optimising nutrient release, and ensuring improved crop yields. The decision to price it on par with existing neem-coated (i.e. slow release) urea is intended to encourage the adoption of environmentally friendly fertilizers without imposing an additional financial burden on farmers.

KAZAKHSTAN

Talks to settle fine over sulphur storage

Talks began at the end of last year between the government of Kazakhstan and the international partners in the North Caspian Operating Company (NCOC), operators of the huge Kashagan oil, gas and condensate field, to settle a potential $5.1 billion fine over what the government claims was illegal storage of sulphur at the project site. The Bolashak oil and gas treatment plant receives and processes associated gas from the offshore Kashagan field and has a reported total permitted capacity of

CONTENTS
What's in issue 410
COVER FEATURE 1
Indonesia's nickel boom
COVER FEATURE 2
Pyrite-based acid
COVER FEATURE 3
Acid plant tower design
COVER FEATURE 4
SRU catalysts

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OBITUARY

James Hyne

November 23, 1929 - December 11, 2023

It is with sadness that we announce the passing of Jim Hyne in Calgary, Alberta, Canada. Jim will be remembered by many people in many different ways. He was an individual who seemed as large as life itself. We are honoured to write a few words about our friend. The longer stories will be told amongst us for some time to come.

Jim was born in Dundee, Scotland to William Simpson Hyne and Winnifred Moore (nee Bissett). Following his early education at Dundee Public School and Morgan Academy, he completed his BSc (Hons) Chemistry in 1951 and PhD in 1954, both at St. Andrew's University, Scotland. In the 1940s and early '50s Jim was an active member of the Grampian Club, a climbing and hillwalking club that was founded in Dundee in 1929. It was at this time that his love of the mountains developed. Jim was particularly drawn to the Munros of the Angus Glens, particularly Glen Clova, an affinity which remained with him throughout his life. During this time, he also served with the United Kingdom Territorial Army, achieving the rank of Sergeant Major.

Jim emigrated to Canada in the summer of 1954 where he held a postdoctoral fellowship in chemistry at the National Research Council of Canada in Ottawa. He continued his military service with the Canadian Cameron Highlanders of Ottawa as 2nd Lieutenant. He joined the staff of the Chemistry Department at Yale University in 1956 as an instructor. Whilst there, he met Ada Leah Jacobson, a native of Boston, Massachusetts, who was working on her own PhD. While Ada was conducting postdoctoral work at Stanford in California, Jim visited her there and proposed marriage. Happily, they were married in New Haven, Connecticut on September 3, 1958. From 1959-60, Jim was an Assistant Professor of Chemistry at Dartmouth College in Hanover, New Hampshire.

In July of 1960, Jim and Ada moved to Calgary in Alberta, where they joined the Chemistry Department of the University of Alberta (Calgary Branch), he as Associate Professor and she as a Research Associate. Their arrival coincided with the opening of the new campus in northwest Calgary. Jim was appointed Administrative Officer of the Chemistry Department, and in 1963 he became the Head of the Department.

In early 1964 Jim, together with representatives from the local oil and gas industry, formed Alberta Sulphur Research Ltd (ASRL), a not-for-profit research group established to investigate the applied chemistry of sulphur and sulphur compounds to support the evolving sour gas industry. The group was housed within the faculty of Science and it integrated faculty, graduate students, postdoctoral appointees, undergraduate summer students, interns and, eventually, full-time research staff, in a relatively unique model of academic - industrial collaboration that has seen the organisation grow and thrive for sixty years. Jim was the inaugural Director of Research for ASRL until 1995. If that were not enough, when the University of Calgary became an autonomous institution in 1966, Jim was appointed the first Dean of the Faculty of Graduate Studies, a position he would hold until 1989.

Jim and his late wife Ada, near their home in Calgary

Throughout his academic career, Jim spearheaded hundreds of research projects, published numerous papers, was named inventor on patents, and was celebrated with many awards and appointments; too many to mention here. As important as his research and administrative accomplishments were in their own right, his mentorship of young scientists, (as scholars, researchers, and individuals), has arguably made a larger impact throughout academia and industry. His encouragement to explore new ideas, to be creative in the laboratory, to persevere through the challenges of building a frontier research facility, and his approach to effective communication, has had an immeasurable influence. Not only did he impact the people under his guidance, but in many cases their families too, who grew up around and were supported by the structures Jim helped to build.

Then there was Jim apart from these institutions, these companies, and these business networks. He owned and operated a ranch west of Peace River, Alberta. He maintained an interest in cattle breeding well into his 80s and would often visit the Perth bull sales back in his native Scotland. He was an avid collector of items that ranged from the beautiful and culturally significant to the esoteric and idiosyncratic. He travelled to many places around the world, always curious and engaged with the people and the culture he experienced. Jim would also combine his travels with visits to his family and his favourite book seller in St Andrews (Mare Wilks). In the early days of their move to Calgary Jim's mother Winnie was a frequent visitor. In the years that followed his sister May and her husband Alf were welcomed into Jim and Ada's home and given many "Grand Tours" of the splendours of Alberta. These visits were continued by his niece Sheila her husband Alister and their children Ashley and Bradley. As well as hosting family Jim and Ada hosted many gatherings, big and small, including notable celebrations on Robbie Burns Day.

Jim is survived by his nephew Edward and his great nieces and nephews Ashley, Bradley and Simon and their families. They continue to live in Scotland in the area of Jim's birth. Much appreciation and gratitude goes out to the health care nurses who were Jim's companions of late. As we bid Jim farewell, we are reminded that we take not here the full measure of this man. We can, however, assert that he will be sorely missed and fondly remembered. ■

730,000 tonnes, but the Kazakh government alleges that this reached 1.7 million tonnes in November 2022. Other allegations include a lack of dust suppression, failure to recycle water, and lack of automated emissions monitoring. NCOC has said that the company carries out its sulphur management activities responsibly and in accordance with the laws of Kazakhstan, as well as in accordance with applicable standards and best practice. It produces around 1.4 million t/a of sulphur and exports 1.0-1.2 million t/a of this overseas. It has denied any wrongdoing and mounted a successful legal challenge to the decision, with a court ruling in June 2023 that the regional environmental protection department's sulphur storage inspection had not been valid. However, the government is still pursuing the penalty at the country's court of appeals. Press reports have suggested that there is a counter-offer of $200 million and a commitment to reduce sulphur storage to minimal levels. The government is also disputing an estimated $13 billion in project costs with the project partners over delays in the implementation of the Kashagan project.

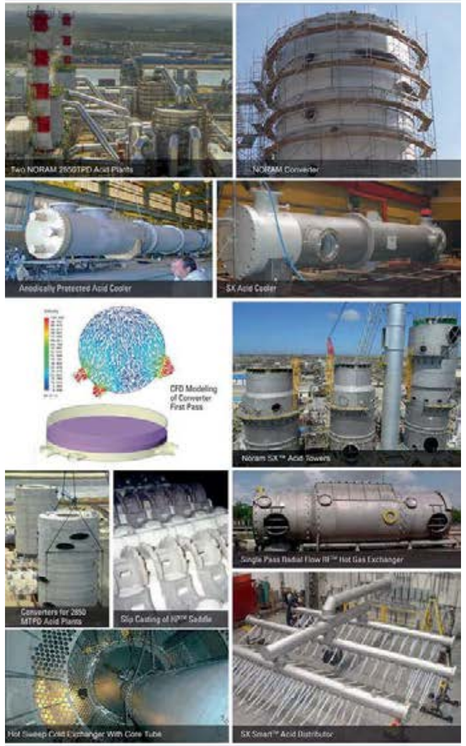
MEXICO

Delayed start-up for new refinery

Mexican state oil company Petróleos Mexicanos (Pemex) has said that production at its new Olmeca refinery at Dos Bocas in the in southern Tabasco state of Mexico would begin at the end of January 2024. During 2024 the refinery is expected to process an average 243,000 bbl/d of crude to produce 274,000 bbl/d of gasoline, diesel and jet fuel. It would ramp up to its full capacity of 320,000 bbl/d in 2025, according to a statement by Pemex CEO Octavio Romero Oropeza. Total throughput by Pemex's six refineries was 794,000 bbl/d of crude oil last year, while its Deer Park refinery in Texas processed 270,000 bbl/d. The new refinery will raise Pemex's crude processing capacity to 1.5 million bbl/d, and the company expects that to rise to 1.8 million bbl/d in 2026. By refining more of its own oil, Mexico is seeking to reduce its imports of petroleum products, including gasoline and diesel, and lower its petroleum trade deficit. Pemex imported 396,000 bbl/d of gasoline in 2023, and 170,000 bbl/d of diesel. ■

The Olmeca refinery, Mexico

PHOTO: PEMEX



CONTENTS
What's in issue 410
COVER FEATURE 1
Indonesia's nickel boom
COVER FEATURE 2
Pyrite-based acid
COVER FEATURE 3
Acid plant tower design
COVER FEATURE 4
SRU catalysts

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1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27

Sulphuric Acid News

INDONESIA

Copper smelter expansion inaugurated

Freeport Indonesia has inaugurated the $250 million expansion at its PT Smelting copper smelter in Gresik, East Java, in a ceremony attended by Indonesian president Joko Widodo. Smelting, a joint venture between Freeport McMoRan and Mitsubishi Materials, has increased copper concentrate processing capacity to 1.3 million t/a, up from the previous figure of 1.0 million t/a, with copper cathode production of 300,000 t/a.

Freeport's expansion of Indonesian smelter capacity was part of a deal to extend its copper concentrates export and mining permits. The company operates one of the world's largest copper and gold mines in Grasberg, Central Papua. The Indonesian government has been pushing for greater downstream processing of domestically produced ores to capture more of the value chain, and is looking at a ban on exports of copper concentrate in June 2024.

Freeport Indonesia has requested it be allowed to continue shipping copper concentrate beyond the date of the ban, as the company's other new smelter will not reach full capacity before December. Freeport is building a new, larger smelter at the Java Integrated Industrial and Ports Estate, also in Gresik. The smelter, called Manyar, will be able to process 1.7 million t/a of copper concentrate at an estimate cost of $3 billion.

The government owns 51.2% of Freeport Indonesia and Freeport-McMoRan the remaining 48.8%, but talks are reportedly ongoing to increase the government's stake in Freeport Indonesia to 61% in exchange for a 20-year extension to Freeport's mining rights in Grasberg after the expiration of its current contract in 2041. ■

HPAL project moving forward

China-based Ningbo Contemporary Brunp Lygend (CBL), a subsidiary of the huge battery maker Contemporary Amperex Technology Limited (CATL), has signed an agreement with Indonesian state owned mining company PT Aneka Tambang (Antam) and battery maker PT Industri Baterai Indonesia (IBI) to develop a nickel and electric vehicle battery project in Indonesia. CBL will invest $420 million as part of the project, which has six segments: nickel mining; a rotary kiln electric furnace for the production of ferronickel from nickel laterite ore; a nickel high pressure acid leach (HPAL) plant to extract nickel and cobalt from laterite ore; and a battery materials, battery recycling and battery manufacturing plant. The Indonesian government had asked CBT to begin work on the project by the end of 2023, once a feasibility study was completed. The facility will have capacity to process 6-7 million t/a of low grade limonite nickel ore, and will be based on land owned by Antam on Obi Island, North Maluku.

Nickel Industries signs contract with Glencore

Nickel Industries Ltd has entered into a nickel matte sales contract with Glencore AG. The contract, commencing January 2024 and running for an initial 6-month term, will see nickel matte from the company's Hengjaya Nickel Project (HNI) sold to Glencore. Nickel Industries says that it represents the company's first direct sale to western customers. Volume and pricing terms were not disclosed.

Commenting on the Company's maiden nickel matte sales contract with Glencore, Nickel Industries' Managing Director Justin Werner said: "We are delighted to have entered into this initial nickel matte sales contract with Glencore, with this contract signalling a maturing of our nickel matte business and an important diversification of our customer base into western markets closely linked with the global EV supply chain. Very pleasingly we have seen strong interest from global battery and EV makers for our matte product and welcome this first contract with Glencore as we continue to broaden of our customer base.

Hengjaya operates four rotary kiln electric furnaces producing nickel matte and nickel pig iron (NPI). Indonesia produced 127,000 tonnes Ni in NPI in November 2023, bringing annual production to 1.25 million tonnes nickel content. But Nickel Industries is moving towards producing more nickel matte for the battery sector, as well as mixed hydroxide precipitate (MHP) via its 10% stake in the Huayou nickel cobalt high-pressure acid leach (HPAL) project, and its decision to move ahead with its Excelsior nickel cobalt HPAL project in the Morowali Industrial Park in Sulawesi. This project, due on stream in October-December 2025, is expected to produce 72,000 t/a of nickel as MHP, nickel sulphate and nickel cathode.

Asiamet reports progress on nickel project

In its end of year assessment of the status of its BKM copper heap leach project on Kalimantan, Asiamet said that the consortium of banks it is negotiating with expects to appoint a lead arrange early in 2024. The company says that it "expects that the BKM Copper Project will be strongly supported by Indonesian banks." The company has also advanced negotiations with Indonesian and Chinese engineering, procurement and construction firms to deliver the next phase of engineering for the required project infrastructure. Commercial proposals have been received with reviews and negotiations well advanced. Subject to internal approvals, letters of intent will be issued and agreements sought to be entered to commence early engineering works in Q1, 2024. Permitting is almost complete, with finalisation of commercial terms for shared use of the forestry access road to the BKM site expected soon. Asiamet also sees "encouraging" costings for producing a pyrite and copper concentrate from the BKM primary resource which sits immediately beneath the leachable copper resources, with the pyrite offering "the potential to be a supplementary source of sulphur for producing the large volumes of sulphuric acid needed in the acid leach process (HPAL) in Indonesia's nickel industry. There is a significant opportunity to increase the overall copper recovered from the BKM resource and deliver pyrite to an external facility for processing."

FINLAND

Metso launches high efficiency scrubber optimiser for gas cleaning plants

Using its technical knowledge base on wet gas cleaning, enabling continuous improvement of the operation and performance of gas cleaning equipment and entire plants, Metso has launched the high efficiency scrubber (HES) optimiser, a digital tool that combines internal process calculations with measurements available at site to enable energy savings in the operation of Venturi-type scrubbers in wet gas cleaning plants. The scrubber captures impurity particles in wet gas cleaning plants. However, a significant pressure drop is required to achieve this. Precise adaptation of the pressure drop to the process conditions – the capacity and duty of the wet gas cleaning in general – can enable substantial energy savings while meeting performance targets. The scrubber and wet electrostatic precipitator (WESP sections can also be jointly optimised, and the program supplements WESP low load optimisation, ensuring that performance targets are met while the WESP equipment protection sequence is running. Commissioning and online support services are available as part of the HES Optimiser license.

CANADA

First Phosphate closes second tranche of financing

First Phosphate says that it has successfully completed an oversubscribed financing round, which has brought in a substantial influx of capital. Ther first two share sales tranches brought in C$7.5 million.

"We are pleased by this large vote of confidence placed in First Phosphate by existing and new shareholders including a number of institutional investors," said company CEO, John Passalacqua. "We are now in position to be able to drill this winter and begin uncovering the full extent of the Bégin-Lamarche high-purity igneous rock phosphate horizon at only 70 km from the deep-sea port of Saguenay. In our experience, proximity to port and access to infrastructure and workforce are the single largest determinants for the economic viability of any phosphate project. Bégin-Lamarche has all these strong requisites. We feel that it will become the first phosphate mine to see production in Quebec. We are now in a position to accelerate its development."

CHILE

Commissioning begins at copper project

Capstone Copper Corp. says that commissioning activities are underway at its Mantoverde Development Project (MVDP) in Chile. The project is expected to increase the company's consolidated copper production by over 40% with a significant decease in unit operating costs.

"The project is on-time and we reaffirm our $870 million total capital cost guidance," said Capstone CEO John MacKenzie. "This marks an exciting time for Capstone, MVDP is transformational four our business and provides the based for incredible growth in the Mantoverde-Santo Domingo District."

First ore was introduced to the new concentrator on November 29th, 2023. The sulphide copper project is on track to reach nameplate capacity of 32,000 t/d by mid-2024. Mantoverde is expected to produce total copper (concentrates plus cathode) of 98,000 t/a at a cash cost of $2.41/lb in 2024.

Following the ramp up at Mantoverde, the company's next phase of growth will be a construction decision and integration of Santo Domingo. The Santo Domingo project includes upgrades to the existing water and power infrastructure as well as development of the Santo Domingo port, approximately 65 km away by road from Mantoverde. The company says that its future growth plan includes Mantoverde Phase 2, an expansion of the sulphide concentrator to process part of the 77% of resources not included in Phase 1, processing Santo Domingo oxides at the underutilised 60,000 t/a SX-EW cathode plant at Mantoverde, as well as Mantoverde-Santo Domingo cobalt production. Part of the plan is a sulphuric acid plant at Mantoverde to process cobalt-containing iron pyrite produced by both Mantoverde and Santo Domingo, lifting cobalt production from 1,500-2,000 t/a to a total of 6,000-6,500 t/a. The acid generated from pyrite processing will then be fed to the SX/EW and other leaching facilities.

Codelco and SQM to cooperate on lithium project

SQM says that it has signed a memorandum of understanding (MoU) with the National Copper Corporation of Chile (Codelco) for the operation and development of the Salar de Atacama lithium deposit during the period 2025–2060. A new joint venture operating company owned 51-49 by Codelco will be responsible for the production of lithium carbonate and lithium hydroxide on the properties that SQM currently leases from the Chilean Production Development Company (Corfo) in the Salar de Atacama.

Ricardo Ramos, CEO of SQM, commented, "I believe that with Codelco we are achieving the objectives that we had set forth at the beginning of the negotiation process to create a positive partnership for Chile, for the Antofagasta region, for the communities and for both companies. We are moving forward. There is a significant amount of work which needs to be done on this great project and we are deeply committed to making it happen."

Chile is the world's second largest lithium producer but has only two mines operational, in the Atacama desert, operated by SQM and US-based Albermarle. SQM sold 156,800 t/a of lithium globally in 2022 which represented around 20% of the global market. Under the deal, SQM will be able to increase its production quota in the Atacama by up to 300,000 t/a of lithium carbonate equivalent between now and 2031. Production after 2031 will be split between the companies according to their stake in the new partnership.

UNITED STATES

Metso building new training centre

Metso is expanding its service centre in Mesa, Arizona to support the growing needs of mining customers, primarily in the copper segment. In addition to expanding its service and repair capabilities, a cutting-edge training centre will be built to continue to improve competence development in the region. The total investment value is around $15.3 million, with the expansion expected to be completed during the first half of 2025. The expansion will increase the repair shop area by nearly 60% and add new high-capacity cranes, CNC machines, welding, and assembly stations. This will increase the capacity and capability to perform heavy equipment repairs and service a wider range of equipment, spanning process steps such as crushing, screening, grinding, HPGRs, filtration, flotation, and pumps, among others. Within the same property, a fully-equipped training centre will also be built, to bridge the knowledge gap between people, equipment, and operational goals. The centre will support multiple ways of learning, outfitted with state-of-the-art simulators and digital training assets, in addition to classroom and hands-on learning areas. Comprehensive and tailored training programs will be

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27

designed and offered to support mining professionals’ technical knowledge, at the part, equipment, and plant level.

WORLD

Electric vehicle policy updates

European countries rushed to update their EV subsidy programmes in December. In Germany, the last-minute 2024 budget has put the brakes on the country’s subsidy scheme, with the decision to end it as of 17 December 2023. The programme, which started in 2016 and has since paid out euro10 billion, was prematurely scrapped in the new slimmed down budget. EVs comprised 18% of light vehicle sales in Germany for the year to November in 2023 but were almost a quarter of the total in 3Q before fleet subsidies expired. Previously, subsidies for EVs between euro 40,000-65,000 were set to expire at end-2023, whereas the policy for EVs below euro 40,000 was expected to extend end-2024. When EV subsidies for businesses expired in September 2023, sales contracted by 29% year on year. Given the private market is significantly larger than fleet sales to businesses, the sales contraction following the 17 December change is expected to be particularly strong.

Meanwhile, in France, consumer cash incentive rules have been revamped to favour vehicles made in France and Europe over China. Some 32% of EV sales in France in 2023 were imported; 20% from China alone. Over 65% of EVs made in France are anticipated to be eligible for the incentives, providing up to euro 5,000 per vehicle. The new criteria include a carbon emissions limit when manufacturing the EV, causing many Chinese vehicles to be excluded.

In China, the Shanghai government extended the free license plate policy through to 31 December 2024, which was previously set to expire at the end of 2023. The city will continue to offer this for EV and fuel cell vehicles; however, the criteria for receiving them has been tightened.

In North America, new guidance has been released on the Inflation Reduction Act (IRA) regarding the production and sale of certain products, including some battery components and critical minerals. The Biden administration is reportedly discussing increasing the 25% tariff on importing specific goods from China, including EVs. The import tariff and subsidies are designed to protect domestic production and avoid a slew of cheaper Chinese vehicle imports. This may be unnecessary as the tariff is already punitively high, and the handful of Polestar, Volvo, and BMW vehicles imported from China will soon have their tariffs offset by a provision allowing manufacturers to earn credits by domestically producing vehicles.

EUROPEAN UNION

Anti-dumping investigation on titanium dioxide

The European Commission has initiated an anti-dumping proceeding to investigate whether imports of titanium dioxide from China have been ‘dumped’ on the EU market and caused material injury to the EU industry. This investigation was triggered by a complaint lodged by the European Titanium Dioxide Ad Hoc Coalition in September 2023, representing EU titanium dioxide producers. The Coalition in its evidence noted that EU imports of TiO2 from China have sharply increased over the past few years, and alleges that this is due to dumping margins estimated at between 45 and 65%, forcing the shutdown of some EU producers.

GERMANY

BASF collaboration on lithium-ion batteries

BASF has entered into an agreement with Korean firm SK On, a leading electric vehicle battery cell manufacturer, to jointly evaluate collaboration opportunities in the global lithium-ion battery market focused on North America and the Asia-Pacific region. The collaboration brings together strong business and product development capabilities to develop industry-leading battery materials for lithium-ion batteries.

Initially, the companies will focus on evaluating collaboration options for cathode active materials (CAM) production. Further details on the collaboration will be revealed at a later stage. Additional collaboration opportunities along the battery materials value chain will be evaluated subsequently, including battery recycling. By leveraging their respective expertise, BASF and SK On aim to develop innovative solutions to support their strong growth ambitions.

“With the collaboration with SK On, we are further strengthening our market position to serve battery manufacturers and electric vehicle producers around the world.” said Dr. Peter Schuhmacher, President of BASF’s Catalysts division, who is also responsible for the company’s battery materials and battery recycling business. “We want to address the need for more sustainable solutions for the electric vehicle industry. And we are ready to work with our customers and partners in all regions to make this a reality.”

ZAMBIA

Cash injection for Mopani

Abu Dhabi-based International Resources Holding (IRH) will invest more than $1 billion in the Mopani copper mine, according to Zambia’s majority state-owned ZCCM Investments Holdings Plc. IRH will pay $620 million for a 51% stake in the business, with the government owning the rest, and has also agreed to make up to $400 million in shareholder loans. ZCCM said it’s also in talks with Glencore about restructuring its $1.5 billion of debt to the company, which previously owned the copper and cobalt mines until ZCCM bought Glencore’s 90% stake in 2021 for a nominal sum.

Mopani reportedly needs $300 million to complete projects started by Glencore and boost annual production 200,000 t/a. Mopani made a loss of $196 million in the first half of 2023, according to ZCCM-IH.

INDIA

Copper smelter to start up in March

Adani Group’s new copper smelter at Mundra on India’s west cost is due to begin production in March this year, according to the company. Phase 1 has a capacity of 500,000 t/a of copper production, boosting India’s domestic output by 80%. India has been a net importer of refined copper since the closure of the Vedanta smelter in 2018. International Copper Association India (ICAI) said that Indian copper production was down to 560,000 t/a in March 2023, against annual demand of around 1.5 million t/a. Copper consumption is rising rapidly in India, forecast to increase by around 11% this year due to new infrastructure projects and the green energy transition. Adani is planning a second phase at Mundra which will bring output to 1.0 million t/a, but all of this is expected to be absorbed by rising domestic demand.

The plant will require 1 million t/a of copper concentrate in its first year of operation. However, over 90% of ore for India’s copper production is imported, mainly from South America, and there are some concerns that the forthcoming Indonesian export ban and continuing strong demand for concentrate in China could lead to a tight copper concentrate market by 2025.

In addition to its copper output, the new smelter will generate 1.5 million t/a of sulphuric acid and 250,000 t/a of phosphoric acid, as well as 250 t/a of silver and 25 t/a of gold.

BRAZIL

Eurochem to begin phosphate production in Q1

The EuroChem group says that it plans to begin producing phosphates at the Serra do Salitre Mining Industrial Complex in Minas Gerais state in the first quarter of 2024, the group’s first mining project outside Europe, following the successful award of an operating license for its sulphuric and phosphoric acid plants. Production is expected to reach about 1 million t/a of phosphate fertilizers per year, which represents 15% of Brazilian demand. Brazil currently imports around 85% of its fertilizer requirements.

“The operating license is a crucial step for the complex that will make EuroChem a significant player in the fertilizer production industry in Brazil and South America,” said Gustavo Horbach, CEO of EuroChem in South America. “The sulphuric acid and phosphoric acid plants, which have received the necessary licenses, are essential to produce fertilizers.”

CHINA

Zijin acid output up in 2023

China’s Zijin Mining Group Company Ltd has announced production results for the fiscal year 2023. For the year, the company reported zinc/lead production of 467,000 t/a, compared to 454,000 t/a for the previous year. Refined copper production was 720,000 t/a against 690,000 t/a a year ago. Sulphuric acid produced as by-product was 3.27 million t/a against 3.02 million t/a a year ago.

Sumitomo Metal Mining reported that Chinese copper cathode output in November was 960,800 tonnes, down 3.3% month-on-month, but up 10.9% year-on-year at 10.4 million t/a to November. Smelter maintenance contributed to the fall, as well as tight supply of blister copper. In addition, the output of newly-commissioned smelters was slower than expected, limiting new production. However, production was expected to be higher in December and January, with full year production at 11.5 million t/a, up 11.3% on 2022. Primary lead output also increased by 14.0% year-on-year with a total capacity of 5.84 million t/a in 2023. Secondary lead output was up 14.9% year on year in spite of significant declines in lead prices, while refined zinc output was up 10.6%, year on year, totalling 6.0 million t/a from January to November 2023. Nickel sulphate production was down 14.8% year on year, with year-end inventory reductions and weak demand.

SAUDI ARABIA

Ma’aden and partners develop unique phosphogypsum recycling process

The Saudi Arabian Mining Company (Ma'aden) has entered into a partnership with Metso and thyssenkrupp Uhde to develop and license an integrated process to reduce carbon emissions and recycle phosphogypsum in Saudi Arabia. A framework agreement between the three partners was jointly announced on 10th January.

The innovative new process, which will form the centrepiece of a new complex in Ras Al Khair, is designed to reduce CO_2 emissions across Ma’aden’s phosphate business. Ma’aden has already been granted a US patent for this integrated CO_2 and phosphogypsum recycling technology.

The partners plan to incorporate the patented technology at the greenfield Ras Al Khair complex. It will capture CO_2 with lime generated from the calcination of phosphogypsum using sulphur. The new process is designed to reduce CO_2 emissions across Ma’aden’s phosphate business, making it more sustainable in the long-term. It will also recycle phosphogypsum waste and transform this into a useful resource.

Ma’aden says the patented approach is dual-purpose and addresses two of the phosphate industry’s most pressing environmental challenges – first, the decarbonisation of production to prevent atmospheric CO_2 pollution and, second, the effective reuse of phosphogypsum, a by-product of phosphate production that is generated in very large quantities. Overall, the new process offers global warming mitigation via sustainable carbon capture as well as providing a viable solution for phosphogypsum recycling.

Hasan Ali, executive vice president, Ma’aden Phosphate, said, “This pioneering patent, combined with our new CO_2 capturing complex, underscores Ma’aden's commitment to sustainability. We look forward to working with Metso and thyssenkrupp Uhde to develop this important project that will truly change and reduce the carbon footprint of our phosphate business. It puts us at the forefront of innovation, turning what was once leftover material into a valuable resource, while significantly reducing CO_2 emissions. It's a giant leap towards a sustainable future.”

Hannes Storch, vice president for metals and chemicals processing at Metso, added: “We are excited to see this unique project moving forward. The new concept for phosphogypsum processing will be a major step forward in the fertilizer industry, contributing to sustainability targets, such as waste recovery and limiting global warming. Metso contributes to the project with our extensive know-how and experience in the field of fluid bed, gas cleaning and sulfuric acid solutions.”

"We are honored to be chosen from our esteemed customer to provide our technology and expertise," stated Lucretia Löscher, COO thyssenkrupp Uhde. "We are providing the innovative process to turn the phosphate industry into a circular economy. This project will be another important milestone for thyssenkrupp Uhde in enabling the green transformation for our customers.”

Ma’aden is the Middle East’s largest commodity mining and metals company and one of the fastest-growing mining companies in the world, generating revenues of $10.7 billion in 2022. The Saudi mining giant operates 17 mines and production sites in the Kingdom, has more than 6,500 direct employees, and exports products to over 30 countries.

The company has huge growth plans for phosphate, aluminium, gold and copper mining over the next 18 years, together with the extraction of new minerals – under plans to capture a greater share of Saudi Arabia’s $1.3 trillion endowment in mineral resources and turn these into commercial opportunities.

Ma’aden also wants to be a role model in responsible and sustainable mining in keeping with the government’s Vision 2030 strategy for the Saudi economy. ■

CONTENTS
What's in issue 410
COVER FEATURE 1
Indonesia's nickel boom
COVER FEATURE 2
Pyrite-based acid
COVER FEATURE 3
Acid plant tower design
COVER FEATURE 4
SRU catalysts

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People

CITGO Petroleum Corporation has named **Dennis Willig** as the company's new Vice President of Refining, where he will oversee operations at the company's three refineries located in Lake Charles, Louisiana.; Lemont, Illinois; and Corpus Christi, Texas. Willig most recently served as Vice President and General Manager of the Corpus Christi Refinery, and prior to that was the Vice President and General Manager of the Lemont Refinery, where he spent the majority of his 28-year career with CITGO. Replacing Willig as the new Vice President and General Manager Corpus Christi Refinery is **Ryan Vining**, who spent the last 24 years at the CITGO Lake Charles Refinery, most recently as General Manager Operations, Maintenance and Reliability. Both appointments are effective from February 1st, 2024.

"Denis Willig's leadership skills, experience and commitment to operational excellence are an excellent fit for overseeing our refining network and maintaining continuity in our operations," said CITGO Chief Operating Officer and Executive Vice President Edgar Rincon. "And adding Ryan Vining as Vice President and General Manager Corpus Christi Refinery further strengthens our leadership team."

Willig replaces Jerry Dunn, who will retire after more than 34 years with CITGO, spent primarily at the Lake Charles Refinery before serving as Vice President Refining for nearly two years.

"Jerry is a well-respected, outstanding leader who has dedicated his entire career to CITGO," said CITGO President and CEO Carlos Jordá. "On behalf of the executive leadership team and all the employees, I want to thank Jerry for always giving his best and making us a better refiner. We wish him well in the next chapter of his life," added Jordá.

Willig joined the CITGO Lemont Refinery in 1995 and advanced all the way to Vice President and General Manager Lemont Refinery before assuming the Vice President and General Manager position at the Corpus Christi Refinery in 2022. He holds a bachelor's degree in chemical engineering from Purdue University.

Vining joined the Lake Charles Refinery as a process engineer in 1999 after graduating with a chemical engineering degree from McNeese State University. He served in several engineering leadership roles, including General Manager Operations, Maintenance and Reliability; General Manager Engineering and Technical Services; Area Manager Reformers, and Manager Process Engineering among others.

Premium Nickel Resources Ltd. has announced the appointment of **James Gowans** as a director and as the new independent chairman of the board of the company, effective from January 1st, 2024. Gowans has over three decades of expertise as a senior executive in the mining industry, with roles at Debswana Diamond Company in Botswana, DeBeers SA, DeBeers Canada Inc., PT Inco and Placer Dome Ltd. He has also served on the boards of several Canadian mining companies, including Cameco, Arizona Mining, Trilogy Metals, Detour Gold, New Gold, Marathon Gold, Paycore Minerals and Treasury Metals, where he currently serves as chairman. He was also CEO and interim president of Trilogy Metals Inc., held roles as CEO, president, and director at Arizona Mining Inc., and served as co-President of Barrick Gold Corporation before becoming a senior advisor to the Chairman of the Board at Barrick Gold Corporation.

John Hick, Lead Director commented: "On behalf of the PNRL Board and management I would like to extend a warm welcome to Jim as he joins our team. This is a strategic step for the growth of PNRL and the Company will greatly benefit from Jim's wealth of experience as we advance the Company's Botswana mines. I would also like to thank Keith Morrison for acting as interim Chairman of the Board while the Company underwent the search for a new independent director to serve as Chairman of the Board."

Marathon Oil and Gas has named **Maryann Mannen** as its new company president, taking on the role that CEO Michael Hennigan had held since 2020. Hennigan will continue serving as Marathon's CEO, as the CEO and president roles are being split. Mannen has been Marathon's executive vice president and chief financial officer since 2021. She is succeeded in that role by **John Quaid**, who previously held the same title with Marathon's MPLX division. Mannen and Quaid will report to Hennigan in their new roles. As president, Mannen will oversee Marathon's refining business, responsible for the company's commercial performance, as well as its health, environment, safety and security functions. Mannen will remain a member of the board of directors for MPLX. ■

Calendar 2024

JANUARY

31-FEBRUARY 2

SulGas Conference 2024, MUMBAI, India
Contact: Conference Communications Office, Three Ten Initiative Technologies LLP
Tel: +91 73308 75310
Email: admin@sulgasconference.com

FEBRUARY

26-28

CRU Phosphates 2024 Conference, WARSAW, Poland
Contact: CRU Events
Tel: +44 (0) 20 7903 2444
Email: conferences@crugroup.com

26-29

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

APRIL

2-4

TSI Sulphur World Symposium 2023, CHALESTON, South Carolina, USA
Contact: Sarah Amirie, The Sulphur Institute
Tel: +1 202 296 2971
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22-25

Sulphuric Acid Round Table, ORLANDO, Florida
Contact: Cathy Hawyard, Sulfuric Acid Today.
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Email: kathy@h2so4today.com

29-MAY 3

REFCOMM 2024, GALVESTON, Texas, USA
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MAY

20-23

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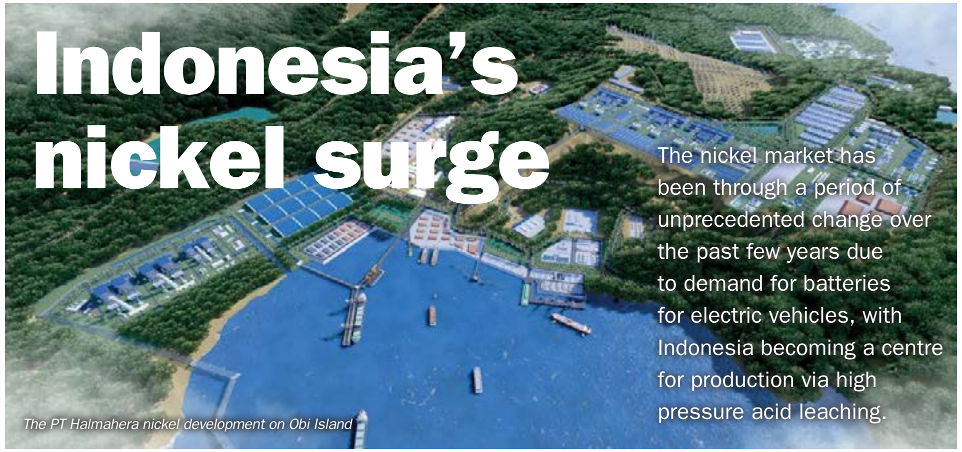


Indonesia's nickel surge

The nickel market has been through a period of unprecedented change over the past few years due to demand for batteries for electric vehicles, with Indonesia becoming a centre for production via high pressure acid leaching.

The PT Halmahera nickel development on Obi Island

World primary nickel production continues to rise rapidly, from 3.06 million t/a in 2022 to 3.42 million t/a in 2023, according to the International Nickel Study Group (INSG), and it is forecast to rise to 3.71 million t/a in 2024. This is set against demand of 2.96 million t/a in 2022 and 3.20 million t/a in 2023, rising to 3.47 million t/a in 2024. This rapid rise, averaging more than 8% year on year, is being driven by demand from the battery industry. Stainless steel remains the main source of demand for nickel, as Figure 1 shows, but this has fallen from 70% of the market in 2019 to 65% in 2022, with battery demand rising from 4% to 15% of nickel demand in just three years. The quantity of nickel used in the battery sector is growing rapidly, as nickel is used in nickel-cadmium, nickel-metal-hydride, nickel-iron, nickel-zinc, nickel-hydrogen and, increasingly in lithium-ion batteries because of the high energy density of nickel-containing cathodes.

The changing battery market

Rapidly rising use of electric vehicles shows no sign of slowing down. Worldwide sales exceeded 10 million in 2022, meaning that EVs represented 14% of all new cars sold, up from around 9% in 2021 and less than 5% in 2020. Figures for 2023 are expected to show a 35% increase on 2022.

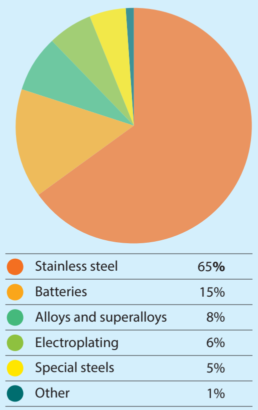
Three markets dominate these figures. China is the leading market for EV sales, representing around 60% of all global EV sales. More than half of the electric cars on roads worldwide are now in China and the country has already exceeded its 2025 target for new energy vehicle sales. Europe is the second largest market, with EV penetration reaching 20% of new car sales. The third largest market is the US, where EV sales increased 55% in 2022, reaching a market share of 8%.

However, at the same time, the preference for different battery chemistries is changing. Previously, two chemistries of lithium-ion batteries have dominated the EV market: nickel-manganese-cobalt ('NMC'), and nickel-cobalt-aluminium ('NCA'). NCA batteries have a high nickel content – the ratio of nickel to the other metals in an NCA battery is around 80%. NMC batteries began at around 33%, but are also steadily moving towards more nickel-rich formulations, as nickel offers greater energy density and storage at lower cost, delivering a longer range for vehicles. But rival iron-based chemistries, particularly lithium iron phosphate (LFP), are becoming increasingly popular, with LFP representing 60% of new EV batteries in China, and this share is rising. Other new technologies are undergoing rapid development, such as sodium ion batteries and various solid state technologies.

One new area of development is grid-scale battery storage systems for renewable energy applications. Renewable energy technologies like wind and solar suffer from variable output and need storage systems to smooth output levels. One area that has attracted particular interest is recycling EV batteries that have lost a significant amount of charging capacity for stationary power storage applications; so-called 'second life batteries'.

In spite of these changes, the future for nickel demand continues to be bright. Typical projections for nickel demand estimate that nickel use in batteries could reach approximately 1.5 million t/a of nickel by 2030, or 30% of total primary nickel demand by that time.

Figure 1: **Nickel demand by sector, 2022**



●	Stainless steel	65%
●	Batteries	15%
●	Alloys and superalloys	8%
●	Electroplating	6%
●	Special steels	5%
●	Other	1%

Source: Nornickel

CONTENTS
What's in issue 410
COVER FEATURE 1
Indonesia's nickel boom
COVER FEATURE 2
Pyrite-based acid
COVER FEATURE 3
Acid plant tower design
COVER FEATURE 4
SRU catalysts

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12
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22
23
24
25
26
27

Class 1 nickel

Lithium-ion batteries with nickel-rich cathodes require high purity nickel, typically in the form of nickel sulphate. As the main feedstock for EVs battery cathodes, nickel sulphate is currently manufactured by dissolving so-called 'Class 1' nickel (nickel with greater than 99.8% metal purity) in sulphuric acid.

Nickel ores broadly exist in two different forms; sulphides, and laterites, which are an oxidised form found mainly in tropical regions. Processing of nickel laterite ores is more difficult and has come to rely upon two main routes; pyrochemical or acid leaching. Pyrochemical routes are generally cheaper, but the nickel that they produce is often compounded with iron. This is not a problem if the destination for the nickel is stainless steel use, but it means that the nickel cannot be used for demand uses that require high purity nickel. Much of the growth in nickel supply, especially in Indonesia, was used in China to produce so-called 'nickel pig iron' (NPI) for steel production.

With new sulphide deposits limited, ways will have to be found of processing laterite ores to produce Class 1 nickel. Heap leaching requires a very low iron content in the ore, and leaching at atmospheric pressures tends to require much more sulphuric acid than high pressure acid leaching (HPAL), to the extent that costs become comparable or potentially higher. The result has been an increasing focus on HPAL, using sulphuric acid at >240°C and 33-35 atmospheres pressure in titanium autoclaves, although the intensely corrosive conditions make for challenging operation.

Table 1: **Mined nickel by country, 2022, tonnes metal**

Indonesia	1,600,000 t/a
Philippines	330,000 t/a
Russia	220,000 t/a
New Caledonia	190,000 t/a
Australia	160,000 t/a
Canada	130,000 t/a
China	110,000 t/a
Brazil	83,000 t/a
Others	460,000 t/a

Source: USGS

The increasing price differential between Class 1 and Class 2 nickel has led to innovation from China in the form of so-called nickel matte production from NPI. The process to covert the NPI to nickel matte involves adding elemental sulphur to NPI or ferronickel in a converter, where it is blown with air to oxidise and separate the iron and produce a high grade nickel matte. This can then be further refined in a similar way to a mixed nickel-cobalt sulphide precipitate to produce Class 1 nickel or battery grade chemicals. However, the process is energy intensive and generates up to five times more CO_2 than conventional Class 1 nickel production.

Indonesia

China remains the largest consumer of nickel, both for stainless steel production and also increasingly for batteries, with around 60% of all nickel currently being consumed in China. However, its domestic reserves of nickel are relatively modest, and so it must rely upon imports from overseas. Indonesia has become the mainstay of the nickel market in terms of production (see Table 1), and for a while exported large quantities of laterite ore to be converted in China to NPI production. However, in 2020 Indonesia banned the export of nickel ore in an attempt to force the development of domestic nickel processing industries in order to capture more of the value chain.

Initially this meant that a lot of Chinese NPI producers offshored their operations back to Indonesia. By July 2023 there were 43 NPI smelters operating, 28 under construction and 24 in the planning stage. But the increasing demand for Class 1 nickel has also led to several new high pressure acid leach projects, again dominated by Chinese investment, this time for battery production. This began in 2018 with the announcement of a 50,000 t/a HPAL project by QMB New Energy Materials, a joint venture between Tsingshan, GEM, CATL and Hanwa. This project eventually came on stream in 2022, by which time it had been leapfrogged by two other Chinese-backed HPAL plants, Huayue Nickel and PT Halmahera Persada Lygend. By the end of 2022, 160,000 t/a of HPAL capacity was operational in Indonesia.

The new plants have been built at a fraction of the cost of previous HPAL plants. Table 2 shows existing HPAL plants. Second generation plants cost several billion dollars, from Ravensthorpe and Ramu both at $2.1 billion, to $5.7 billion for Ambatovy and $5.9 billion for Goro. Conversely, PT Halmahera on Obi Island, and Huayue Nickel and PT QMB New Materials, both located in Morowali, Central Sulawesi all cost less than $1.5 billion, for an average capital intensity of around $30-35,000 per annual tonne of nickel compared to an average of $100,000 per annual tonne of nickel for the second generation plants. The difference is put down to existing infrastructure at established industrial parks, often with existing NPI production, as well as knowledge obtained from the development and operation of the Metallurgical Corporation of China's (MCC) Ramu operation in PNG, whose engineering division, China ENFI Engineering was the developer of the flowsheet for PT Halmahera Lygend on Obi Island. Like Ramu, Halmaher used a three-stage preheating, autoclave, and three-stage flash technology, as well as a high-steam, high-leaching rate to achieve recoveries of around 85% nickel and cobalt in MHP. The application of a tested flowsheet also allowed the operation to ramp up to nameplate capacity in only 12 months, compared to an average of four years for the second generation projects. This cheaper and more rapid start-up has removed many of the concerns that the industry had over the previously difficult, expensive and occasionally unreliable HPAL process and helped pave the way to more new project announcements.

Nickel Industries has taken a final investment decision (FID) for its Excelsior Nickel Cobalt high-pressure acid leach (HPAL) project in the Morowali industrial park in Indonesia's central Sulawesi. The project, also known as the Dawn HPAL+ project, is expected to produce 72,000 t/a of nickel as mixed hydroxide precipitate, nickel sulphate and nickel cathode with production due to start during 4Q 2025.

Indonesia's Merdeka Battery Materials plans to build two HPAL plants, each with a capacity of 60,000 t/a. China's stainless steel giant Tsingshan Holding Group will be a strategic partner to develop an industrial park to house the projects. Development of the first plant is under way at an estimated cost of $1.28 billion, with operations also planned for 2025.

PT Vale Indonesia has signed a cooperation agreement with Zhejiang Huayou Cobalt to develop a 60,000 t/a HPAL plant at Malili, South Sulawesi as mixed hydroxide precipitate (MHP) with cost estimated at $1.8 billion. The plant is due for completion in 2027. It follows an earlier announcement by the two companies in conjunction with Ford to develop a larger 120,000 t/a nickel MHP plant in Pomalaa, with start-up planned for 2026.

Table 2: **HPAL projects**

Operator	Capacity (t/a Ni)	Location	Start-up	Notes
First generation				
Sherritt	37,000	Moa Bay, Cuba	1959	Expansion planned
Second generation				
Centaur	9,000	Cawse, Australia	1998	Shut down 2008
Glencore (was Anaconda)	45,000	Murrin Murrin, Australia	1999	
Preston Resources	10,000	Bulong, Australia	1999	Shut down 2003
Sumitomo	24,000	Coral Bay, Philippines	2005	
First Quantum (was BHP)	36,000	Ravensthorpe, Australia	2007	Restart 2020
Trafigura (was Vale)	60,000	Goro, New Caledonia	2010	Shut down 2020
Sumitomo	60,000	Ambatovy, Madagascar	2012	
MCC	33,000	Ramu, Papua New Guinea	2012	
Sumitomo	36,000	Taganito, Philippines	2013	
Third generation				
PT Halmahera	37,000	Obi Island, Indonesia	2021	
(Ningbo Lygend)	18,000		2023	
PT Huayue	30,000 x 2	Morowali, Indonesia	2022-3	
PT QMB	50,000	Morowali, Indonesia	2022	
Under development				
Nickel Industries	72,000	Morowali, Indonesia	2025	
Merdeka	60,000	Konawe, Indonesia	2025	
Vale/Huayou	60,000	Malili, Indonesia	2027	
Vale/Huayou/Ford	120,000	Pomlaa, Indonesia	2026	
BASF/Eramet	42,000	Weda Bay, Indonesia	2026	

Source: USGS

Anugrah Neo Energy Materials and China's Gotion Indonesia Materials have also agreed to build an HPAL plant on Sulawesi Island with a production capacity of 120,000 t/a of nickel in mixed hydroxide precipitate. No start date has been announced.

Overall, Indonesia's share of world nickel production is forecast to rise from its present 55% to more than 70% over the next five years.

Waste

One of the issues for the new HPAL plants is dealing with waste from the process. HPAL generates an acidic slurry which must be neutralised and properly dealt with. It is estimated that for every tonne of nickel produced via HPAL around 1.4-1.6 tonnes of waste is also produced. This has often led to large quantities of solution being disposed of via tailings ponds or ocean discharge of liquids, depending on access to sites for so called deep sea tailings placement (DSTP), which has been controversial. Some facilities such as Ramu Nickel discharge the tailings at the same pH as the ocean, making them effectively inert, but others discharge acidic waste with a knock-on effect on sea life. Tailings disposal is particularly challenging to deal with in environments such as Sulawesi where there is limited space for large dams due to the island's topography, thick vegetation and high rainfall. At PT Halmahera tailings are being treated as backfill to the mining operations.

Nickel prices

The plethora of new nickel projects, especially for nickel pig iron production, in Indonesia have led to a surge of new nickel production and falling prices on the international market. Prices fell by 45% during 2023, to below $16,500/t by the end of the year, and are well down from their highs in 2022 when there were fears of an interruption in supply from Russia. The International Nickel Study Group estimated that there was a 104,000 tonne surplus in 2023 which is forecast to rise to 239,000 tonnes in 2024, the third consecutive year of surplus supply and the largest annual surplus to date. One issue has been the slowdown in the Chinese economy, restricting new demand for stainless steel. Nevertheless, as previously mentioned, new demand for batteries is expected to lead to an increase in nickel demand to 3.47 million t/a this year, and much of the surplus is in Class 2 rather than Class 1 nickel. Nickel stocks at the London Metals Exchange are actually at very low levels, and it is expected that there will be support for marginally higher prices over the next year or so. The lower capital costs for new Indonesian HPAL plants means that the projects are less sensitive to lower nickel prices than previous HPAL plants, although the startup of a 200,000 t/a nickel matte facility in China may also relieve some of the pressure on Class 1 nickel prices.

Sulphur and acid demand

The rapid boom in nickel leaching in Indonesia is leading to an equally rapid growth in sulphuric acid demand. CRU estimates that by 2027, acid demand could have risen from around 5 million t/a in 2022 to a total of 17 million t/a. Some of this demand will be satisfied by acid production in Indonesia. Smelter acid production from copper production will account for around 3.2 million t/a by 2027, and another 1 million t/a from pyrite roasting. However, the rest is likely to be accounted for by dedicated sulphur burning acid capacity at the nickel processing sites. A total of 12.8 million t/a of sulphur burning acid capacity is projected to be onstream by 2027. This will in turn necessitate 4.3 million t/a of sulphur consumption, most of which will need to be supplied by imports.

Longer term there are some HPAL projects planned in Australia, but they have not made as much progress as quickly as the ones in Indonesia. ■

CONTENTS
What's in issue 410
COVER FEATURE 1
Indonesia's nickel boom
COVER FEATURE 2
Pyrite-based acid
COVER FEATURE 3
Acid plant tower design
COVER FEATURE 4
SRU catalysts

SULPHUR
ISSUE 410
JANUARY-FEBRUARY 2024

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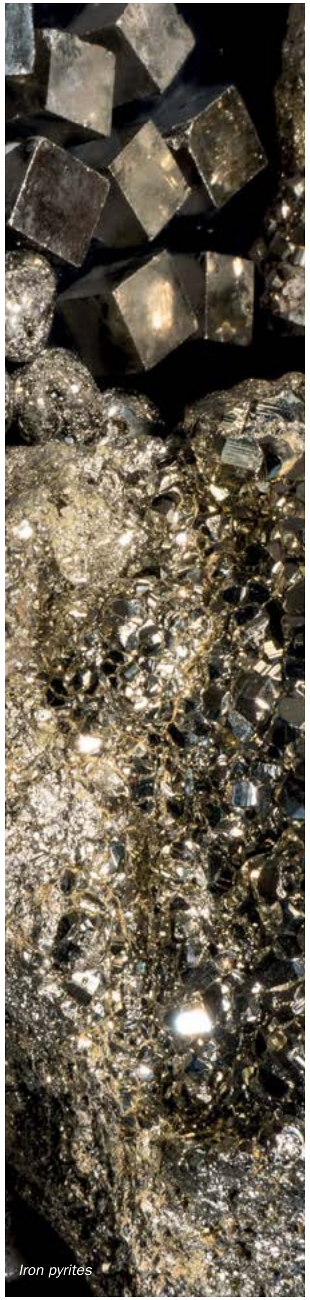
PHOTO: GECAMINES



Iron pyrites

The future of pyrite production

Pyrite roasting as a source of sulphuric acid continues to be a significant, albeit minor sector of the overall acid market.

Iron pyrites (FeS_2) are the most common sulphide mineral in the Earth's crust. There are extensive deposits around the world, and prior to the development of Frasch mining, they were the dominant source of sulphur for sulphuric acid production, throughout the 19th and early 20th centuries. However, they fell out of favour as a source of sulphur, overtaken first by Frasch mining which began in 1895 in the US, and then by Claus sulphur recovered from oil and gas processing, which has come to dominate sulphur production, with acid derived from smelter off-gases the main secondary source of sulphur in all forms (SAF).

Global sulphuric acid production from pyrites reached a peak of over 30 million t/a in the 1970s, at which time it represented 22% of sulphur production in all forms. However, it has been in long-term decline since then, down to less than 7% of sulphur production in 2021. Production largely ceased in the United States in 1988, Brazil and Bulgaria in the 1990s, Albania and Spain in 2001, India in 2003, and Zimbabwe in 2008 with the closure of the Iron Duke mine. Nevertheless, some production continues in Finland, Russia, and particularly China, which now represents over 90% of world pyrite roasting acid production.

Production

The production of acid from pyrites is a pyrometallurgical process. The pyrite (pyrrhotite – Fe_7S_8 – can also be used) rock is crushed or passed through a grinding mill to produce smaller particles with a larger surface area. There may also be a beneficiation step, using a process such as froth flotation, where chemicals are added to create a frothy mixture where the pyrite particles adhere to air bubbles and rise to the surface, allowing them to be collected and concentrated.

The crushed pyrite is then passed into a roaster. Metso uses an air blown circulating fluid bed system in its process. The pyrite is heated to a temperature of 600–1000°C, depending on the process, at which temperature the sulphide part of the mineral oxidises to sulphur dioxide and trioxide and the iron oxidises to a calcine mixture consisting of Fe_2O_3, Fe_3O_4, and $FeSO_4$, as well as oxides of any trace minerals in the pyrite (such as arsenic). The arsenic can be separated from the iron cinder in a two stage process with the arsenic volatilised in an oxygen free section before oxidation occurs, leaving it to be later recovered from the gas stream via a wet gas cleaning system. Waste hot gases pass to a heat recovery section such as a waste heat boiler to generate process steam. The sulphur oxide rich gas can finally be passed to a downstream conventional sulphuric acid plant.

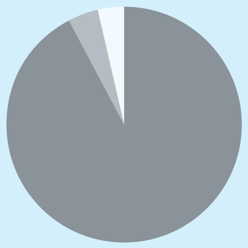
Process economics

Pyrite was originally mined for its sulphur content, and as a convenient source of sulphuric acid. However, the recovery of large volumes of sulphur from oil and gas as a by-product and the recovery of sulphur rich off-gases from copper and other base metal smelting have collectively largely undercut the economics of pyrite mining for acid production, hence its gradual discontinuing in many of the countries that formerly used it, as noted above. Pyrite rock tends to be cheaper than elemental sulphur as a raw material, and the operating costs for a pyrite based acid plant can be lower or comparable, but the lower capital cost of a sulphur burning acid plant makes for faster payback in the medium term (though pyrite plants can be more profitable in the long term, depending on the price of sulphur).

In addition, the solid iron cinder contains around 30-60% iron. The production of 1 tonne of sulphuric acid usually results in the creation of 0.8–1.5 tonnes of iron cinder, and China produces more than 11 million t/a of it. The cinder is not very valuable, and sometimes is merely disposed of as tailings, but it can be used in the manufacture of cement or as ballast in road construction. And it can also be used a source of iron in steel manufacture, which has had particular application in China. China makes around 55% of the world's steel, and the country imports large quantities of iron ore in order to do so. In 2023 China imported a record 1.18 billion tonnes of iron ore for steel manufacture. The iron calcine from pyrite manufacture can be used in lower grade steel manufacture and helps offset the process economics. Delivered costs of iron ore to Chinese ports are at present around \$120/t c.fr, and even at a fraction of this the calcine still represents a valuable by-product. In addition, there are also often trace 'impurities' such as copper and gold in the calcine, and recovery of these minerals can also assist with the economics of the process.

There are however also additional drawbacks and costs associated with pyrite production, one of the foremost of which is acid mine drainage. When exposed to air, like in a mine, pyrite will fully oxidize in a matter of years. Microorganisms can also form on the mineral and speed up the reaction. In the presence of water this process generates sulphuric acid which can lead to environmental issues within and near the mine. As a result, modern mining practices prioritise the mitigation of environmental impacts associated with pyrite mining and processing, adding to the cost.

Figure 1: **Global pyrite-based acid production, 2021**



● China	15.6
● Finland	0.7
○ Others	0.6
Total	17.9

Source: USGS

Acid production

After its long slow decline from its peak in the 1970s, global pyrite production has actually been at a fairly stable level over the past two decades. In 2021 it accounted for around 18 million t/a of acid production worldwide, most of this in China (see Figure 1). While production in several countries has been declining or ceasing, Chinese production was actually on an upward trend in 1990s and 2000s, with many of the smaller producers – there were over 350 producers of pyrite based acid in 2006 – closing at the same time that larger, more efficient and lower cost plants were completed. In 2006 Outotec completed the world's largest pyrites roaster at Tongling Nonferrous Metals, which produces 400,000 t/a of sulphuric acid, and Hunan Hengyang started up a 300,000 t/a acid plant based on pyrites in 2008. Some pyrite roasters have converted their acid plants to sulphur burning, though the sulphur price spike of 2008 and continuing strong demand for both sulphuric acid and iron, continue to make pyrites roasting economical in parts of China. Chinese pyrite acid production peaked at 17.7 million t/a in 2010, but still amounted to 15.6 million t/a in 2021, representing about 17% of Chinese acid production that year.

Geographically, much of China's sulphuric acid output is concentrated in Hubei and Yunnan provinces, with significant production also in Guizhou, Sichuan, Shandong and Anhui. Yunnan, Hubei, Guizhou and Sichuan are major fertilizer producing regions and capacity there is dominated by sulphur burning plants, while Shandong is a coastal chemical producing region, and Anhui has a lot of smelter capacity. Pyrite-based acid production is concentrated in the eastern provinces of Guangdong, Anhui, Jiangxi and Liaoning (more than 75% of pyrite based production).

The future of pyrites

Outside of China, the next largest producer of acid from pyrites is Finland. Finland's pyrites have mainly come from First Quantum Minerals Pyhasalmi mine, which produces the bulk of Finland's pyrites. But this looks likely to come to and end soon. Underground mining at the site ended in 2022 when the zinc and copper deposits there were exhausted. FQM says that it expects to continue to produce 330-350,000 t/a of pyrite from pyrite rich tailings currently stored in one of the mine's tailings ponds. However, pyrite recovery is not currently scheduled to last beyond 2025.

There have been predictions of the demise of China's pyrite roasting acid industry for many years now, but the industry was kept alive via demand for iron and the burgeoning phosphate industry in China, which required ever-increasing amounts of sulphuric acid. However, China is now recovering increasing amounts of elemental sulphur from sour gas extraction in Sichuan and its increasing number of major oil refineries, and acid production has also been boosted by a large increase in copper smelting capacity, and pyrite-based acid must compete with both sulphur burning and acid offtake from smelters. In spite of this glut of acid capacity, China has continued building new pyrite roasting acid capacity, although this has been partially balanced by closures among older and less efficient capacity, and operating rates have slipped to around 70%. Nevertheless, there was still 21.2 million t/a of pyrite acid capacity in China in 2022, representing around 16.5% of total acid capacity. A stable or slow decline of this seems likely over the coming years, but the pyrite based acid sector will continue to be a small but significant part of China's acid production. ■

CONTENTS
What's in issue 410
COVER FEATURE 1
Indonesia's nickel boom
COVER FEATURE 2
Pyrite-based acid
COVER FEATURE 3
Acid plant tower design
COVER FEATURE 4
SRU catalysts

SULPHUR
ISSUE 410
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17
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19
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21
22
23
24
25
26
27

Small-scale sulphur recovery

Small quantities of sulphur in a refinery or gas feed can present challenges for conventional large scale sulphur recovery techniques.

PHOTO: SHELL GLOBAL

A Shell Sulferox installation

Around 40% of the world's natural gas reserves contain enough hydrogen sulphide to be classified as sour. However, the percentage of H_2S can vary widely, from as high as 90% in some fields, to the limits of what can be defined as sour (around 4ppm). Likewise refinery streams can vary significantly according to the sulphur content of the feed. Biological sources often have a small amount of sulphur, for example in refineries producing renewable diesel and jet fuel from sources such as used cooking oils, waste animal fats or vegetable oils such as rapeseed. Units processing gas from biological sources may also deal with smaller sulphur quantities in process streams.

Extraction of the H_2S is usually achieved using a regenerative solvent, which extracts CO_2 as well as H_2S to produce acid gas. But where small volumes of H_2S are present the acid-gas stream may consist mainly of CO_2. Claus plants are generally set up to process significant quantities of sulphur in a feed, but can struggle where levels of H_2S are low and/or volumes of gas being processed are small. In the past low levels of hydrogen sulphide were sometimes flared, but in e.g. the US, regulations prevent the flaring of gas with more than 230 mg/m^3 of H_2S (approx. 350 ppm). If conventional Claus processing is not suitable, a variety of techniques can be used to treat smaller quantities of sulphur, either removing or recovering it, depending upon the situation.

Scavengers

Where there are very low levels of sulphur in the gas stream (<0.1 t/d), such as in sewage plants, or lone gas wells where flaring is not possible, scavenger systems are typically used which bind the H_2S either chemically or physically. There are dry scavengers and wet scavengers. The smallest scale removal systems typically use solid-based ('dry') scavengers. Iron oxide is a common scavenger, reacting to form iron sulphide and water. The iron sulphide can then be disposed of in landfill without requiring special permits. However, the system can be capital and labour intensive for larger volumes.

Regenerative solid beds using zeolites can be used, using adsorption to take the H_2S from the system, but generating an H_2S-rich gas stream as the adsorber is regenerated. Large vessel size, limited capacity, and the need for parallel trains for regeneration during service can increase capex and space requirements. Additionally, dealing with sulphur waste creates potential issues for both operations handling and OPEX considerations.

There are also a wide variety of liquid scavengers, soluble in variously water, oil or organic solvents, including copper carbonate, zinc oxide, hydrogen peroxide, triazine, sodium nitrite, chlorine dioxide, sodium chlorite, etc etc. These products depend on the type and composition of the scavenger and the conditions at which the reaction takes place. Like solid scavengers, liquid scavengers can be divided into regenerative and non-regenerative types. Non-regenerative scavengers include aldehydes such as formaldehyde, although safety and handling issues generally militate against their use. The most commonly used non-regenerative liquid H_2S scavenger used is triazine. However, while the reaction byproducts are biodegradable, unreacted triazine is highly toxic to aquatic life and treatment of the waste stream is required. Nitrate/nitrite solutions have similar removal capacity compared to triazine, though they can produce nitrogen oxides, nitric acid, and insoluble precipitates from reacting with H_2S.

Caustic scrubbing

A special case of liquid scavenger is caustic scrubbing systems. These use a caustic stream, usually containing a solution of sodium hydroxide, to react with the hydrogen sulphide. Caustic scrubbing is typically employed where the amount of sulphur to be removed is less than 10 t/d. The type of scrubber used depends upon the CO_2 content of the gas to be treated. Where CO_2 levels are low, the gas can be processed through a recirculating caustic solution. However, CO_2 can react with the solution leading to high rates of consumption and sodium carbonate precipitation, and specialised designs are required for higher CO_2 streams which allow preferential reaction of the H_2S. The product of the scrubber is a mix of sodium sulphide (Na_2S) and sodium bisulphide (NaHS), depending on the ratio of H_2S to caustic in the solution, which can be sold depending on the proportion of sodium carbonate in the mix from CO_2 in the gas stream.

Liquid redox

Liquid reduction-oxidation (redox) systems are in effect a regenerative scavenger. Redox systems usually use iron and chelating agents for the reaction. Sour gas passes through an absorber column where the H_2S is stripped from the gas. This spent solution is sent to an oxidizer unit to regenerate. The iron is initially reduced from ferric (Fe^{3+}) state to ferrous (Fe^{2+}) by the H_2S, then oxidised back to iron-(iii) in the oxidiser unit. The oxidation process produces a H_2S-rich waste gas stream, but can also result in elemental sulphur production due to the reactivity of the oxidising agents. This process can be used to remove less then 20 t/d of H_2S, or where complete stripping of sulphur is required.

Merichem offers the *LO-CAT* process, a proprietary liquid redox process that converts H_2S to solid elemental sulphur. The process uses an aqueous solution of iron, whose catalytic performance is enhanced by a proprietary blend of chemicals. Direct treatment of a sour gas stream uses a separate absorber and oxidizer. This configuration is a lot like an amine unit – a closed-loop circulating solution – but in lieu of steam for regeneration, the *LO-CAT* process uses air to oxidise the iron catalyst back to Fe^{3+}. When hydrocarbons are not present in the vapor stream an autocirculation unit can be used that combines the absorber and oxidiser into a single vessel and eliminates pumping of the working solution. The process produces a sulphur cake that is mostly solid sulphur, but also contains some moisture and proprietary chemicals and may not be suitable for all end users.

Shell offers the *SulFerox* process, similar to LO-CAT but using a different chelating agent. Various contactor types are available, such as sparged towers, spray towers and pipeline contactors. After contacting the sour gas and solution in the contactor, the gas/liquid mixture is separated, yielding treated sweet gas and the depleted *SulFerox* solution. After optional degassing, the reduced iron chelate solution is regenerated via reaction of Fe^{2+} back to Fe^{3+} with oxygen from an air source in the regenerator vessel. The sulphur product can be obtained as a filter cake as per *LO-CAT* or alternatively as molten sulphur.

Biological processes

Biological processes selectively remove H_2S by using it in bacterial respiration, converting it to mercaptans or elemental sulphur and sulphate. The operating temperature range is very limited due to the biological nature of the process. Shell markets its *Thiopaq* system, originally developed by Paques BV for the treatment of biogas, which is produced by the anaerobic digestion of wastewater. Co-operation with Shell led to further development of the process for application at high pressure in oil and gas environments. Shell says that it can be economically applied to projects recovering up to 150 t/d of sulphur. For the natural gas and petrochemical environments, the process is licensed by Paqell BV, a joint-venture company of Shell Global Solutions International BV and Paques BV.

Low capacity Claus

Below about 20% H_2S in the acid gas feed to a Claus the flame in the reaction furnace becomes unstable. In such cases, the acid gas and air can be preheated before mixing in the front-end burner. Maintaining a proper feed temperature is crucial for operation of the Claus and tail gas reactors, and this is another area where alternatives are available for small processors. Large facilities use steam or hot oil when available, but these can be expensive options for small processors, requiring additional infrastructure and operations. For smaller units, however, an electric reheater may be applied to perform this task. These reheaters are effective, inexpensive to install and simple to control.

However, when the acid-gas stream contains less than 10% H_2S, it may be too difficult to achieve the necessary recovery efficiency. In such a situation, the acid-gas stream can be treated in an additional sweetening step with a solvent that preferentially absorbs the H_2S and leaves most of the CO_2 behind. After solvent regeneration, the acid gas feed to the Claus plant is sufficiently enriched in H_2S content. So-called acid gas enrichment can bring H_2S concentrations up from around 1% to 25%, allowing normal Claus operation. Care must be taken to avoid contamination of the enrichment solution, however. If hydrocarbons, amine, or corrosion inhibitors enter the solution, the performance of the solvent will suffer and require potentially expensive replacement.

Selectox

A derivative of the Claus process is the *Selectox* process, developed by Parsons and Unocal and licensed through UOP. Once-through *Selectox* is suitable for lean acid gas streams (1-5% hydrogen sulphide), which cannot be effectively processed in a Claus unit. The process is similar to a standard Claus plant, except that the thermal combustor and waste heat boiler are replaced with a catalytic reactor. The *Selectox* catalyst promotes the selective oxidation of hydrogen sulphide to sulphur dioxide, i.e., hydrocarbons in the feed are not oxidised. These plants typically employ two Claus catalytic stages downstream of the Selectox reactor, to achieve an overall sulphur recovery of 90-95%.

For feeds greater than 5% hydrogen sulphide, the Recycle *Selectox* process can be used. In this variation a portion of the process gas leaving the condenser downstream of the *Selectox* reactor is recycled so as to limit the outlet gas temperature from the reactor to >205°C. *Selectox* produces a conventional 99.9% pure sulphur product. ■

■ CONTENTS
What's in issue 410
■ COVER FEATURE 1
Indonesia's nickel boom
■ COVER FEATURE 2
Pyrite-based acid
■ COVER FEATURE 3
Acid plant tower design
■ COVER FEATURE 4
SRU catalysts

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SULPHUR index 2023

A complete listing of all articles and news items that appeared in *Sulphur* magazine during 2023.

Asia's new mega-refineries: the Hengli Petrochemicals refinery in Singapore.

PHOTO: HENGLI GROUP

ARTICLE	Issue	Pg
Conference/meeting reports		
Middle East Sulphur Conference 2023	Jul/Aug	24
SulGas Mumbai 2023	Mar/Apr	26
Sulphur and Sulphuric Acid 2023 Preview	Sep/Oct	30
Sulphur and Sulphuric Acid 2023 Review	Nov/Dec	26
Sulphur World Symposium 2022	Jul/Aug	24
TSI World Sulphur Symposium 2023	May/Jun	24
Digital technology		
Next generation sulphur plant analysers	Nov/Dec	44
When digitalisation meets reality	Jul/Aug	34
Health, Safety and Environment		
Controlling SO_2 emissions	Mar/Apr	24
Do you have a plan for weak acid incident?	Jan/Feb	28
Hydrogen safety in sulphuric acid plants	Jan/Feb	26
Phosphates		
New phosphate demand – India and Brazil	Jul/Aug	16
The future of phosphate production	Nov/Dec	20
Product forming and handling		
Age and friability for different forms of elemental sulphur	Jul/Aug	44
Life cycle of a sulphur melting plant	Mar/Apr	47
Sulphur dust suppression	Jul/Aug	20
Refining		
Impact and mitigation of processing bio-feeds in a refinery	May/Jun	32
Optimising refinery assets with fertilizer production	Nov/Dec	40
Sustainable refineries	May/Jun	20
Sulphur industry/markets		
A looming sulphur shortage?	Jan/Feb	20
Advances in sulphur battery technology	Mar/Apr	18
Demand for sulphur fertilizers	Sep/Oct	18
Developments in sulphur polymers	May/Jun	22
New sulphur projects	May/Jun	16
The impact of Ukraine on sulphur markets	Jan/Feb	17
Sulphuric acid markets		
Is LFP the next big thing?	Sep/Oct	24
Metals markets after China's slowdown	Mar/Apr	20
Sulphuric acid markets	Nov/Dec	23
Sulphuric acid recycling	Sep/Oct	26
Sulphuric acid technology		
A beacon of energy efficient waste heat recovery	Jul/Aug	27
A new era in catalyst geometric shape selection	May/Jun	26
Innovative redesign of an economiser	Nov/Dec	34
Seeking out energy in sulphuric acid plants	Nov/Dec	38
Sulphuric acid plants as a source of carbon free energy export	Mar/Apr	36
The art of candle filter wetting	Jan/Feb	47
Sulphur recovery and associated technologies		
A better understanding of SRU ammonia salt formation	Mar/Apr	28
A novel combustion solution	Sep/Oct	56
Another lesson from an SRU shutdown	May/Jun	48
Best practices for sulphur pipeline design	May/Jun	42
Closing the skills gaps in sulphur recovery	Jul/Aug	30
CO_2 recovery in sulphur plants	Jan/Feb	36
Freezing the furnace	Jul/Aug	40
Improving the performance of the SRU thermal incinerator	Mar/Apr	39
Monitoring for refractory failure in Claus reactors	Sep/Oct	54
Keep your sulphur recovery unit online and efficient	Sep/Oct	38
Protecting your assets with PFA	Sep/Oct	44
Reaping the rewards of recycling	May/Jun	45
Sneaky SO_2 breakthroughs	Mar/Apr	42
Sulphur plant revamps to meet future challenges	Nov/Dec	47
Sulphur recovery in the energy transition	Jan/Feb	32
Sulphur run-down liquid level prediction	Jan/Feb	42
TGU catalust poisoning and deactivation	Sep/Oct	48
Unlocking the power of sour gas reserves	Sep/Oct	32
Upgrading refractory solutions	Nov/Dec	32

Country	SULPHUR INDUSTRY NEWS	Issue	Pg
Argentina	Trafigura to instal diesel hydrotreater	Nov/Dec	12
Bahrain	BAPCO modernisation programme to start this year	Jan/Feb	11
Canada	Chemtrade announces 3Q results	Nov/Dec	11
	Midstrean Solutions buys KANATA Energy	Mar/Apr	11
	S&P forecasts rise in oil sands production	Jul/Aug	9
Chile	Refinery reduces FCC sulphur emissions	Nov/Dec	10
China	PetroChina producing sour gas from Tieshanpo	Jul/Aug	10
Denmark	JV to accelerate global SAF production	Sep/Oct	11
	Sustainable aviation fuel plant on track for 2026	Jul/Aug	10
	Tospoe to license waste to biofuel process	Mar/Apr	11
India	New SRU for Numaligarh refinery	Jan/Feb	12
Iran	South Pars celebrates 25th anniversary	Nov/Dec	12
Iraq	Iraq to invite bids for sour gas development project	Nov/Dec	11
Kazakhstan	Funding for Kashagan gas plant	Nov/Dec	11
	Gas processing plant to start up in 2025	Mar/Apr	10
	NCOC fined for excess sulphur storage	May/Jun	9
	Sour gas reinjection resumes at Kashagan	Jul/Aug	9
Kuwait	Al Zour to ramp up oil product exports in 2023	Mar/Apr	10
	Al Zour to reach capacity by the end of the year	Jul/Aug	10
	Axens to license gas treatment plants	May/Jun	9
Libya	Bids invited for gas processing complex	May/Jun	10
Mongolia	Contract signed for new refinery	Nov/Dec	12
Nigeria	Dangote refinery commissioned	Jul/Aug	10
Oman	Duqm refinery nearing completion	Jan/Feb	12
Panama	Topsoe technology selected for renewable fuels	Jan/Feb	12
Qatar	Bedeschi to supply sulphur handling equipment	May/Jun	9
Saudi Arabia	Aramco evaluating proposals for tail gas treatment	Sep/Oct	10
	Aramco to begin refinery construction	May/Jun	10
	Contract tenders expected for Jafurah phase 2	Jan/Feb	10
	Hyundai wins gas plant expansion project	Nov/Dec	12
South Africa	Joint venture for sustainable aviation fuel	Mar/Apr	10
Taiwan	Quality award for gas scrubbing system	Jul/Aug	9
UAE	ADNOC awards $1.3 bn contract for artificial islands	Sep/Oct	10
	ADNOC forms new gas processing company	Jan/Feb	10
	Bids in for Hail and Ghasha	Jul/Aug	10
	Contract for offshore services	May/Jun	10
	Hail and Ghasha contracts awarded	Nov/Dec	10
	More sulphur from ADNOC this year	Jan/Feb	10
	Shah achieves record output	Sep/Oct	10
	Tecnicas Reunidas wins Ghasha contract	Sep/Oct	10
	Tecnimont awarded preliminary Hail/Ghasha contract	Jan/Feb	11
UK	CRU to enter partnership with UniverSUL Consulting	Mar/Apr	10
	Fluor wins contract for SAF production	Sep/Oct	10
	Lithium sulphur battery market could see 30% growth	Jan/Feb	12
US	Analyser for H_2S breakthroughs in gas production	Mar/Apr	11
	Analysis of impurities in hydrocarbon gas streams	Nov/Dec	11
	Battery can use non-chemical grade sulphur	May/Jun	9
	Increase in sulphur fertilizer use	Jan/Feb	10
	Ioneer signs sulphur supply contract with Shell	Jan/Feb	10
	KP to partner Agra on sustainable aviation fuel	Nov/Dec	11
	Sulphur recovery analyser	Sep/Oct	11
World	Most new refinery capacity in Asia and Africa	Sep/Oct	11
	Oil production cuts lead to price hikes	Nov/Dec	10

Country	SULPHURIC ACID NEWS	Issue	Pg
Australia	Alliance Nickel delays feasibility study	Nov/Dec	16
	Ardmore supplying NZ phosphate producers	Jan/Feb	13
	Avenira looking at LFP production	Sep/Oct	13
	Chemetics to provide sustainable acid technology	Mar/Apr	12
	Codelco to buy Lithium Power	Nov/Dec	16
	Concentrator plant for copper nickel project	Jan/Feb	13
	Conico to include HPAL plant	Nov/Dec	16
	Construction begins at Arafura	Jul/Aug	12
	Glencore to close Mt Isa	Nov/Dec	16
	Port Pirie smelter restarts	Jan/Feb	13
	Poseidon continuing with Kalgoorlie restart	Jul/Aug	12
	Worley Chemetics to supply acid technology	May/Jun	11
Bangladesh	Ma'aden renews fertilizer supply deal	Sep/Oct	14
Brazil	Award for sulphur burning acid plant	Mar/Apr	13
	MoU for treatment of gypsum	Sep/Oct	12
Bulgaria	Pirdop sees small fall in acid output	Mar/Apr	15
Canada	Chemtrade wins lawsuit over Canexus acquisition	Jan/Feb	14
	First Phosphate looking at Prayon offtake agreement	Mar/Apr	16
	First Phosphate signs acid supply deal	Sep/Oct	12
Chile	Antofagasta output slightly up after poor Q4	May/Jun	13
	Ceibo attracts $30 million of investment	Jul/Aug	13
	Cochilco says costs are rising	Nov/Dec	16
	Copper output falls in higher input prices	Mar/Apr	15
	Metals output up	Sep/Oct	13
China	MECS awarded spent acid regeneration plant contract	May/Jun	12
	Zijin to develop Manono lithium project	Nov/Dec	16
	Zinc market boosted by government support	Jul/Aug	12
Czech Rep.	Nuberg awarded sulphuric acid plant project	Mar/Apr	14
D R Congo	New smelter for Kamoa	Jan/Feb	15
	Production at Kamoa-Kakula up after debottlenecking	May/Jun	11
Finland	Eurobattery increases stake in nickel cobalt project	May/Jun	12
	Metso introduces battery black mass recycling process	Jul/Aug	11
	Metso Outotec launches digital optimiser for WESP	Jan/Feb	14
	Metso Outotec shareholders to vote on name change	Mar/Apr	14
Germany	Auribis and Metso working on smelter decarbonisation	Nov/Dec	14
	Aurubis profits up 20%	Sep/Oct	12
	Lead smelter reopens after sale	May/Jun	12
	Trafigura buys Ecobat Stolberg lead smelter	Mar/Apr	16
India	Copper smelter looking to March 2024 startup	Sep/Oct	12
	Coromandel acid plant commissioned	Nov/Dec	14
	Deal for phosphate rock import	Jan/Feb	15
	FACT seeking part privatisation	Sep/Oct	12
	Greenfield copper to start operations from March	Nov/Dec	14
	Hindustan Zinc to convert to green energy	Jan/Feb	15
	Larsen & Toubro to build phosphate plant	May/Jun	11
	Reopening for Sterlite Copper smelter?	Mar/Apr	16
	Vedanta invites bids to restart Sterlite	Jul/Aug	12
	Vedanta to carry out work at Sterlite	May/Jun	11
Indonesia	Elessent Clean Technologies opens office	Jan/Feb	13
	New smelter off-gas acid plant	Mar/Apr	13
	Nickel Industries buys into Huayue project	Sep/Oct	13
	Nickel Industries to proceed with HPAL plant	Nov/Dec	15
	Nickel Industries seeking financing for Excelsior	Jul/Aug	13
	Thickeners for HPAL plant	Jan/Feb	14
	Work begins on new HPAL plant	Jan/Feb	14
Iran	Copper leach operations begin in NW Iran	Jul/Aug	13
Kazakhstan	Metso Outotec to supply SX/EW plant	Jan/Feb	14
	New copper concentrator for Kazakhstan	Nov/Dec	15
Morocco	OCP announces green investment strategy	Jan/Feb	15
	OCP to 'solarise' phosphate production	May/Jun	13
	Phosphate exports down 12% in 2022	Mar/Apr	16
Pakistan	Shutdown for Fauji DAP plant	Jan/Feb	14
PNG	Ramu back to full production after earthquake	Nov/Dec	15
Portugal	New copper and zinc concentrator	Nov/Dec	15
Russia	Nornickel launches SO_2 abatement project	Nov/Dec	16
Saudi Arabia	FLSmidth wins major Ma'aden beneficiation order	Sep/Oct	14
	Ma'aden names Phosphate 3 project partners	Mar/Apr	14
	Metso signs MoU for phosphogypsum processing	Mar/Apr	14
Serbia	Restart for Zijin Bor Copper after smelter overhaul	Mar/Apr	15
Sweden	Boliden scrap smelting returns to pre-covid levels	May/Jun	12
Taiwan	SAR awards contract for spent acid regeneration	Jul/Aug	11
Togo	Phosphate output up	Jul/Aug	12
US	Acid catalyst price hike	Nov/Dec	15
	Approval reversed for phosphate project	Jul/Aug	11
	Copper project to receive SX/EW package	Jan/Feb	15
	MECS wins two contracts for electronic grade acid	Mar/Apr	12
	Sumitomo buys Saconix	Jul/Aug	11
	Work begins at Thacker Pass lithium project	Mar/Apr	12
Uzbekistan	Metso Outotect to deliver two sulphuric acid plants	Jan/Feb	13
	Phosphate production to rise this year	Sep/Oct	12
Zambia	Contract awarded for copper expansion	Sep/Oct	14
	Copper/cobalt slag project	Nov/Dec	14
	FQM to convert acid plant to smelter off-gas	Nov/Dec	14
Zimbabwe	Zimplats commissions concentrate plant	Jul/Aug	12

CONTENTS
What's in issue 410
COVER FEATURE 1
Indonesia's nickel boom
COVER FEATURE 2
Pyrite-based acid
COVER FEATURE 3
Acid plant tower design
COVER FEATURE 4
SRU catalysts
SULPHUR
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6
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8
9
10
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12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27

New low-density titania catalyst for improved sulphur recovery

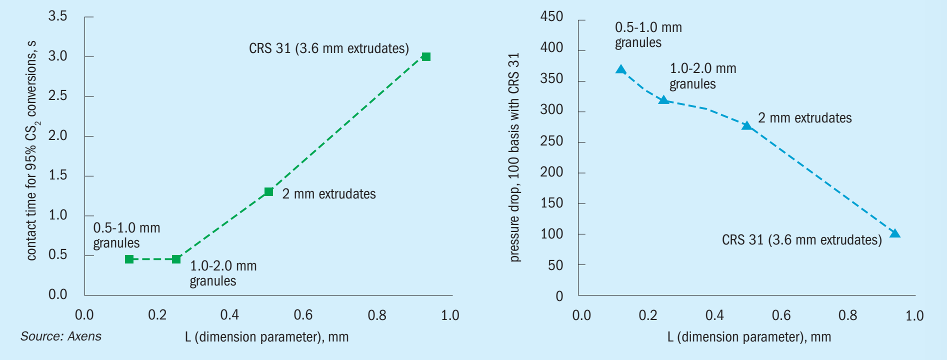
Axens has developed a new titania-based catalyst named CRS 41, which has a much larger porosity than its renowned predecessor, CRS 31 catalyst. Thanks to an improved catalyst manufacturing process and a new recipe, the porosity of CRS 41 has been increased while preserving the mechanical resistance for loading, allowing customers to optimise their capex by either reducing the Claus reactor size or loading volume of TiO_2 catalyst.

Johann Le Touze, Thomas Serres, Mathieu Chevrier, Eric Roisin (Axens)

Increasingly stringent environmental legislation requires maximising sulphur recovery yields. That explains the growing role of titania (TiO_2) catalysts in SRUs, which is accompanied by the arrival of high-activity tail gas treatment catalysts on the market. Titania-based catalysts are used because they can efficiently convert all sulphur species to elemental sulphur, even under conditions that deactivate conventional alumina catalysts. Furthermore, the use of titania facilitates the conversion of COS and CS_2 at low temperature, which is essential if hydrocarbons are present in the acid gas feed. Axens' titania-based catalyst, CRS 31, has extensive commercial experience with thousands of tonnes loaded worldwide, and is considered to be the benchmark titania catalyst. It contains high amounts of TiO_2, which is very active towards hydrolysis of sulphided species. However, not all the titanium dioxide of CRS 31 contributes to the catalytic activity, since not all of it is accessible to the gaseous reagents.

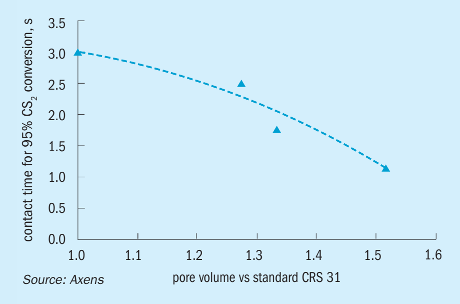
From the standard 3.6 mm diameter extrudates of CRS 31 to smaller diameter extrudates and low diameter granules, performance can be critically improved. As gases move slowly toward the inner areas of the extrudates, the catalyst's core sees a low amount of gas. Inner parts of the catalyst thus contribute poorly to the overall performance. The accessibility of these parts can be strongly favoured by shortening the pathway of gases towards the catalyst's core, i.e. by reducing the particles size. In addition, the minimum contact time required to reach a minimum of 95% conversion can be drastically reduced (less catalyst in the reactor) with smaller particles, as illustrated in Fig. 1. Further size reduction has little impact once all the material in the catalyst is fully active. Compared with 0.5-2 mm granules considered 100% active, CRS 31 needs a sixfold longer contact time to reach the same performance. These results suggest that about only one sixth (≈17%) of the CRS 31 catalyst is actually performing at maximum activity.

Fig 1: **Impact of catalyst dimensions on Claus R1 performance: CS_2 hydrolysis (left) and pressure drop (right). Dimensional parameter L is the catalyst volume divided by its outer surface, in mm.**



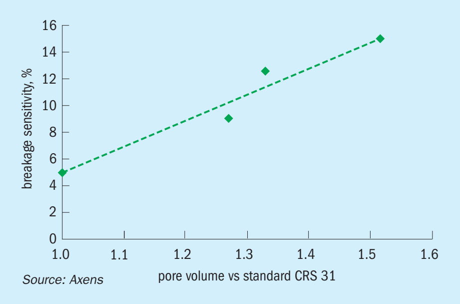
Source: Axens

Fig 2: **Impact of increase of porosity from standard CRS 31 on performance under 1st converter conditions**



Source: Axens

Fig 3: **Impact of increase of porosity from standard CRS 31 on breakage sensitivity**



Source: Axens

However, catalyst size reduction has a huge drawback in terms of pressure drop. Indeed, reducing the diameter of the extrudates by a factor close to two triples the pressure drop generated by the catalyst bed, which would lead to hydraulic issues.

Another possibility to achieve better performance when catalyst activity is limited by gas diffusion is to increase the accessibility to the active sites by increasing the catalyst porosity and/or its outer surface area (with more complex shapes). The increase of porosity results in larger "roads" inside the catalyst which help gases access the active sites1. A 95% CS_2 conversion could be achieved with half the amount of titania in the converter when the pore volume is increased by 50%. From results shown in Fig. 2, such catalyst achieving 95% CS_2 conversion at a contact time of 1.25 seconds would see at least 40% (2.5 times less active than 0.5-2 mm granules) of its titania working at maximum activity. It should also be noted that increasing the titanium dioxide content will have no significant impact on performance since only a low content of TiO_2 operates at full activity.

However, Axens' experience has shown that major drawbacks can come from the increase of porosity e.g., the catalysts show critical brittleness.

Claus catalysts are sock-loaded in SRU converters and may fall from a height of several metres (from the hopper outlet to the flexible loading sleeve outlet). When extrudates hit hard surfaces (like ceramic beads, steel or catalysts), the shock generates shards. Even if these shards are highly active, they will also generate pressure drop.

Axens developed a test to check the resistance of Claus catalysts to free falls, where extrudates are projected on a steel plate using compressed air. The method is derived from ASTM 8353, where catalysts are dropped from a height of 7.6 m through a pipe on a steel plate. In this protocol, the use of compressed air enables to the size of the setup to be reduced while mimicking the shock undergone by the extrudates falling freely from a height of 5 m, which is a typical fall height during actual sock loading. The sensitivity of catalysts to breakage is then calculated as the volume of extrudates broken from the shock (excluding shards and fines). In the case of catalysts with higher pore volumes than CRS 31, the brittleness monitored with the breakage sensitivity becomes critical. As shown in Fig. 3, the breakage sensitivity is tripled when the pore volume is 50% higher than that of CRS 31. The breakage of extrudates generates several shards per extrudate and the pressure drop rises accordingly.

An increase of porosity favours an increase in the breakage sensitivity of extrudates. Observation of the inner parts of extrudates via scanning electron microscopy (SEM) reveals that cracks are already present inside the extrudates with high porosity before the breakage test. Such cracks on the extrudates microstructure are totally absent in CRS 31 (see Fig. 4).

Any shock from a free fall leads to the propagation of these cracks and favours the generation of shards.

Several parameters can be optimised to improve the performance of titania Claus

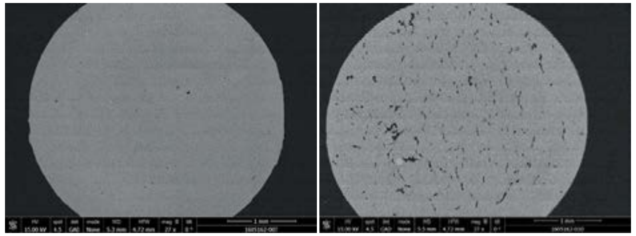


PHOTO: AXENS

Fig.4: SEM picture of a cross-section of CRS 31 (left) and titania extrude with high porosity (right)

CONTENTS
What's in issue 410
COVER FEATURE 1
Indonesia's nickel boom
COVER FEATURE 2
Pyrite-based acid
COVER FEATURE 3
Acid plant tower design
COVER FEATURE 4
SRU catalysts

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11
12
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14
15
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20
21
22
23
24
25
26
27

catalysts. This study shows that reducing the catalyst dimensions or increasing its porosity highly benefits the product performance. However, major drawbacks result from these parameter changes since pressure drop will rise dramatically with the reduction of catalyst dimensions and/or with the shards generated during the loading operation of too porous catalysts. The development of Axens' in-house testing methodology to measure breakage sensitivity of Claus catalysts has helped to target catalyst improvement pathways while keeping critical mechanical properties under surveillance.

Development of new low-density titania-based Claus catalyst

When making titania extrudates, scale-up is critical because the mechanical and textural properties can only be assessed at an industrial level. Several operating conditions validated at pilot scale cannot be fully transferred at industrial level. Since the launch of CRS 31 in 1981, Axens has accumulated significant experience on scale-up issues. As a matter of fact, Axens is able to shape some titania supports at the pilot scale with exceptional textural properties associated with good mechanical resistance. However, when applying the pilot recipe on the production line, those outstanding titania extrudates cannot be fully reproduced because of loading densities that are too high or due to insufficient mechanical properties.

The use of calcium sulphate as a binder in Claus titania catalyst has been previously reported to be beneficial on crush strength and catalyst stability under operation[2]. This binder improves the mechanical strength of titanium oxide extrudate, which would be too brittle without it. As reported above, the beneficial effect of this binder is limited when high performance catalysts are targeted.

Consequently, Axens decided to develop a new generation Claus titania catalyst – CRS 41 – to run an extensive study directly at its production line. It is the first time Axens has followed such a method for an extruded catalyst. The workshop was devoted to the new CRS 41 for a couple of months. Manufacturing operating conditions were studied thoroughly by a versatile team of manufacturing and development engineers and data scientists. New additives selected by molecular modelling by Axens' R&D teams were used.

Table 1: **Specifications of CRS 31 and CRS 41**

Catalyst parameter	CRS 31	CRS 41
Catalyst type	high performance titania	high performance titania
Form/shape	Cylindrical extrudates	Cylindrical extrudates
TiO_2, wt-%	≥ 90	≥ 90
Average size, mm	Diameter: 3.5 Length: 6-7	Diameter: 3.5 Length: 7-9
Sock loading density, kg/m^3	880	700
Surface area, m^2/g	130	130
Total pore volume, cm^3/g	0.36	0.55
Side crushing strength, daN/mm	2	2
Loss on ignition, wt-% (at 550°C)	1	1

Source: Axens

The use of Axens' production line was mandatory to find the optimal textural properties in association with satisfying mechanical properties. A new set of operating conditions and a new recipe were identified to manufacture this new titania catalyst, CRS 41.

Table 1 compares the key specifications of CRS 31 and CRS 41.

Porosity

CRS 41 is a highly porous TiO_2 catalyst. CRS 41 has a total pore volume of 0.55 cm^3/g compared to 0.36 cm^3/g for CRS 31. It is worth noting that the macroporous volume of CRS 41 (pores of larger than 0.1 μm) is four times higher than CRS 31, as shown in Fig. 5.

The benefits of increased macroporous volumes on the Claus activity of alumina has been previously reported[2,3]. The proposed explanation to this phenomenon is that larger pores tend to ease the diffusion of the product of the Claus reaction (S6 and S8 molecules) out of the porous structure of the catalyst. It is anticipated therefore that the performance of CRS 41 will be better than CRS 31 on a weight basis.

Surface area

In heterogeneous catalysis, the chemical reaction takes place at the interface between the gaseous reagents and the solid catalyst at the catalyst surface. Hence, the specific surface area is a critical parameter. CRS 31 and CRS 41 exhibit comparable high surface areas of typically 130 m^2/g.

Density

CRS 41 is produced with a sock loading density of 700 kg/m^3, much lower than that of CRS 31 (880 kg/m^3). The reduction in density allows a given reactor volume to be filled with a lower weight of catalyst, allowing cost savings. Importantly, this reduction in density does not have a negative impact on the performances of the catalyst on a volume basis. The performance of CRS 41 is actually higher than that of the same volume of CRS 31.

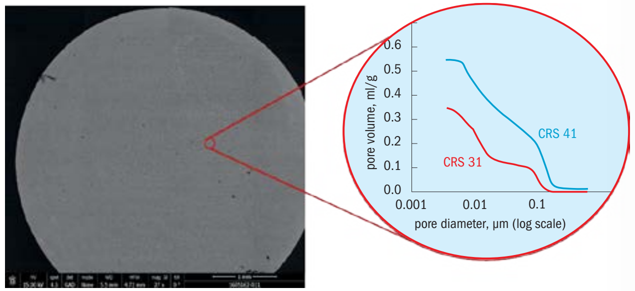


PHOTO: AXENS

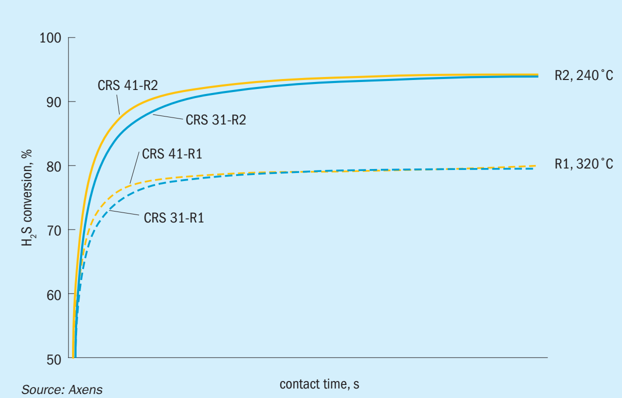
Fig.5: SEM picture of a cross-section of CRS 41 titania extrudate exhibiting high porosity and no cracks

Catalytic conversion performance evaluation

Claus conversion

A pilot test was carried out to compare the performance of CRS 31 and CRS 41 in terms of H_2S conversion. This experiment was conducted under specific conditions at a temperature of 320°C (simulating first Claus reactor operations) and of 240°C (simulating second Claus reactor operations). The test utilised a mixture comprising H_2S, SO_2, and H_2O with concentrations of 2, 1, and 30 mol-% respectively. The results of the test revealed that both catalysts exhibited comparable performance in their ability to convert H_2S. The result of the test is provided in the Fig. 6.

Fig 6: **CRS 31 vs. CRS 41 Claus conversions**



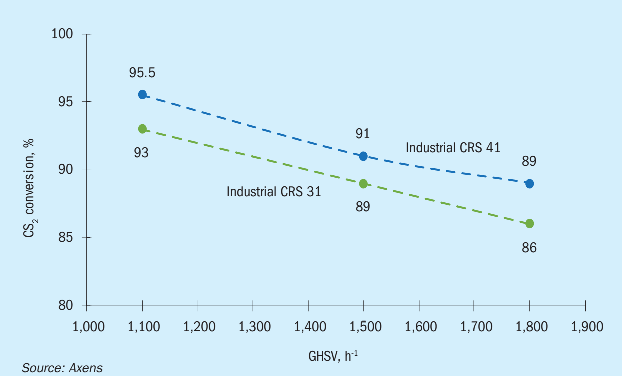
Source: Axens

COS and CS_2 hydrolysis

The pilot test was conducted under specific conditions, at a temperature of 310°C, using a mixture of H_2S, SO_2, H_2O, and CS_2 at concentrations of 8, 4.5, 30, and 0.5 mol-%, respectively. These conditions were selected to simulate real-world operating conditions and provide accurate results.

The performance of the catalysts was measured through the conversion of CS_2. The pilot test results in Fig. 7 show that CRS 41 requires less contact time to reach a desired conversion of CS_2.

Fig 7: **CS_2 conversion of CRS 31 vs. CRS 41**



Source: Axens

Cost effectiveness

Utilisation of the new catalyst CRS 41 featuring a lower density, has the potential to bring a significant benefit: an improved cost-effectiveness. Indeed, for a given volume of catalyst, CRS 41 allows customers to reduce their expenses on titanium dioxide catalysts at every turnaround.

With CRS 41, customers can also optimise their capex by either reducing their Claus reactor size or the loading volume of TiO_2 catalyst, without compromising the overall performance.

Conclusion

Axens has developed a new titania-based catalyst named CRS 41, which has a much larger porosity opening than the renowned CRS 31. Thanks to improved catalyst manufacturing and the new recipe, the porosity of CRS 41 has been increased while the required mechanical resistance for loading is preserved.

The large porosity of CRS 41 results in a significant improvement in product performance, allowing customers to achieve higher COS/CS_2 conversions by reducing the reactor size or the titania requirement by 10%. The new CRS 41 features a reduced sock loading density of 700 kg/m^3, which makes it around 20% lighter than CRS 31, for a more sustainable use of the TiO_2 resources. Thus, the cost-to-fill with CRS 41 is more attractive without compromising the pressure drop and the performance. ■

Acknowledgement

Thanks to Aurore Higon, Adrien Goigoux, Jérémy Thome and all manufacturing staff of Axens' Salindres plant.

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■ CONTENTS
What's in issue 410

■ COVER FEATURE 1
Indonesia's nickel boom

■ COVER FEATURE 2
Pyrite-based acid

■ COVER FEATURE 3
Acid plant tower design

■ COVER FEATURE 4
SRU catalysts

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15
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18
19
20
21
22
23
24
25
26
27

New impaction technology for acid plant towers

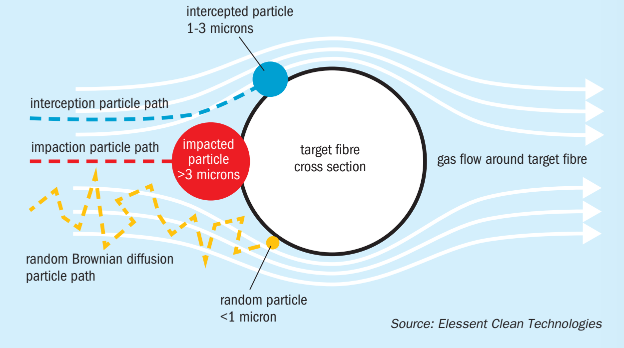
MECS, Inc. (MECS) has developed a new impaction-based mist eliminator called Brink® Prime Impact™, which offers equivalent or improved efficiency at higher throughput and the same pressure drop as traditional impaction beds, resulting in the ability to debottleneck existing inter-pass absorption towers and final absorption towers in sulphuric acid plants or design new or replacement towers with smaller diameters, thus reducing investment cost.

Douglas Azwell, Evan Uchaker, Rob Ewing (MECS, Elessent Clean Technologies)

Fibre bed mist eliminators have a long history of use in industrial applications and are utilised in a wide variety of processes. Originally invented and developed by Joe Brink in the 1950s, the use of the products that comprise this technology has become ubiquitous with removal of liquid mist and soluble solids from a gas stream throughout industry.

The devices employ micron-sized fibres to remove entrained droplets and particles from gas streams via three principal mechanisms: direct impaction, interception and Brownian diffusion. Fig. 1 shows a graphical representation of the three collection mechanisms.

Fig. 1: **Graphical representation of particle capture in fibre bed mist eliminators**



Source: Elessent Clean Technologies

Impaction mechanism: The impaction mechanism (typically effective for particles larger than 3 microns) collects a mist particle in a gas stream when it directly impacts onto a fibre. The larger the particle, the more mass it contains and therefore at a set velocity the more inertia it has that works to continue propelling the particle forward in flight when the gas flow changes direction due to an obstruction, which is in this instance a fibre in our discussion. If the gas velocity is sufficiently fast, the mass of the particle moving within the gas will have adequate momentum to cause it to impact on a fibre and adhere by weak Van der Waals forces rather than continue following the gas streamline around the fibre. Therefore, the larger the particle diameter, the more mass and thus momentum the particle has, and the easier it is for capture by the impaction mechanism.

Interception mechanism: The second mist collection mechanism is direct interception. Mist particles collected via this mechanism are intercepted from the gas stream if they cannot ride the streamline between two fibres (or if the particle touches the tangent of a fibre as it passes within the barrier zone between the freely moving gas and the fibre surface, adhering to the fibre by means of weak Van der Waals forces). Consider a particle 1.0 micron in diameter which follows a gas streamline passing within 0.5 micron of a fibre. As the particle attempts to pass the fibre, its tangential fringe will make contact with the fibre, whereupon adhesion as governed by Van der Waals forces will cause the particle to stick to the surface of the fibre and therefore be collected by interception. This mechanism is similar to the action of a mesh filter or sieve. Interception efficiency is largely independent of fibre bed velocity but is most effective for particle sizes greater than 0.5 micron and less than approximately 3 microns.

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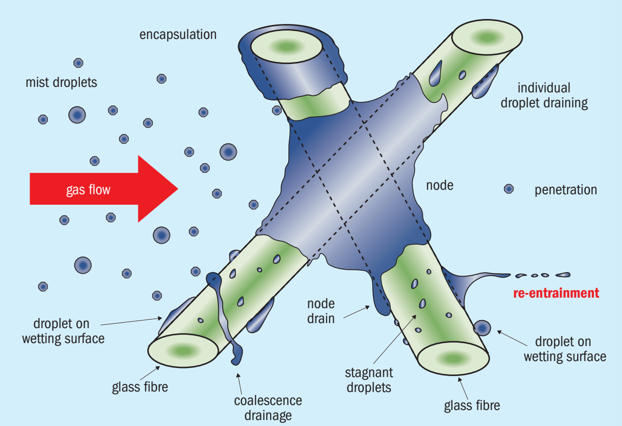
Brownian diffusion: Impaction and interception are the primary collection methods employed by devices which are designed for removal of larger mists from a gas stream. In order to remove sub-micron mist particles out of a gas stream however, a third mist capture mechanism called “Brownian motion” or “Brownian diffusion” must be utilised. All molecules in a gas stream are in constant, random, thermally induced motion. This molecular motion causes collisions between gas molecules and suspended mist particles. As mist particles are bombarded by surrounding molecules of gas, the momentum exchange causes a randomly oriented “zigzag” effect on mist particle motion. Since these collisions have little energy, this mechanism is only effective for very small particles (typically less than 1 micron) and decreases in intensity as the particle size increases. Therefore, the smaller the particle, the greater its random motion (also known as particle diffusivity) and the more likely an incident particle will collide with a fibre and stick (collect) by weak Van der Waals forces during transit through the fibre bed. This of course assumes that there is enough residence time (low enough velocity) for the random motion to walk the particle into the collecting fibre.

The flow of process gas through a fibre bed is complex and the path the process gas takes through a fibre bed is torturous. Many other factors contribute to determining mist capture including the amount of collected mist retained within the fibre bed at steady state, mist residence time as it passes through collecting fibres, mist properties, fibre bed uniformity, and general fibre bed properties to name a few. Brownian diffusion requires large residence time of a droplet within a fibre bed to allow time for capture, so operation of an impaction fibre bed at high velocities largely diminishes the effectiveness of the Brownian capture mechanism for these devices.

For all types of fibre beds which rely upon these mechanisms, technology provider experience, based on development of semi-empirical models supported by rigorous piloting and field measurements, is critical to accurately predict diffusion fibre bed collection efficiency and operating pressure drop. The MECS field-collected mist sampling data base has over 50 years of mist measurements in support of Brink® fibre bed products and designs.

Fig. 2: **Illustration of liquid within fibre bed and re-entrainment**



Source: Elessent Clean Technologies

Re-entrainment: It is important to take into account the effect of the gas flow through the fibre beds and the resulting disturbance on liquid contained within the matrix of the fibres within the device. As the gas flows around and past the liquid the drag force and Van der Waals attraction of the liquid to the surface of the fibre establish an equilibrium. If the gas velocity is high enough, the Van der Waals attraction is overcome and at least a portion of the liquid can be sheared by the gas back into the downstream gas flow. Any fibre bed has the ability of this mechanism to degrade performance of the device and if significant enough the resulting overall efficiency of the fibre bed is degraded. This is why it is imperative to use re-entrainment control devices or methods to prevent this mechanism from significantly degrading performance.

Fig. 2 demonstrates liquid appearance and interaction with media in a fibre bed to include representation of reentrainment.

Proper use of impaction technology in acid plants

Mist capture devices frequently found in operating sulphuric acid plants are mesh pads, impaction fibre beds and diffusion fibre beds. Mesh pads and low velocity impaction fibre beds (350 ft/min devices such as the MECS® CS-IP model) are typically found in drying towers (DTs). These devices rely upon the impaction mechanism for capture of larger diameter sulphuric acid droplets emanating from the sulphuric acid saturated tower packing below them in the tower. Fig. 3 shows a typical mesh pad and impaction (CS) fibre bed.

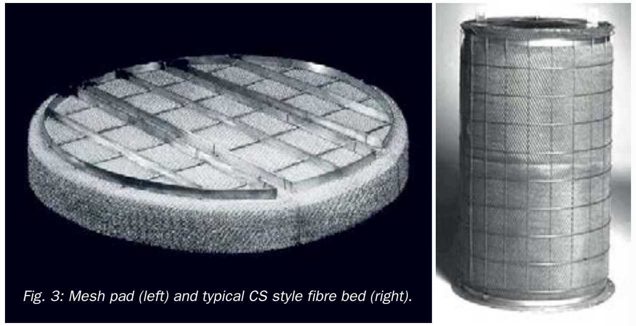


Fig. 3: Mesh pad (left) and typical CS style fibre bed (right).

Table 1: **Comparison of typical impaction device used in sulphuric acid service**

Device	Operating velocity (ft/min)	Pressure drop (in. w.c.)	Orientation	Use in sulphuric acid plants	Efficiency @ particle size (micron)
Mesh pad	250 to 660	2	typically horizontal	DT only	99+% > 5 90+% 3 to 5 65+% 1 to 3
MECS® CS-IP	approx. 350	4 to 4.5	vertical bolted onto tubesheet	DT only	99.9+% 3 to 5 96+% 1 to 3 75+% 0.8 to 1
MECS® CS-IIP	approx. 500	8 to 8.5	vertical bolted onto tubesheet	IPAT or FAT	99.9+% > 5 99.9+% 1 to 5 93+% 0.7 to 1 75+% < 0.7

Source: Elessent Clean Technologies

There are other applications for impaction fibre beds in sulphuric acid. Enhancement of MECS’s original impaction technology led to the development of the MECS® CS-IIP product which is used in the final absorption tower (FAT) and operates closer to 500 ft/min. The MECS® CS-IIP product offers some enhancement in the collection of 1-micron sized droplets and is appropriate for superior overall mist control in select applications. For instance, some US and Canadian based sulphuric acid plants use MECS® CS-IIP impaction fibre beds in their interpass (IPAT) towers and many ex-US plants use impaction fibre beds in both their IPAT and FAT towers. A word of caution however is that impaction driven devices are not used in areas where the local or regional emissions regulations have opacity requirements since impaction-driven device efficiency is lower on less than 1-micron sized droplets (which is also the most optically active and thus opacity sensitive region of droplet size). Also, since impaction fibre beds rely upon velocity to achieve adequate capture, pressure drop is device specific and cannot be tailored. At less than 80% production rate (gas velocity), collection efficiency will plummet and there is risk from an emissions standpoint, thus turndown rate with impaction device use is severely limited.

In the case of impaction-based devices, the higher velocity used to drive collection efficiency has a potential drawback: re-entrainment. Thankfully, re-entrainment can be overcome by creative use of materials and with differing composition and density within the fibre bed to allow vertical drainage paths for liquid removal while the gas freely passes through the device horizontally. This is an advantage of MECS impaction fibre bed technology compared to mesh pads used in sulphuric acid service, as the fibre beds operate under a drier state since gas flow through and liquid flow down the fibre bed are not along the same orientation with respect to the collection media.

It is important that these material combinations are thoroughly vetted, as improper design can actually induce worse re-entrainment than a design lacking re-entrainment suppression media. However, even the creative use of these materials has an ultimate limit necessitating additional means to enable pushing impaction bed technology further.

Brink® Prime Impact™

While considering improvement to its existing technology, MECS reviewed the original development data for its MECS® CS-IIP product originally conducted during the 1970s. The data demonstrated higher theoretical efficiency when using impaction fibre beds at higher velocity. However, this came at a trade-off as the developers at the time noted that the amount of re-entrainment was significantly higher than with lower velocity designs. Thus, there was an optimisation struck between the velocity through the bed and degree of re-entrainment generated giving way to the overall collection efficiency measured. Based on this understanding, MECS was able to consider packing alteration using materials in different forms and/or new materials of construction to realise re-entrainment reduction improvements to reduce exit emissions at higher bed velocity without the negative side effects of re-entrainment. These improvements culminated in the development of a new impaction fibre bed product offering – Brink® Prime Impact™ (Brink® PI).

PI impaction elements use a proprietary combination of fibres and re-entrainment prevention techniques to enable operation of these beds with a higher velocity limit without suffering additional pressure drop or suffering from poorer collection efficiency overall. One of the interesting aspects of this product given the mix of layers contained within the device, the pressure drop is consistent with operation of the MECS® CS-IIP even though it is designed to operate at 20% higher bed velocity. Effectively this means that fewer fibre beds can be used for the same pressure drop at overall improved droplet removal from the gas stream as compared to the previous high velocity impaction products. A mechanical review revealed that when using 20% fewer Brink® PI in an IPAT or FAT as compared to MECS® CS-IIP elements, the cost savings for a new tower can be in excess of 5% from reduction of the number of beds alone. Alternatively, these Brink® PI devices can be used in existing impaction installations that have undergone rate expansion and there is insufficient space for additional elements.

Field trial results of Prime Impact™

After some internal prototyping to determine fabrication details, in 2020 MECS moved forward with production of field prototypes to enable real-world operational comparison to MECS® CS-IIP impaction fibre beds in a client site. Fig. 4 shows a picture of the new Brink® Prime Impact™ bed.

J. R. Simplot (Pocatello, Idaho, U.S.A.) had an existing installation of MECS® CS-IIP fibre beds in their IPAT tower and were looking to replace their old fibre beds with a new set due to high pressure drop buildup following years of service. After some initial discussions concerning the new product and its capabilities, Simplot agreed to replace the older MECS® CS-IIP elements with a new set of Brink® PI impaction fibre beds and allow MECS to perform on-site testing using a modified version of

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24
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US EPA Method 8 complete with Andersen (cascade-style) Impactors for determination of inlet and outlet mist loading and particle size distribution

The Brink® PI fibre beds were installed during a routine maintenance shutdown at J. R. Simplot in the fall of 2020 and testing was conducted in early summer 2023. During the run from 2020 to 2023, the client experienced excellent stick test results (Fig. 5), reduction in overall acid carryover to downstream ductwork and pressure drop consistent with previously installed MECS® CS-IIP elements at around 8-inches w.c.

The MECS modified version of US EPA Method 8 enables measurement of acid mist, acid vapor and sulphur trioxide. The modification entails the use of an Andersen cascade impactor that provides a mist particle size distribution as opposed to a single mass loading. In this way, it is possible to assess the performance of a mist removal device for particles ranging in size from 0.1- to beyond 10-micron in diameter. It is critical to know the performance capabilities of emission control equipment to meet design criteria for different chemical processes and applications. Such information can also be useful for troubleshooting events. Analysis of the data revealed a few interesting facts:

- J. R. Simplot's IPAT gas to the inlet of the mist eliminators had a lower mist load than expected – only around 16.4 mg/ACF. MECS normally expects up to 50 mg/ACF as the inlet mist loading to fibre beds in IPAT installations based on 60 years of sampling in this service. The value measured at Simplot is reflective of excellent maintenance and operation protocols.
- The performance on submicron droplets was excellent as compared to impaction fibre beds, including the MECS® CS-IIP, and surpassed the theoretically expected performance (Fig. 6).
- Pressure drop of the Brink® PI fibre beds was consistent with expectation at 7-inches w.c., even after nearly three years of operation where an increase in pressure drop would be expected due to the buildup of sulphates and any remaining dust and dirt which makes it through upstream catalyst passes.

Fig. 6 shows a logarithmic plot of the efficiency versus particle size and the resulting efficiency achieved at the J. R. Simplot facility as recorded during sampling work performed in June 2023.

Fig. 4: Brink® Prime Impact™ fibre bed.

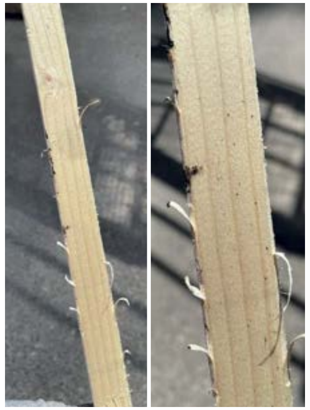
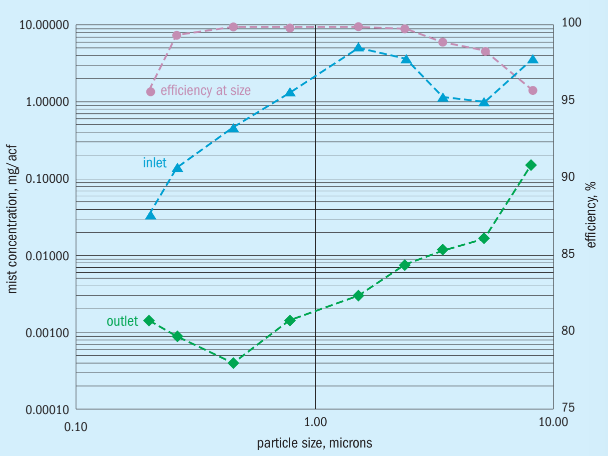


Fig. 5: Clean stick test results from J. R. Simplot's IPAT installation of PI fibre beds at 18 months of service.

Design options and case studies

Whenever a new technology is introduced to the market, it is imperative to consider the implications of using the advancement in either new equipment or existing operations. Table 2 demonstrates design options which are available to provide a perspective on the new Brink® PI impaction beds and their capabilities. For this example, MECS first considered the implications on replacement of MECS® CS-IIP fibre beds in an existing installation where equipment limits are pushed and then what these new Brink® PI beds can enable for the design of a new tower. The data is based on an IPAT in an average sized 2,500 s. t/d sulphur burning sulphuric acid plant at sea level. The gas flow is 111,471 ACFM (189,389 Am^3/hr) at a temperature of 176°F (80°C) and 75" w.c. (1905 mm w.c.) static pressure at the inlet to the impaction beds.

Fig. 6: **Brink® Prime Impact™ efficiency at J. R. Simplot IPAT installation June 2023**



Source: Elessent Clean Technologies

Table 2: **Design options of Brink® PI versus conventional MECS® CS-IIP option**

	Existing plant		**New tower**	
	CS-IIP	PI	CS-IIP	PI
No. of elements required	9	9	12	9
Pressure drop (inches w.c. / mm w.c.)	11 / (271)	8 / 203	8 / 203	8 / 203
Cost savings for tower design	n/a	no tower modification required	n/a	> 5+% reduction in total installed IPAT price
Carryover reduction	standard	better than CS-IIP	standard	better than CS-IIP

Source: Elessent Clean Technologies

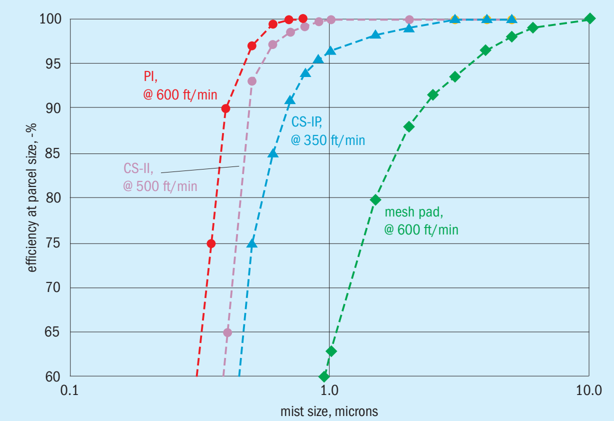
As presented in Table 2, the use of Brink® Prime Impact™ fibre beds offers a wide array of advantages for both existing plants looking to expand production capability and for new plants which are attempting to minimise tower cost. The Brink® PI fibre beds offer a lower pressure drop at the same gas flow rate as their MECS® CS-IIP predecessors, so there is no operational drawback from an energy consumption standpoint when considering pressure margin required to push the gas through the plant. Since overall efficiency and re-entrainment of the Brink® PI fibre beds is superior to MECS® CS-IIP fibre beds (see Fig. 7), there are no operational issues to consider. When considering the possibility of replacement of existing MECS® CS-IIP fibre beds with Brink® PI there is a great advantage to Brink® PI use if the client is considering a plant expansion in the future as well. For new plants, the smaller diameter tower when using Brink® PI beds (since fewer beds are required) enables savings in tower cost. Overall, the Brink® PI product offers a significant advantage in the sulphuric acid market.

The following cases highlight the advantages of Brink® PI fibre beds.

Case 1 – existing plant

A client has pushed their production over the years beyond their original boilerplate and as a result the 9 MECS® CS-IIP elements installed in their IPAT operate at 11 inches w.c. (271 mm w.c.) upon installation. The bed velocity is beyond what MECS recommends and there are plans for modification to their IPAT to add additional elements to rectify. While they have been running at higher rate, they have noticed increased downstream ductwork corrosion, heat exchanger vestibule drainage and corrosion, and fourth pass catalyst destruction. MECS evaluates the process data and determines that the existing MECS® CS-IIP elements can be replaced with 9 Brink® PI impaction beds and operate with much reduced acid mist carryover and lower pressure drop at 8 inches w.c. (203 mm w.c.). Not only does this save money in reduction of downstream catalyst, ductwork and heat exchanger repairs but the 3 inches w.c. (76 mm w.c.) savings directly translates to around \$40,000 – \$60,000 per year in energy savings for plant blower operation.

Fig. 7: **Comparison of mesh pad, MECS® CS-IP, MECS® CS-IIP and Brink® Prime Impact™ fibre bed efficiencies on sulphuric acid droplets**



Source: Elessent Clean Technologies

Case 2 – new tower

This case features a client who is considering a tower replacement. They have used MECS® CS-IIP elements in prior towers with good success. While evaluating options they are intrigued by the possibility that Brink® PI offers better efficiency at the same pressure drop as MECS® CS-IIP elements with up to 25% fewer beds. Additionally, the option of making the tower doghouse smaller with the 5+% savings in capital expenditure is appealing. They also consider the fact that fewer elements mean fewer bolts securing the elements to the tubesheet, fewer gaskets and an easier installation for better downstream ductwork, heat exchanger and catalyst protection from the effects of carry-over sulphuric acid droplets coming from the IPAT.

Conclusions

Impaction elements are commonly used in inter-pass absorption towers and final absorption towers to remove entrained sulphuric acid, especially when stack opacity is not regulated or operators are satisfied with the droplet removal efficiency. MECS has developed a new impaction-based mist eliminator called Brink® Prime Impact™, which offers equivalent or improved efficiency at higher throughput and the same pressure drop as traditional impaction beds, resulting in the ability to debottleneck existing towers or design new or replacement towers with smaller diameters, thus reducing investment cost. Brink® Prime Impact™ elements have performed well in industrial service for over 3 years, showing clean stick tests and excellent mist removal at the initial installation, an inter-pass absorption tower in the United States. ■

CONTENTS
What's in issue 410
COVER FEATURE 1
Indonesia's nickel boom
COVER FEATURE 2
Pyrite-based acid
COVER FEATURE 3
Acid plant tower design
COVER FEATURE 4
SRU catalysts

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22
23
24
25
26
27

Case study: Replacement of upper part of a co-current flow quench tower

Gavin Floyd (Eco Services Operations Corp.) and Roland Günther (STEULER-KCH GmbH)

This case study reports on the successful collaboration of two experienced partner companies to replace the problematic upper part of a co-current flow quench tower in a spent acid plant and shows the benefits of using resistant, pre-lined workshop fabricated equipment.

Eco Services' Dominguez Plant operates a spend acid unit production facility in Long Beach, California. After the spent acid furnace and the waste heat boiler the acid gas with a temperature of 358°C has to be cleaned and cooled down to 80°C in a co-current flow quench tower (see below).

The original quench tower was built in 1989 for the predecessor company Stauffer.

Quench tower damage

Due to the high thermal, chemical and mechanical stress in the quench tower the acid resistant brick lining system had suffered from frequent damage during its 30 years of operation (see below, right).

The problem

Eco Services had to repair the acid resistant brick lining system at every turnaround. The costs for the repairs were very high and the duration of the shutdowns was often 2-3 weeks long. Eco Services used several different materials for the repair, including monolithic spray systems with anchors etc. several times but the materials were not resistant. Due to unforeseen damage in the upper part of the quench tower, Eco Services experienced lost production and high maintenance costs associated with this tower.

View of upper part of quench tower before replacement (above); damage to inside and outside of quench tower before replacement of upper part (right).

Finding a solution

Eco Services explained the issues with this acid resistant brick lining system to STEULER-KCH GmbH at the Sulphur + Sulphuric Acid Conference in Houston in 2020 and asked for a repair proposal.

After receiving the inquiry and reviewing the detailed technical information (steel and brick lining drawings, complete stress data, process description, loads of the piping etc.) STEULER-KCH GmbH recommended installing a new, acid and heat resistant brick lining system that would be installed in their workshop in Germany and then delivered together with the upper part of the steel apparatuses as a pre-lined workshop fabricated equipment ready for service on site to the Martinez Plant in LA.

Besides the detailed technical design for the lining system STEULER-KCH GmbH was also responsible for designing, building, and delivering the new, necessary upper steel part.

Pictures below show various manufacturing and installation stages involved of the project. During a shutdown the damaged existing upper part of the quench tower was removed and the new pre-brick lined equipment was installed. The works on site was carried out by Eco Services contractors under technical supervision of a STEULER-KCH GmbH rubber- and brick lining specialist.

1. Step: Steel fabrication

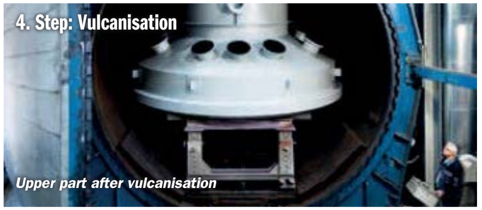
Grinding of welds to radius 5 mm

2. Step: Surface treatment

Sandblasting inside and outside grade Sa 2½ roughness 65 µm

3. Step: Rubber lining and outside painting

Rubber lining, Vulcoferran 2206 4 mm thickness single-ply soft rubber lining based on bromobutyl rubber (BIIR)



4. Step: Vulcanisation

Upper part after vulcanisation

5. Step: Brick lining

Installation of inner layer of special shaped graphite bricks with tongue and groove

6. Step: Transportation to site

Tranportation of the upper part to site

Main benefits

The main benefits of the pre-lined lining systems in this case were:

- everything delivered from a single source;
- execution of the highest level in the workshop;
- no expensive weather protection and scaffolding on site;
- lower travel and accommodation expenses;
- no loss of time on site due to internal regulations;
- no harmful influences (gas, steam, acid etc.) during work on site;
- better and safer cost control;
- no visa application and safety instruction on site for many fitters;
- very limited time on site and extreme reduction of shutdown period;
- working conditions/environment under defined conditions in the workshop;
- no transport costs for materials and tools to site and back;
- significantly lower cost for installation. ■

7. Step: Installation on site

Old upper part after lifting out

New upper part before lifting in

Installation of rubber and brick lining in connection area after welding new part to existing quench tower

CONTENTS
What's in issue 410
COVER FEATURE 1
Indonesia's nickel boom
COVER FEATURE 2
Pyrite-based acid
COVER FEATURE 3
Acid plant tower design
COVER FEATURE 4
SRU catalysts

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17
18
19
20
21
22
23
24
25
26
27

Back to the roots: single versus double absorption

With increased demands to reduce SO_2 emissions and lower energy consumption, **Eduardo Almeida** and **Nelson Clark** of Clark Solutions highlight the advantages of single absorption sulphuric acid plants compared to double absorption plants.

In the 1950s, led by environmentalist pressure following events such as the Great Smog of London in 1952, industries emitting sulphur dioxide (SO_2) began searching for alternatives. Specifically in the sulphuric acid industry, the solution was to increase the conversion of SO_2 to SO_3 from 96 – 97% to 99.6 – 99.7%, favouring thermodynamics by the intermediate removal of oxidised SO_3. This transformation changed single absorption plants into double absorption, reducing emissions by both increasing energy consumption and decreasing specific steam generation.

This situation was not a problem until the end of the 20th century and the beginning of the 21st century when energy costs and environmental restrictions became more relevant. This made single absorption plants with tail gas treatment more economically and environmentally viable.

Current scenario

As a result of a more than 60-year hiatus, single absorption (SA) plants have been set aside in most countries, and double absorption (DA) plants have become the global standard. As environmental legislation advances and becomes stricter, SO_2 emission limits for sulphuric acid plants will gradually decrease. The typical 2 kg SO_2/tonne produced H_2SO_4 is being reduced worldwide, with a new standard in development that requires emissions below 0.5 kg SO_2/t H_2SO_4.

SO_2 emission control in DA plants is not straightforward. As the campaign progresses, the efficiency of catalyst conversion decreases, and the usual method of control involves reducing plant capacity, which has a significant economic impact. Some double absorption plants address this issue by adding a 5th catalytic bed and using more sophisticated and efficient catalysts. However, this solution results in a substantial increase in energy consumption for the plant.

Additionally, plant start-ups and shutdowns in DA plants typically lead to emission levels above regulations. This is increasingly deemed unacceptable by public administration and nearby communities

On the other hand, with advancements in flue gas desulphurisation (FGD) technologies, the versatility of single absorption plants becomes more attractive. SA energy consumption is considerably lower, specific steam production is higher, and there is the possibility of a co-product generated from gas washing at the end of the process.

Sume current DA plants are adding a tail gas treatment system downstream from the final absorption tower. However, a more attractive alternative is transforming a double absorption plant into a single absorption plant.

Converting from double to single absorption

The core of a double absorption plant lies in the intermediate circuit, where oxidised SO_3 in two or three catalytic beds is absorbed in an intermediate absorption tower before returning to the reactor. This flow proceeds towards one or two catalytic reactors where the absence of SO_3 significantly favours the course of the oxidation reaction and overall conversion.

The intermediate circuit is complex, generally consisting of a SO_3 absorption tower and its internals and appendices (liquid distributors, mist eliminators, packing, pump, tank, acid cooler), gas-gas heat exchangers, pipelines, valves, instrumentation, and, last but not least, footprint/civil basis.

From the perspective of conversion efficiency, the intermediate circuit allows the possibility of raising conversion up to 99.9%, although the trade-off is higher energy consumption and a loss of plant operational flexibility.

Inside the gas-gas heat exchangers, the process gas cools down the gas heading towards absorption and reheats the stream exiting the tower that returns to the reactor. This process becomes extremely restricted at low capacity when limited heat exchange area prevents or hinders ideal temperature conditions. In such instances, the plant experiences lower conversion and acid condensation on cold heat exchanger locations.

To transform a double absorption plant into a single absorption plant, two aspects must be considered: Removal of intermediate absorption circuit and tail gas (TG) system addition.

Intermediate circuit elimination

In SA plants, the gas passing through the reactor, containing three or four beds, does not undergo an intermediate removal of SO_3. This eliminates the need for gas-gas heat exchangers. Instead, heat removal equipment can be installed to recover the heat generated from oxidation.

This configuration may include boilers, economisers, and superheaters to achieve virtually any desired steam specification. Of course, the intermediate absorption tower must be disabled or transformed into a final absorption tower, and the choice of tower characteristics will determine the best course of action. Acid coolers can be repurposed, and depending on their configuration, circulation tanks may be reused or reallocated.

After these modifications, the single absorption plant can benefit from maximum recovery of heat generated in the catalytic reactor. This energy can increase steam generation by more than 25% compared to DA plants.

Additionally, by eliminating the intermediate circuit, the plant's total pressure drop is reduced by roughly 30 to 40%, significantly decreasing the energy consumption of main blowers and increasing the time between shutdowns.

Fig. 1: Single absorption plant using hydrogen peroxide scrubber in GRP

PHOTO: CLARK SOLUTIONS

Tail gas scrubber system addition

The removal of the intermediate circuit reduces the SO_2 content after the catalytic reactor to pre-double absorption levels, ranging from 6 to 20 kg SO_2/t H_2SO_4. Utilising cutting-edge catalysts enables conversions of 98.5%-99.0% to be achieved in reactors with three or four beds in an SA plant. In addition to eliminating the intermediate acid circuit, a catalytic bed can be removed, still achieving SO_2 conversions up to 98.5% using modern catalysts and adjusting gas inlet concentrations.

To address residual non-converted SO_2, a tail gas treatment is added between the absorption tower and the stack. This treatment can be approached in two different strategies: coproduct generation or SO_2 regeneration. The former generates a solution that could either be sold or used in other applications when the sulphuric acid plant is part of an industrial complex. The latter consumes negligible washing solution with the associated costs of steam consumption.

In the coproduct generation approach, a plastic or metallic scrubber is installed. SO_2 reacts with a selected solution, generating the coproduct. The choice of coproduct should ideally align with a strategic destination, considering factors such as high added value and logistical advantages in its use. Numerous options exist, as SO_2 is an acid gas with properties favourable to acid-base reactions.

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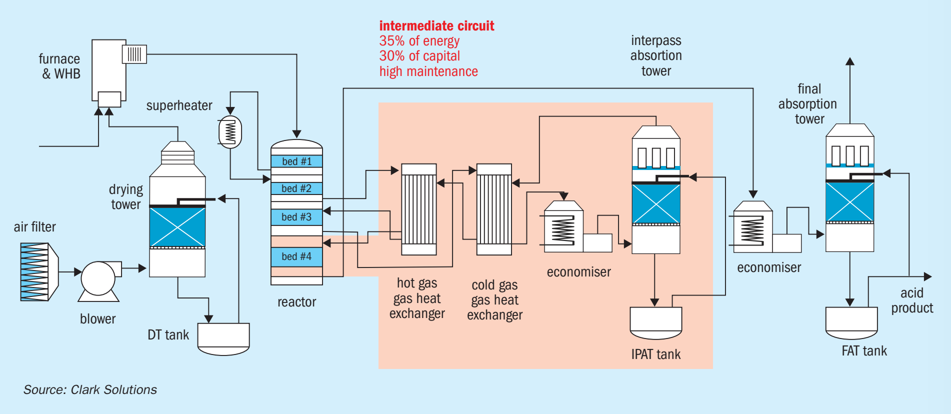
Fig 2: **Intermediate circuit in DA**



Source: Clark Solutions

Washing solution: ammonia

Due to issues related to vapour pressure between coproducts, ammonia scrubbers should utilise two packed beds operating with different concentrations of ammonia solutions. The following reactions take place on the packed beds:

$$NH_3 + SO_2 + H_2O \rightarrow NH_4HSO_3 \quad (1)$$

$$2NH_3 + SO_2 + H_2O \rightarrow (NH_4)2SO_3 \quad (2)$$

$$(NH_4)_2SO_3 + SO_2 + H_2O \rightarrow 2NH_4HSO_3 \quad (3)$$

Ammonia reacts with SO_2, producing ammonium sulphite and bisulphite. This solution circulates towards an acidulator, where sulphuric acid is added, releasing SO_2 from sulphite and bisulphite and yielding ammonium sulphate, a high-value product.

$$(NH_4)_2SO_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 + SO_2 + H_2O \quad (4)$$

$$2NH_4HSO_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 + 2SO_2 + 2H_2O \quad (5)$$

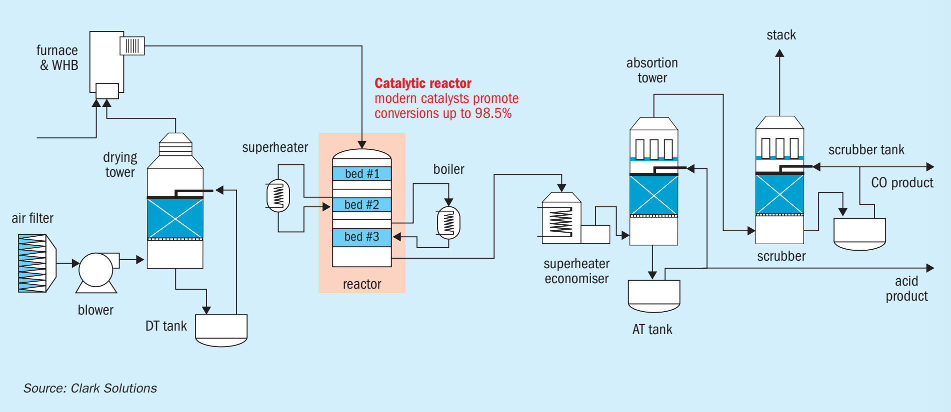
In addition to ammonium sulphate, a portion of the recovered SO_2 can be recycled back to the plant's drying tower.

Washing solution: hydrogen peroxide

Unlike the other standard washing methods, using peroxide will produce diluted sulphuric acid that can be directed to the process either as dilution water or used for leaching processes. The reaction strongly depends on both sulphuric acid and hydrogen peroxide concentration in the washer recirculating solution. As a general rule, the optimal concentration of acid in this solution is about 35-40%. Higher concentrations will require a double-deck solution, marginally increasing system investment.

$$SO_2 + H_2O_2 \rightarrow H_2SO_4 \quad (6)$$

Fig 3: **Single absorption plant with tail gas scrubber**



Source: Clark Solutions

Washing solution: caustic soda

Using caustic soda is the most traditional method of absorbing SO_2 in atmospheric emission treatment systems. The caustic soda solution reacts immediately with SO_2 inside the scrubber:

$$NaOH + SO_2 \rightarrow NaHSO_3 \quad (7)$$

$$NaHSO_3 + NaOH \rightarrow Na_2SO_3 + H_2O \quad (8)$$

$$Na_2SO_3 + SO_2 + H_2O \rightarrow 2NaHSO_3 \quad (9)$$

Caustic soda reacts with SO_2, yielding sodium sulphite and bisulphite. pH control of the solution allows for the preferred coproduct to be produced. The sulphite or bisulphite can then be removed as a valuable commercial product. The SO_2 can be regenerated by introducing the solution into an evaporator, where SO_2 is recovered and can be sent back to the plant drying tower.

$$2NaHSO_3 \overset{\Delta}{\rightarrow} Na_2SO_3 + SO_2 + H_2O \quad (10)$$

In this case, the sulphite and bisulphite production can be adjusted, both to minimise and maximise production. This situation involves reducing acid plant conversion to increase coproduct yield.

Other methods of eliminating SO_2 with alkaline solutions are viable. Lime or calcium hydroxide can be used to produce calcium carbonate. In this scenario, scrubbers with large nozzles without a packed bed, e.g., Clark Solutions MaxiJet, are necessary to minimise fouling. Other chemicals, such as magnesium hydroxide, zinc hydroxide, among others, can also be employed.

Regenerative approach

A different approach involves regenerating all SO_2 absorbed by the washing solution. In this case, the objective is to capture almost all SO_2, leaving the stack free of this component. Subsequently, the recovered SO_2 can be regenerated by treating the scrubbing solution. This generates a SO_2 stream that can be returned to the acid plant and/or utilised for some specific purpose as a pure stream.

The most common regenerative systems utilise either amines, sodium sulphite/bisulphite (as mentioned before), or sodium bisulphite/phosphate. All of them operate with reversible reactions, each with its benefits and disadvantages. Clark Solutions recommends the sodium bisulphite/phosphate approach using the SOPHOS technology, which ensures a decrease in the washing solution oxidation, and consequently, losses.

All cited regenerative approaches consist of two towers and auxiliary equipment. The absorption tower is where the lean washing solution reduces the SO_2 content from the gas to meet environmental restrictions standards. The washing solution will be rich at the absorber bottom; therefore, it is fed to an evaporator or stripper. The increase in temperature reverses the reaction, releasing the SO_2, which is then conditioned and returned to the sulphuric acid plant drying tower and/or dried for compression and other uses.

Advantages of single absorption over double absorption

A single absorption plant can offer numerous advantages compared to a double absorption plant, both in the case of a transformation and the construction of a new facility. Advantages include:

- Smaller capex:
  - Fewer equipment requirement by eliminating the intermediate acid circuit.
  - Lower blower and engine costs due to reduced pressure drop.
  - Lesser catalyst volume with tail-gas treatment leading to lower SO_2 emissions.
- Lower opex:
  - Reduced blower pressure discharge and energy consumption.
  - Tail gas system opex:
    - Compensated with coproduct added value.
    - Very low for regenerative configurations.
- Less maintenance cost:
  - Lower catalyst usage in single absorption plants, reducing maintenance expenses.
  - Single-stage blowers with reduced maintenance costs.
  - No intermediate acid circuit, lowering equipment maintenance costs.
- Higher reliability:
  - Fewer equipment and valves.
  - Single-stage blowers in single absorption plants typically experience fewer issues than those in double absorption plants.
  - Elimination of gas-gas heat exchangers, prone to acid condensation and failures.
- Higher turndown:
  - Single absorption plants can operate at lower capacities, limited only by blower capacity, whereas double absorption plants face limitations due to reheating difficulties in the intermediate circuit.
- Higher steam generation:
  - Improved heat utilisation without the intermediate circuit leads to surplus steam generation, around 0.3 t/t H_2SO_4 more compared to double absorption.
- Lower emissions:
  - Emissions easily controlled by the tail-gas treatment system, achieving levels lower than 0.1 kg SO_2/t H_2SO_4 if needed.
- Cleaner start-ups and shutdowns:
  - Continuous control by the tail-gas treatment system in single absorption plants, ensuring emissions are managed during all operational phases.
- Faster and cheaper start-ups:
  - Smaller plant size, fewer catalysts, and equipment result in about 30% less fuel and time required to start a single absorption plant compared to a double absorption plant.
- Safer:
  - Lower risk of hydrogen accidents in single absorption plants compared to double absorption plants, with fewer reported incidents due to hydrogen exposure.
- Sustainability:
  - Currently, companies are reinventing themselves to achieve greater efficiency with fewer resources. This involves producing more acid and energy while minimising capital, operational, and maintenance costs. This embodies the essence of sustainability.

Conclusions

Advantages of a single absorption plant compared to a double absorption plant have been listed, highlighting that in the current scenario, single absorption presents more economic and versatile appeal compared to double absorption. Single absorption plants should capture the attention of investors, both for constructing new facilities and for remodelling existing double absorption plants, aiming to eliminate the environmental and economic weaknesses associated with double absorption.

Clark Solutions offers an extensive range of options for evaluating, building and converting sulphuric acid plants to single absorption, including tail gas treatment systems. ■

CONTENTS
What's in issue 410
COVER FEATURE 1
Indonesia's nickel boom
COVER FEATURE 2
Pyrite-based acid
COVER FEATURE 3
Acid plant tower design
COVER FEATURE 4
SRU catalysts

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Cobalt-molybdenum catalyst activation in low temperature TGUs

Part 1

Cobalt-molybdenum (CoMo) catalysts are integral components of tail gas units (TGUs), playing a vital role in reducing harmful sulphur dioxide (SO_2) emissions arising from Claus sulphur recovery units. Effective activation of these catalysts is essential for their optimal performance. The consequence of sulphiding at low temperatures and atmospheric pressure in low temperature TGUs is to compromise effectiveness of catalyst activation. In the first part of this two-part article, **Michael Huffmaster**, Consultant, explores CoMo catalyst activation at low pressure, focusing on sulphiding reaction pathways and the impact of temperature and the composition of the sulphiding media on reaction kinetics, specifically the concentration of H_2, H_2S, and H_2O.

Cobalt-molybdenum (CoMo–Al_2O_3) catalysts are integral components of tail gas units, playing a vital role in reducing harmful sulphur dioxide (SO_2) emissions from Claus sulphur recovery units in refineries and gas plants. The catalyst function is to convert all sulphur species from the Claus unit to hydrogen sulphide (H_2S) in the hydrogenation reactor. This H_2S is recovered via an amine system and recycled to the upstream Claus unit. Relatively sulphur-free off gas is incinerated and released to atmosphere.

A reduction in SO_2 emission to the atmosphere has been achieved via sulphur recovery units and removal of sulphur from fuels over the past 50 years. Air quality, thus quality of life, has improved. This progress needs to continue in our contemporary practices and innovations.

Claus and TGU processes are complementary, combining to recover sulphur from amine acid gas and sour gas, found in gas treating and refining applications. The Claus process produces elemental sulphur and typically achieves 96% sulphur recovery. The TGU improves the overall sulphur recovery to 99.9%.

The role of the catalyst in the hydrogenation reactor is providing catalytic sites for conducting TGU reactions at operating temperature. Effective activation of CoMo catalysts is essential for their optimal performance. As important as it is for TGU operation, activation is not well understood, owing to complicated chemistry[1,4] and because conventional TGU in-situ techniques produce good results.

The advent of low temperature tail gas catalysts has led to units constructed without the capability to achieve temperatures of 300 to 315°C traditionally applied for activation of these catalysts. Many low temperature TGU (LT TGU) offer only 240°C reactor inlet or lower. The consequence of low temperature activation has been weak catalyst activity.

Activation utilising H_2S and H_2 proceeds with reduction and sulphidation of MoO_3 through a number of steps, involving complex and poorly delineated chemistry[1,14]. Sulphidation of CoO is more straightforward, but its interaction with MoS_2 nanoparticle edge to promote active sites is also complicated and not well defined. Examining research and proposed reaction mechanisms helps clarify the impact of temperature and the composition of the media on sulphiding kinetics at atmospheric pressure, specifically the concentration of hydrogen (H_2), hydrogen sulphide (H_2S), and water (H_2O).

Improving effectiveness of catalyst activation in low temperature tail gas units lies in utilising heat of exothermic activation reactions and managing process parameters to achieve bed temperatures greater than 260 to 270°C. As constraint, operations must be in concert with catalyst activation limitations for temperatures and guidelines to achieve good metals dispersion while avoiding damage such as cobalt reduction.

TGU and low temperature impact

The TGU process converts SO_2, elemental sulphur and other sulphur species, to H_2S which is then recovered and recycled to the Claus unit. Additionally, CO is converted via water-gas shift. A conventional TGU is shown in Fig. 1. Its line-up includes an inlet heater or reducing gas generator, hydrogenation reactor, and amine circuit.

Key equipment changes related to conventional vs. low temperature operation are highlighted in Fig. 2. These changes provide reactor preheat using a high pressure steam heater exchanger in lieu of a burner or reducing gas generator and delete a low pressure steam energy recovery exchanger.

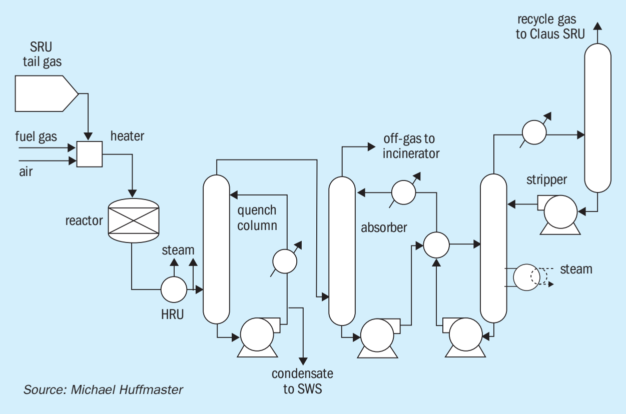
A heater is used to raise the feed gas to the required TGU reactor inlet temperature. The reactor inlet temperature is set to ensure reactions proceed sufficiently to achieve conversion of sulphur species necessary to meet stringent environmental regulations. The relationship of sulphur species conversion with catalyst kinetic activity coefficient and reactor space velocity is addressed in other papers[6], but the designer's role is to provide sufficient catalyst to achieve the operating company's required conversion based on catalyst vendors' activity data for selected operating temperatures.

Introduction of enhanced catalysts with strong activity at low temperatures enabled TGUs to operate with 200 to 220°C reactor inlet temperature. In conventional TGUs the heater is a line burner (or reducing gas generator) or a high temperature heat media exchanger and is required to deliver process temperatures of 250 to 300°C. Low temperature TGUs often feature a heat exchanger (steam or heat media), which reduces capital cost, improves operability and can offer extended catalyst life, all desirable features.

A consequence of the low temperature configuration is preheater downgrade and inability to achieve more than 240°C as the inlet temperature to the reactor. This limitation arises because heat exchangers use condensing MP steam at 600 psi or 42 bar. Field reports suggest operating systems may see 5 to 10 degrees lower temperature. The reactor temperature inlet of 240°C in low temperature TGUs is also the maximum temperature for catalyst sulphiding. In contrast, conventional TGUs are capable of reactor inlet temperatures of 300 to 315°C for final heat soak during sulphiding, which achieves strong activation.

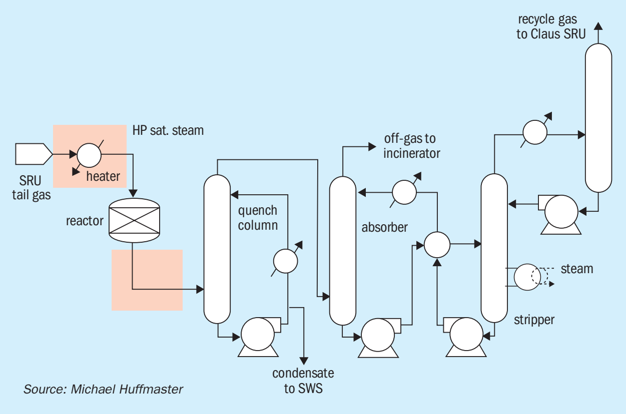
Research published at Brimstone (Huffmaster *et al*, 2019) examined the influence of activation variables, in particular range of temperatures. Examination of temperature, time, and H_2 concentration revealed diminished activity from low temperature activation. As shown in Fig. 3, the best achieved activation at 220°C was 66% of the activity of fresh catalyst.

Fig 1: **Conventional TGU lineup**



Source: Michael Huffmaster

Fig 2: **Low temperature TGU lineup**



Source: Michael Huffmaster

The effect of low hydrogen concentration was found to exacerbate low temperature activation, needing 10% or 0.15 bar for minimal 66% activity and falling below 55% at lower values of 1.5% or 0.02 bar. Furthermore, this finding was consistent across all TGU catalysts vendors suggesting the fundamental character of CoMo-Al_2O_3 catalyst is closely tied to activation[9].

Performance in several low temperature TGUs of in-situ sulphided catalyst was approximately 50% of full catalyst activity; this activity level is typically associated with spent catalyst. Of these field-applied activation practices, some only realised 225°C bed inlet temperature and exhibited very shallow exotherms. Undoubtedly other influences affected these units such as high initial water load, low hydrogen partial pressure, and slow temperature ramp up.

This reveals design shortcomings on preheat even for low temperature units. As well, operations adopt very conservative practices, erring on the side of caution, and duly following decades-long practices heeding catalyst supplier's cautions to raise temperature slowly to avoid temperature excursion as excessive temperature could damage catalyst. These conservative practices combine for less than effective activation at low temperature, not even achieving 240°C in the bed.

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8
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25
26
27

Tail gas unit catalyst

The CoMo-Al_2O_3 catalyst is widely applied in refineries for hydro desulphurisation (HDS) and hydro treating, accounting for 10% of worldwide catalyst volume. Because these are major markets, they enjoy scientific and technical interest. Tail gas applications do not attract the same level of interest as HDS, but they use similar catalysts. Much of the HDS developments and basic research can be useful as applied to TGU catalysts.

The manufactured form of TGU catalyst is oxidic, with MoO_3/CoO metals on a high surface area γ-alumina support, which is highly porous, with minimal diffusional resistance, designed for heterogeneous gas phase application. Metal oxides are impregnated and dispersed on an activated alumina support to provide a large number of catalytic sites. TGU catalysts are Type I, calcined to disperse and distribute the impregnated metals. Type II catalysts utilise a chelate to improve dispersion and are not calcined.

CoMo catalysts require activation to have catalytic function in the process environment of hydrogen and hydrogen sulphide. Activation is achieved by heating in a controlled process with hydrogen and H_2S, traditionally finished at 315 to 345°C.

The activated MoS_2/CoS form of these catalysts are active for these tail gas reactions:

Metal-catalysed hydrogenation

$$SO_2 + 2H_2 \rightarrow S + 2H_2O$$

$$S + H_2 \rightarrow H_2S$$

$$CS_2 + 3H_2 \rightarrow CH_3SH + H_2S$$

$$CH_3SH + H_2 \rightarrow CH_4 + CH_2S$$

Shift reactions

$$CO + H_2O \rightarrow CO_2 + H_2 \text{ (water gas shift)}$$

$$COS + H_2 \rightleftharpoons CO + H_2S \text{ (sour shift)}$$

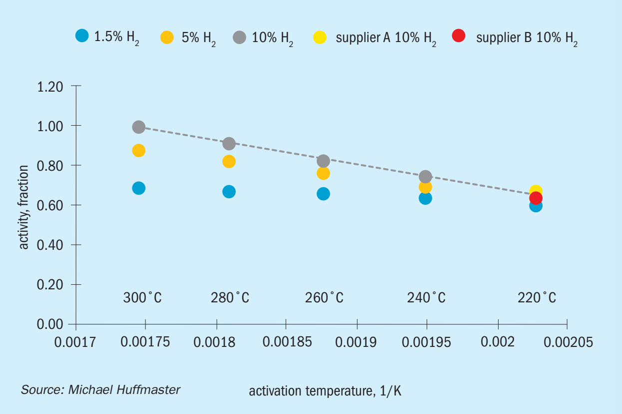
Alumina-catalysed hydrolysis

$$COS + H_2O \rightleftharpoons CO_2 + H_2S$$

$$CS_2 + H_2O \rightleftharpoons COS + H_2S$$

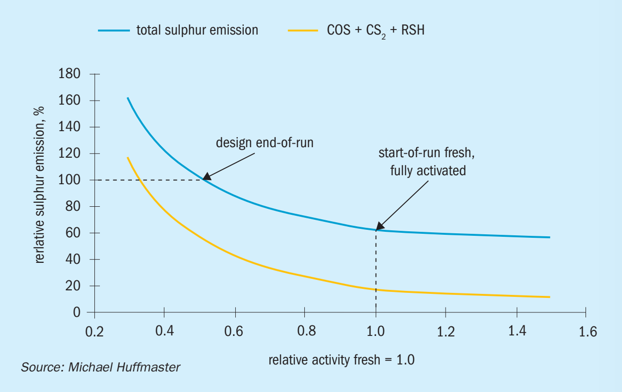
Note: SO_2 participates in other reactions, including reduction by CO; reduction by CS_2; Claus reaction with H_2S which proceeds on alumina until SO_2 is extinguished.

Fig 3: **Catalyst activity vs. activation temperature – isothermal**



Source: Michael Huffmaster

Fig 4: **Expected sulphur emission vs catalyst activity: basis of chart is sulphur to incinerator including H_2S**



Source: Michael Huffmaster

Strong activity at operating temperature enables the reactor to achieve high conversion of sulphur species, required for the TGU to attain high sulphur recovery and low emissions. Low temperature catalysts developed over the last 20 years express strong kinetic activity at temperatures as low as 200 to 230°C when fully activated.

The consequence of weak activation from low temperatures is diminished catalytic function. The consequence of diminished function and low operating temperature is reduced conversion of target reactions. This condition increases the concentration of sulphur species such as COS, CS_2, and CH_3SH in the reactor outlet, which slip past the amine system and raise emissions.

An example of expected sulphur emission as a function of relative catalyst activity is shown in Fig. 4. Relative activity reflects decline of catalyst activity through aging and poisoning. The emissions include sulphur species COS, CS_2, and RSH which pass through the absorber, as well as slip of H_2S at the absorber and other sources such as pit vent, sulphur degasser or sour water tank vents. At the design point, approximately half the emissions are from COS, CS_2, and RSH. Sulphur emissions vary with conversion achieved on COS, CS_2, and RSH. Conversion is impacted by relative activity and residence time. Sulphur species conversion is reasonably represented as following first order reaction mechanics[6]:

$$\text{conversion} = (1 - e^{-kt}),$$

where k = activity coefficient and t = residence time or 1/space velocity

The design point shown is to achieve 100 % target emission at end of run (EOR), typically set at catalyst relative activity = 0.5, thus ensuring there is sufficient catalyst inventory to achieve required conversion at EOR. At start of run (SOR) with fresh, fully activated catalyst the relative activity = 1 and expected emissions are about 63% of permitted or design.

Emissions would be higher if activation is weak and emissions could possibly exceed design when catalyst ages. If a low temperature activation achieves relative activity = 0.7 then initial emission is 78% of design. With activity decline by half over normal service life, relative activity = 0.35 and emissions would be 140% of design. Throughput could be reduced to 70% to maintain emission compliance.

Catalyst activity declines over life due to aging and poisoning, so sufficient catalyst inventory is needed for the unit to meet required environmental performance at EOR. For LT TGU, activity decline from aging is slower at low temperatures, although starting with weak activation means weaker activity over life and could require shortened catalyst cycles to stay in environmental compliance. Reactor temperature increase improves conversion and could extend life, although that capability will be limited in LT TGU design.

The function of the catalytic reactor depends on design parameters such as space velocity (gas rate/catalyst inventory) and operating temperature. If performance is limited then the operator may increase temperature, reduce throughput, or reduce catalyst service life. Reducing service life by increase in catalyst replacement frequency adds to operating cost but has less severe economic impact than out-of-cycle or unscheduled outage for catalyst replacement.

Activation OF Co Mo Al_2O_3 catalyst

Tail gas catalysts and HDS catalysts are prepared in the form of highly dispersed molybdenum oxides on supports such as γ-alumina with 250 to 300 m^2/g surface-area to which promoters like cobalt (or nickel) are added. These are subsequently converted into the catalytically active phase by sulphidation, a controlled process conducted typically in H_2S/H_2 atmospheres at temperatures between 300 and 400°C:

$$\underset{\textit{inert oxide}}{MoO_3 + H_2 + 2H_2S} \xrightarrow[\textit{magic happens}]{300\text{-}400°C} \underset{\textit{active catalyst}}{MoS_2 + 3H_2O}$$

Whereas it would be useful to know the mechanism of sulphiding, as it is important to the delivery of effective catalysts, the activation chemistry of CoMo-Al_2O_3 catalyst is complex and not that well understood[1,4]. Research and field experience define major steps that help analyse activation and influence of process variables.

Research effort in industry and academia have probed the chemistry of HDS catalyst reaction and activation for over four decades. The investigations have followed the Topsoe Co-Mo-S model[2,3]. The range of catalyst forms covered includes model compounds, e.g., MoO_3 and CoMo, alumina supported catalysts, and commercial catalysts, some calcined, others not. Conditions range from ambient temperature to 400°C and system pressures from atmospheric to 20 atm with H_2/H_2S (5 to 15%). Insights also come from MoS_2 monolayer-related HER studies and semiconductor research.

Research papers inform reaction pathways and kinetic steps to consider. Model compounds utilised in research are simpler systems; promoted systems enhance catalytic performance but add complexity. Alumina supports improve dispersion as well enhance sulphiding but have interactions and add complexity[4]. Several essential activation steps have been elucidated, especially by advances in intense spectrographic techniques. Advancement in computational techniques for molecular properties and interactions are beginning to quantify thermochemical properties for reaction intermediates, providing the opportunity to refine sulphidation kinetics.

Research shows that the impact of high partial pressures is that sulphidation completes in a shorter time or at a lower temperature, although catalysts differ between studies. A few studies offer some information to help understand low hydrogen partial pressure.

Research identifies that above 240°C crucial steps occur, namely, transition and reduction to MoS_2 followed by transformation from amorphous to the nanoparticle or slab through crystallisation.

This is of significant note for low temperature activation. The crystallisation process also needs evaluations for how it is best represented. A number of variables need consideration and an approach other than traditional nucleation theory may help, due to observations of clustering and organising[14].

Findings in these articles inform important steps and transitions in the activation pathway. They help understanding of TGU catalyst activation because TGU catalyst and HDS catalysts are similar in composition and function and activation, incorporating MoS_2 nanoparticles promoted by cobalt. A summary and pathway for sulphidation of CoMo catalyst using a tail gas unit sulphiding procedure is discussed in the box on page 46.

TGU sulphiding can be summarised in three steps:

- **Initial sulphur uptake** (170 to 240°C): Sulphiding is initiated at 170 to 200°C in H_2 and H_2S at 1 atm pressure. MoO_3 and CoO are converted to their respective sulphides, proceeding through a number of parallel pathways and intermediates to form amorphous MoS_2 and CoS. This first phase is characterised by sulphur replacing oxygen, then reduction of molybdenum to mixed valence, and loss of oxidic crystal structure.
- **Reduction and transition** (240 to 260°C): In raising the temperature from 240°C to 260°C a critical transition occurs with molybdenum becoming mostly Mo+IV, an ordering of MoS_2 and seeding initial nucleation sites.
- **Annealing and transformation** (260 to 315°C): This phase ramps to 315°C with the catalyst reacting up to stoichiometric sulphur and the transformation of amorphous MoS_2 to crystalline. Activated catalyst has nanoparticles of crystalline MoS_2 (monolayer or 2 to 4 layer slabs) with CoS promotion on the edges which are active catalytic sites on the alumina substrate. This completes activation.

Sulphiding reactions can initiate at ambient temperature in a H_2/H_2S environment, but TGU sulphiding is initiated at 180 to 200°C. Reactions from initiation to 240°C are captured as first phase.

Delving deeper into the chemical pathways, first consider small crystallites of MoO_3 (20–40 Å) intermixed with CoO, populating the surface of an alumina

CONTENTS
What's in issue 410
COVER FEATURE 1
Indonesia's nickel boom
COVER FEATURE 2
Pyrite-based acid
COVER FEATURE 3
Acid plant tower design
COVER FEATURE 4
SRU catalysts

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4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27

Activation reactions delineate potential pathways

For a CoMo catalyst the activation reactions are:

$$MoO_3 + H_2 + 2H_2S \rightarrow MoS_2 + 3H_2O$$

$$CoO + H_2S \rightarrow CoS + H_2O \qquad \text{(also } Co_9S_8\text{)}$$

For molybdenum, several pathways may be followed including oxy-sulphide and MoO_2 and possibly MoS_3.

$$MoO_3 + H_2 \rightarrow MoO_2 + H_2O$$

$$MoO_2 + 2H_2S \rightarrow MoS_2 + 2H_2O$$

Or

$$MoO_3 + 3H_2S \rightarrow MoS_3 + 3H_2O$$

$$MoS_3 + H_2 \rightarrow MoS_2 + H_2S$$

Or

$$MoO_3 + 2H_2S \rightarrow MoOS_2 + 2H_2O$$

$$MoOS_2 + H_2 \rightarrow MoS_2 + H_2O$$

Finally, to be active, amorphous MoS_2 must assemble into a lattice and incorporate cobalt, and transition into a crystalline structure and edge decoration by Co.

A study[10] on MoO_3 reduction by hydrogen to MoO_2 identified a path through an intermediate

$$MoO_3 + H_2 \rightarrow MoO_2 + H_2O$$

$$MoO_2 + 3MoO_3 \rightarrow Mo_4O_{11}$$

$$Mo_4O_{11} + 3H_2 \rightarrow 4MoO_2 + 3H_2O$$

Reaction is applied at 550°C for commercial production of MoO_2. This does not proceed below 400°C, so it is not a viable pathway for TGU CoMo sulphidation.

substrate[5]. These crystallites are well dispersed and only a few molecular layers thick (~ 2.5 average), expressing a surface area on the order of the alumina substrate.

This particle size can be estimated from knowing crystallites are distributed to a depth within pores of 60–90 Å. The size of these, within limits, are 20 to 40 Å, which fits within 40% of pore diameter. Stacking on the order of 2 to 4 layers fits with 6.5 Å per layer for the MoS_2, as pores are not obstructed. This gives us a crystallite or platelet of 6 to 12 units across of MoO_3 or MoS_2. Roughly 50% to 70% of the molecular entities would be exposed to the sulphiding medium, with the balance as interior layer or in contact or interacted with the substrate.

When the surface portion of the oxidic crystal is exposed to the sulphiding environment, it reacts with vigour. Internal layers are hidden by a very low permeability outer layer or shell such that diffusional resistance retards their reaction. Additionally, a portion of the crystal atomic structure interacts with the substrate to form quite stable chemical bonds during calcining[5]. The interacted portion of the oxidic crystals have higher activation energy barriers to sulphide. The temperature required for sulphiding $CoAl_2O_4$ was 625°C[1], therefore it would not sulphide at TGU conditions.

On this landscape consider sulphiding reactions pathways for metal oxide: crystals of MoO_3 and CoO dispersed on γ-Al_2O_3 are exposed to a H_2S/H_2 mixture at ~ 1 atm:

- Initial sulphiding: reactions are initiated at 150 to 170°C and this chemistry prevails to 200°C, (sulphiding can initiate at ambient temperature)
  - Surface layer in the MoO_3 crystal lattice exchanges terminal oxygen (Mo=O) for sulphur, forming oxy-sulphides[4,5,11,18]
    $MoO_3 + H_2S \rightarrow MoO_2S + H_2O$
    $MoO_2S + H_2S \rightarrow MoOS_2 + H_2O$
    Mo+VI is reduced to Mo+V and Mo+IV; possible structures are:
    $Mo^{6+}O_2^{2-}S^{2-}$ or $Mo^{6+}O^{2-}S_2^{2-}$ or
    $Mo_2^{5+}O_2^{2-}S_2^{2-}S_2^{2-}$ or $Mo^{4+}O^{2-}S_2^{2-}$
  - Cobalt oxide is sulphided
    $Co + H_2S \rightarrow CoS + H_2O$ (also Co_9S_8)
  - Bridging ligands of sulphide and disulphide, $S^{=}$ and $S_2^{=}$ bond to adjacent molybdenum, disrupt the MoO_3 lattice and create more terminal oxygen; the process continues, sulphur replacing terminal oxygen, relaxing the lattice, creating more terminal oxygen[5,7].
- The formal structure of MoO_3 is lost. Sulphides formed are amorphous.
- Hydrogen can now be dissociated on CoS or $MoOS_2$ to form atomic hydrogen above 150°C[13]. Molecular hydrogen and sulphur are too bulky to enter the crystal interior. Molybdenum oxides are not reduced by molecular hydrogen at these temperatures (below 400 to 550°C)[10].
  - Atomic hydrogen diffuses into the crystallite interior and reduces MoO_3[11]
    $MoO_3 + 2H^* \rightarrow MoO_2 + H_2O$
    reducing Mo+VI to Mo+IV.
  - The oxy sulphide can also reduce with atomic hydrogen, forming a MoS_2 shell
    $MoOS_2 + 2H^* \rightarrow MoS_2 + H_2O$
  - MoO_3 (or oxy sulphide) can also react with H_2S to form amorphous tri-sulphide
    $MoO_3 + 3H_2S \rightarrow MoS_3 + 3H_2O$
    $MoOS_2 + H_2S \rightarrow MoS_3 + H_2O$
    Mo+VI may be reduced to Mo+V and Mo+IV; possible structures are:
    $Mo^{6+}S_3^{2-}$ or $Mo_2^{5+}S_4^{2-}S_2^{2-}$ or $Mo^{4+}S^{2-}S_2^{2-}$
  - At 200°C most exposed active surfaces of metal crystallites are converted to sulphide or oxy sulphide and interiors have been reduced by atomic hydrogen to MoO_2[11,12].
- In the range 200 to 240°C more of the oxy sulphides and MoO_2 are converted to MoS_2; hydrogen reacts directly with Mo-S sites[7] and S_2^{2-} ligands are converted to S^{2-}, depending on hydrogen partial pressure. Molybdenum valence is varied and the MoS_2 formed is amorphous[4,5].
  - $MoOS_2 + H_2 \rightarrow MoS_2 + H_2O$
  - $MoO_2 + 2H_2S \rightarrow MoS_2 + 2H_2O$
  - $MoSS_2 + H_2 \rightarrow MoS_2 + H_2S$
- Reduction – transition, a crucial change in the 240 to 260°C range:
  - Mo+IV increases to 70% from 17%[7].
  - Evolution of H_2S, potentially reflecting S_2^{2-} ligands reducing to S^{2-}[4,11].
  - Some studies find Mo-O signal disappears at this transition indicating conversion of $MoOS_2$ and remaining MoO_2 (in 20 atm H_2 Mo-O bond signal extinguishes at 150°C)[4,5].
  - The Mo-S coordination number (CN) is ~ 4 after the transition, indicating amorphous MoS_2[4]; Molybdenum atoms are bonded to four sulphur atoms; Haandel indicates nucleation of crystalline MoS_2 begins.
- Annealing – transformation, temperature increased from 260°C to 300-350°C
  - Nucleation continues and amorphous MoS_2 transforms via crystallisation into slabs; bond length for Mo-Mo increases to (3.17Å) corresponding to crystalline MoS_2[4].
  - Hydrogen facilitates crystallisation transition, reducing activation energy [8,13].
  - Sulphur uptake continues until completed with S:Mo ratio of ~2.
  - Coordination number of Mo-S increases to 6, indicating a MoS_2 crystalline structure[4].
  - The S:Co ratio is ~ 1; Have CoS and Co_9S_8; latter is dominate, but not active[19].
  - Incorporation of CoS on the edge of the MoS_2 slab[19].
- MoS_3 reduction to MoS_2 – enhanced by higher H_2 partial pressures or higher temperatures; decomposes at 310°C; studies report MoS_3 are (Mo_3) cluster structures, amorphous, poorly organised but of Mo+IV valence[20].

Transition of amorphous MoS_2 into crystallites is accomplished with annealing, forming nanoparticles or slabs and Co interacting on the edge of 2H MoS_2 two-dimensional nanocrystal-active catalyst sites. Molybdenum is bonded to six sulphur atoms, each sulphur atom is bonded to three molybdenum shown in Fig. 5.

The sulphiding reaction pathways identify crucial aspects of activation, including important transition point at temperature of 240 to 260°C. Also required is the presence of hydrogen sulphide or a sulphur source, hydrogen, and annealing amorphous MoS_2 to form activated crystalline slabs[8,12].

Sulphidation practice varies, with completion at 300°C or 345°C or 400°C. Many reports state sulphiding is completed at 300°C. Others report further refinement and activity enhancement with annealing at 350 to 400°C. Most activation studies heat soak at final temperature, typically for two hours.

In commercial catalysts metals are well dispersed. This is an important feature because dispersion lowers the temperature of sulphidation reactions to as low as ambient from as high as 300°C on non-supported model substances[5]. Additionally, the presence of cobalt promotor enhances sulphiding. Alumina substrate is also an active catalyst in tail gas system for hydrolysis reactions.

The chemical formula of molybdenum disulphide is MoS_2. The most stable crystalline form is 2H, a monolayer, with a hexagonal plane of S atoms on either side of a hexagonal plane of Mo atoms. Strong covalent bonds are between the Mo and S atoms, but weak van der Waals bonds hold layers together. Each molybdenum atom is bonded to six sulphur atoms (Mo-S CN = 6) and each sulphur atom is bonded to three molybdenum atoms.

Layers slide on each other with little friction, which is why MoS_2 finds use as a lubricant. Layers can be mechanically separated to form 2-dimensional sheets of MoS_2.

Molybdenum disulphide belongs to a class of materials called 'transition metal dichalcogenides'. Transition metal atoms are groups 4-12 in the periodic table and a chalcogen is group 16. Applications include catalysis, solid state lubricants, semiconductor/electronics, hydrogen-evolving reactions, batteries, photocatalysts, and a growing list.

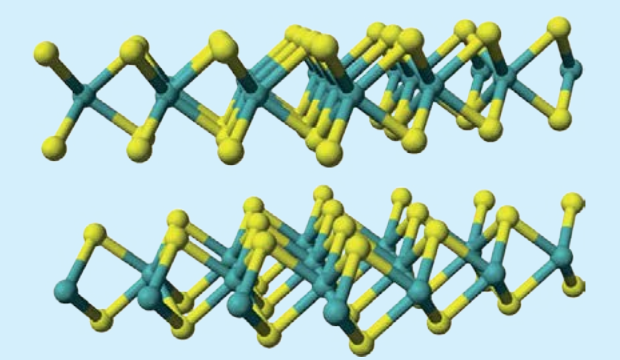
Pressures and composition

Partial pressure of the reactants H_2S and H_2 is set by concentration and total pressure. Most published studies are at pressures of 1 to 20 bar and 5–15% H_2S in hydrogen. Sulphidation reactions proceed readily at lower temperatures when conducted at higher pressures. For low pressure conditions there are a few HER studies[8]. The 2019 tail gas low temperature activation study was at 2.5 to 10% H_2 at 3.5% H_2S and 5% H_2S in H_2 at 1 atm. HDS gas activation conditions may be as high as 20 to 30 bar of hydrogen with 1 to 3% H_2S whereas tail gas pressure is 1 atm with 1-4% H_2S and 2-8 % H_2.

Sulphidation reaction rates are in proportion to hydrogen sulphide partial pressure and metal surface area. Whereas high H_2S partial pressure increases reaction rates, a greater concern is very low H_2S partial pressures. At very low H_2S concentrations, hydrogen can reduce cobalt oxide to metal, especially at elevated temperatures[17].

Hydrogen partial pressure impacts reaction rates. With chemisorption and dissociation the high pressure impact is muted (reaction rate α square root pressure) but over a range of 1000-fold partial pressure its effects are still significant. Low hydrogen concentrations, less effective at reducing molybdenum, hinders the proper sulphidation of the catalyst; formation of metal sulphides, essential for catalytic activity, is incomplete.

Fig 5: **Ball-and-stick model of the part of the crystal structure of molybdenite, MoS_2. This work has been released into the public domain by its author, Benjah-bmm27**



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The role of hydrogen is important in several intermediate reactions and influenced by its partial pressure. An important step in completing sulphidation is reducing S_2^{2-} ligands (oxy sulphides and S_2^{2-} bridging ligands form at lower temperatures) and hydrogen is an important driving force for this reaction, which begins above 200°C, developing the MoS_2 matrix and may continue into the 240 to 260°C transition[4,5,7]. Atomic hydrogen is thought to reduce MoO_3 to MoO_2[13]. If MoS_3 is present hydrogen helps reduce it to MoS_2 below the thermal decomposition temperature of 315°C. Hydrogen readily adsorbs onto terminal sulphur so oxy-sulphides are a catalyst for dissociation of molecular hydrogen.

Low pressure activation may also push the transition temperature higher and may reduce rate of growth of slab structures. Hydrogen is crucial to development MoS_2 crystals. HER studies on hydrogen effect on amorphous MoS_2 transition to crystal identify hydrogen presence reduces activation energy (1.6 eV vs 3.5 eV). Bulk nucleation and crystallisation were noted in 0.005 atm H_2 at 300°C, whereas no crystallisation occurred absent hydrogen at 300°C in one hour[8].

Water

Water dampens thermal response, being adsorbed or desorbed on the alumina. Heat of chemisorption used is 50 kJ/mol. Energy to desorb 0.01 wt fraction from one kilogram catalyst is 28 kJ, about 10% of the energy of activation. At 10% v water in gas at 1 atm and 200°C, equilibrium water on alumina is 0.0126 wt fraction. This effect is more pronounced at higher relative humidity, e.g., lower temperature and higher water concentration.

Water is the product of reduction and sulphidation reactions. Equilibrium for gas–solid reactions is established by product/reactant ratios of the gaseous species, so water vapour exerts a back pressure for weaker reactions. Water inhibits the reduction of molybdenum oxide or cobalt oxide or moly oxy-sulphide by hydrogen. Elevated water concentrations reduce the grain size of MoO_2.

MoO_3 and MoO_2 are hydrophobic in contrast to most metal oxides and less affected by water. The amorphous MoO_2 may have affinity for water on exposed metal atoms and increase the number of oxygen vacancies, which would reduce the rate of sulphur uptake. The impact of water on oxy sulphides is unknown, but hydrogen bonding on terminal oxygen could diminish hydrogen dissociation.

Heat effects

The reaction sequence outlined and the physical features of oxide crystals offer an explanation for observed sulphiding reaction behaviour: early vigour and strong response to temperature which moderates after initial sulphiding. Once about one-third of sulphur uptake is reached, the thermal response is muted even as temperatures are raised above 240°C.

A mechanism of molybdenum–oxygen-sulphur ring-structure activation complexes supports the stepwise oxygen replacement by sulphur and conversion of MoO_3 which progresses through oxy-sulphide intermediates[15]. The calculated enthalpy by density functional theory (DFT) for these intermediates suggest an even distribution of the "overall" heat of reaction energy among sulphur addition steps[16]. With successive activation barriers and smaller Gibbs energy functions the Kp are smaller ~ 10 – 1000 vs 10^6 overall, and the main driving force for the slower reactions as H_2S partial pressure (and H_2S: H_2O ratio).

It is known that initial sulphiding reactions express strong exotherms. Clearly the initial sulphiding step has a higher proportion of heat of reaction or a low activation energy for a stronger kinetic activity coefficient. Intermediates, such as oxy sulphides or reduction reactions must proceed slowly and require higher temperature, suggesting higher activation energies. The characterisations of thermochemical properties for reaction intermediates though DFT calculations is an area of developing research which will help better understand the sulphidation process.

Heat of reaction goes in part to heat the catalyst and in part to heat the sulphiding gas flowing through the bed. With gradual heat release steps, a greater portion of the energy is carried with the gas, and with higher gas rates more heat is carried with the gas and temperature rise is smaller.

Heat of reaction is from published thermodynamic data bases. Enthalpy of formation for MoS_2 now taken as -230 kJ/mol (NBS, AIP) vs previously used value of -276 kJ/mol NIST/JANAF. The molybdenum disulphide heat of formation is less negative and the corresponding expected heat effects are smaller – reduced from previously published values. Enthalpy of formation for MoS_2 now taken as -230 kJ/mol (NBS, AIP) vs previously used value of -276 kJ/mol NIST/JANAF.

The overall heat of reaction for the activation of MoO_3 is taken as 174.86 kJ/mol in this work. Additionally, the published heats of formation are for crystalline solids, meaning there needs to be apportioning of the heat of reaction related to activation to crystallisation transformation as well.

Heat of reaction goes in part to heat the catalyst and in part to heat the sulphiding gas flowing through the bed. Gas flow can preheat the lower bed but with gradual heat ramp steps a greater portion of the energy is carried out of the bed with the gas and bed temperatures are lower. With higher gas rates more heat is carried with the gas and temperature rise is smaller.

Laboratory and research activations are usually temperature controlled. *In situ* field activation is adiabatic. Although the exothermal response of sulphiding is not a major consideration for laboratory work, the exotherms of field activation must be addressed and controlled.

Time and temperature

Time and temperature dependencies have not been well defined for transformation since many published studies are conducted to 300 to 350°C or higher. For activation at low temperature this blind spot is rather critical. Activation at lower temperatures prolongs the reduction and sulphidation process. The lower thermal energy available at these temperatures slows kinetics; longer exposure times may help reduction and sulphiding of metal oxides, but may not be sufficient to ensure full activation. This extended duration might lead to the adverse outcome of less transformation, increased MoS_2 stacking, and more cobalt in the inactive Co_9S_8 motif, further affecting catalyst efficiency.

The time period for many these referenced studies was two to three hours. Where data are available on metals composition and spectrograph at various temperatures from 220 to 280°C, they clearly support that at fixed exposure times higher temperatures advance sulphidation and crystallisation[7,8,14]. General tail gas studies have historically applied "full" activation at 300°C for three hours. The 2019 study at lower temperatures extended times up to 18 hours, with improved activation at extended times, but not realising full activation potential[9]. Field practices are typically 8 to 12 hours including a heat soak.

A more strongly calcined catalyst has a greater number of strong interactions between substrate and metal, forming $CoAl_2O_4$ (spinel) or $Al_2(MoO_4)_3$[18]. Metal-substrate bonds must be overcome in order to form sulphide, requiring substantial activation energy; this requires higher temperatures and higher H_2S or H_2 partial pressure. Many of these metal-substrate bonded metals are not sulphided by TGU procedures, as they require temperatures in the 600 to 1,000°C range[18]. Generally, a higher fraction of cobalt interacts with substrate, but as much as 20% of molybdenum may be bound in this way and unavailable for catalysis[1,5.]

Accomplishing the transformation step, crystallisation, by heating may seem counterintuitive; however sulphiding conditions are well below melting point so amorphous MoS_2 is figuratively frozen. Annealing generally heats to just below melting point – or a point of atomic mobility, holds and cools.

Annealing occurs by the diffusion of atoms within a solid material, so that the material progresses towards its equilibrium state. Heat increases the rate of diffusion by providing the energy needed to break bonds. The movement of atoms has the effect of redistributing and eradicating irregularities and defects. THe melting point of MoS_2 is 2883 K (JANAF) or 2375°C (NIH/NBS). The onset of mobility of atoms in a solid is generally taken as Hüttig temperature, melting point/3. For MoS_2 this would be 610 to 688°C, normally the minimum for a reforming process such as annealing. American Chemical Society suggests MoS_2 sublimes at 435°C, indicating a somewhat earlier onset of atomic mobility.

Many literature references discuss annealing at temperatures in the range of 400 to 800°C and some specific studies report defect reduction/property improvement from 2H MoS_2 as low as 300°C. Overall, it is indeed extraordinary and fortunate that crystallisation will occur in the 260 to 315°C temperature range.

For activation of low temperature catalysts at 260°C and below the process must be assessed in the lab and by field trial. This will hopefully be reported in the near future. Modelling can address managing exotherms and the degree to which catalyst bed temperatures can be raised safely. The question is how much benefit to activation can be obtained by prolonging elevated bed temperatures. ■

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- **Sulphur handling equipment meeting today's challenges**

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CONTENTS
What's in issue 410
COVER FEATURE 1
Indonesia's nickel boom
COVER FEATURE 2
Pyrite-based acid
COVER FEATURE 3
Acid plant tower design
COVER FEATURE 4
SRU catalysts
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ISSUE 410
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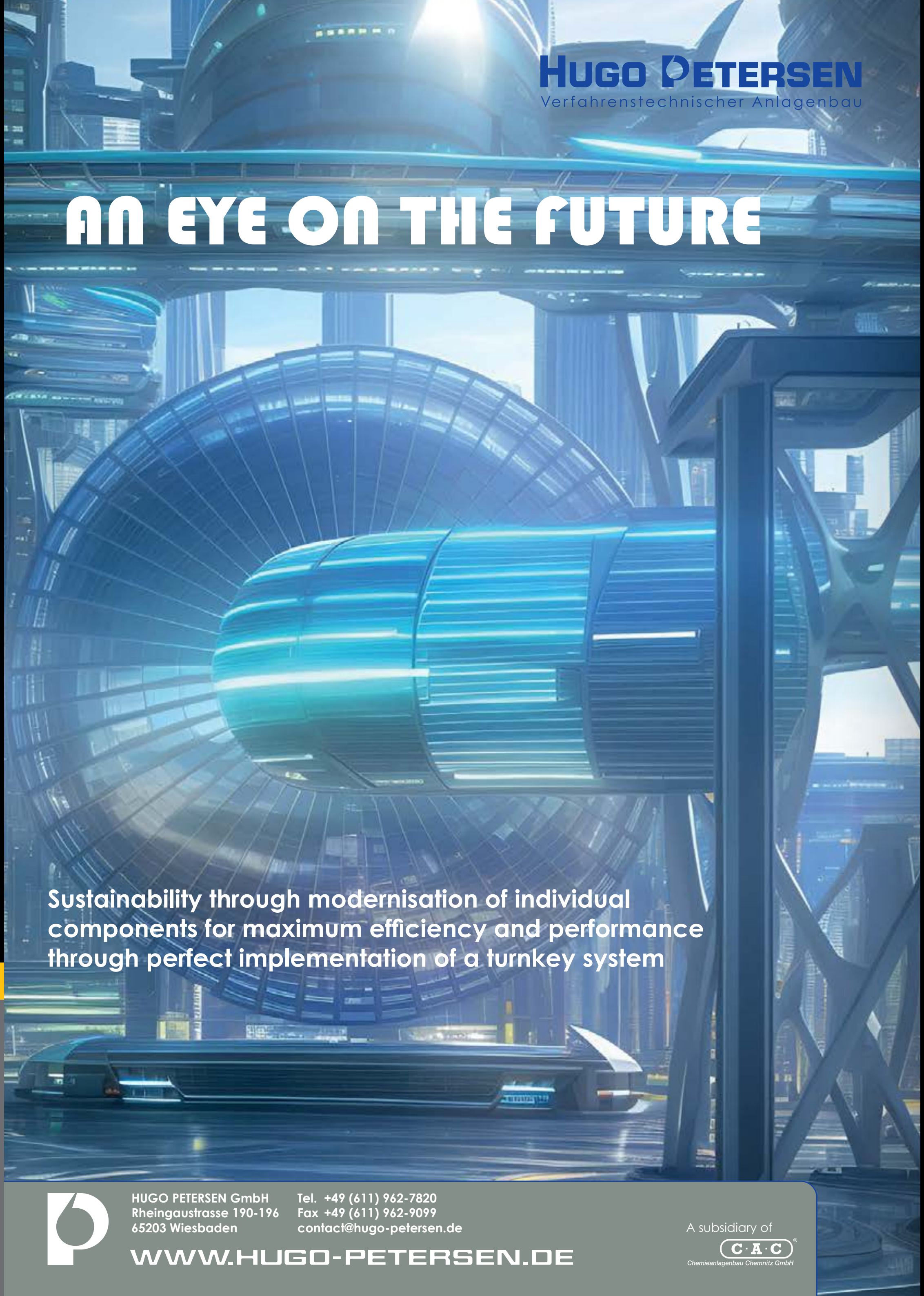
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27



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