May June 2022

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Sanctions hit sulphur markets Sulphur content of crude Meeting pipeline quality specifications Water-related issues in SRUs

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CAR INTERNATION

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What goes up...



ulphur prices keep on climbing. A quick check as I was writing this showed some indicators above \$600/t, around four times what they were last year. As the title of this editorial suggests, what goes up must of course eventually come back down, but of course as always the question is: when?

Commodity prices were already at high levels before February 24th, when Russian tanks crossed the border into Ukraine, and the war and sanctions have added an extra spike of panic buying to the mix. But even before that happened some analysts, such as Goldman Sachs and JPMorgan Chase & Co, had been predicting that we were entering a new commodities super-cycle after the 12 year downturn following the slowdown in the Chinese economy and the banking collapse of 2008-09. Goldman's head of commodities research, Jeff Currie, actually suggested last week that the current covid-related shutdowns in China had removed almost 2 million bbl/d of oil demand from the market and were masking underlying shortages, which would inevitably be exposed as China reopened. Indeed, he has been saying for a year now that all of the apparent supplyside issues we have seen over the past year; labour shortages, war, sanctions, bottlenecks in supply chains, shortages of truck drivers, covid-related disruptions etc, are merely symptoms being caused by the real story; that of rising global demand across the board. Some of this, he argues, comes from government policies to deal with the covid crisis, leading to a new era of commodity-intensive growth, as governments put greater emphasis on job creation and environmental sustainability rather than the focus on financial stability that followed the 2009 financial crisis, typified by the Green New Deal in Europe and president Biden's \$2 trillion American Jobs Plan

Certainly this demand-led growth can be seen in metals markets, where the new focus on batteries is leading to rapidly rising demand for nickel, cobalt, lithium, copper and aluminium. Metals mining has seen structural under-investment after the collapse of the previous commodities boom, and is now racing to catch up. Trafigura estimates that 10 million t/a of additional copper will be required by 2030, while nickel demand is likely to almost double, and lithium demand may increase fivefold. This is good news for demand for sulphur, though it will also lead to more smelter acid trying to find a home. The phosphate industry, the mainstay of demand for sulphur and sulphuric acid, also continues to grow, albeit at slower and more steady levels. While mature markets such as North America and Europe, and now increasingly China are seeking to gradually reduce phosphate overapplication, many regions of the world remain under-supplied, and growth is continuing, especially in Brazil and India. With phosphate prices high, there is no indication as yet that high sulphur prices are impacting upon demand.

So is this the start of a new commodity supercycle? At the moment, the consensus seems to be yes, though one of the worries about the current boom is that this time the surge is making its way into the general economy, leading to the return of serious inflation after an absence of nearly 30 years. Interest rates will inevitably follow, and while some might suggest that this is merely a return to 'normal' after a decade of quantitative easing when governments pumped vast sums of money into the economy without causing inflation, and loans were cheap, it will also no doubt catch out those who over-borrowed during the 2010s. China was already facing a mountain of bad debt, especially in the property sector, as witnessed by the troubles of property giant Evergrande, which sailed close to insolvency last year. It is also possible that we are seeing the reverse of major trends that brought lower prices and more stable markets, such as a return to protectionism after several decades of globalisation; even if the Ukraine conflict were resolved tomorrow, permanent damage has clearly been done to east-west relationships. Globally, ageing populations may also lead to lower savings rates and higher inflationary pressures, while demographically we are nearing the end of a period when rapid labour force growth in developing countries and the increased participation of women in the jobs market also helped dampen increases in wages and input costs. Only continuing technological change seems to continue to point towards lower prices.



Richard Hands, Editor

BCInsight

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Is this the start of a new commodity super-cycle?"

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MARKET INSIGHT

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

SULPHUR

The global sulphur market has continued to firm, with key benchmark prices at elevated levels not seen since 2008. Lower liquidity emerged in April, with some buyers operating on a hand-to-mouth basis. The latest round of economic and financial sanctions in the wake of the Russia-Ukraine conflict has made financing arrangements more challenging. Further price increases are expected through May, particularly while sulphur from Russia and in some cases nearby markets explore alternate transport routes. The tight balance is expected through the remainder of the first half of 2022 before easing with the potential for a price correction increasingly likely as the market grapples with the ongoing conflict.

The Brazil c.fr price has risen to \$510-520/t, the highest level on Argus' records, and other benchmarks are expected to increase to similar levels in the short term. A lack of available vessels because of selfsanctioning, steep insurance premiums and rising freight costs continue to hamper supply from the Black and Baltic seas. As international buyers continue to seek alternative supply to Russian product, sourcing from the Middle East and North America has supported increased export prices in these regions. The Middle East spot range increased to \$454-464/t f.o.b. in April and is expected to rise further in the outlook. The benchmark has risen by 53% since the

turn of the year. The range for Middle East contract supply for second-quarter delivery was concluded at \$380-405/t f.o.b. Middle East to end-users and trading firms, a \$105-120/t rise on the first quarter.

Adnoc set its April official sulphur price for liftings to the Indian market at \$420/t f.o.b. Ruwais, up by \$85/t from the March price. Kuwait's K% set its April sulphur lifting price at \$435/t f.o.b., up by \$92/t from the March price. Muntajat set the April Qatar sulphur price at \$430/t f.o.b. Ras Laffan/Mesaieed, up by \$97/t from the March QSP of \$333/t f.o.b. These increases came largely as a response to the bottlenecks to Russian supply seen since the start of the conflict.

There is still an appetite among some non-OECD countries to procure Russian sulphur, with product that has become available as a result of self-sanctioning by buyers - and attracting higher logistics costs and risks - being priced at the lower end of the global range. Should the financial, legal and logistical framework be in place, then a two-tier pricing structure for sulphur will continue to develop. No Turkmen sulphur was delivered by rail to Kavkaz in the first quarter, and transport along the Volga-Don canal was yet to restart at time of writing. Turkmen product has continued to be loaded at Poti, Georgia, under lower freight costs relative to other Black Sea ports, but delays to loading persist as a result of inland bottlenecks.

The IEA has cut its global oil demand growth forecast for this year following Covid-19 lockdowns in China. Shanghai has partially loosened its Covid-19 quarantine policies after implementing a city-wide lockdown from 1 April, as the government pushes ahead with its economic growth plans. The city is home to the world's largest and busiest container port, which is subject to delays owing to logistical bottlenecks. This is creating disruption across global supply chains that are already under severe stress. The Chinese economy is the biggest single driver of global growth, and slashed forecasts will ratchet up the problems associated with rising inflation and economic stagnation in the country.

Metals-based demand for sulphur is providing support for prices to firm further as margins are boosted by rising commodity prices. At present, demand is deemed sufficient to maintain pricing at historically elevated levels and is likely to prevent a significant downturn in the second quarter. But the balance between the cost of sulphur feedstock and the revenue generated from goods sold is becoming a delicate one. This is evident in the industrial sector in western Europe, where demand erosion is becoming a real possibility. Manufacturers of caprolactam/ammonium sulphate, which use sulphur or sulphuric acid in their production processes, have struggled to pass on elevated costs to consumers. This has forced many sulphur users to reduce operating rates.

Developments in the processed phosphates sector underpin our view for sulphur price changes through the rest of 2022. We forecast a softening by June as export restrictions on Chinese fertilizers come to an end. The rate of softening



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will increase through the third quarter as demand erosion and normalised exports from China alleviate the supply concerns that have persisted since the fourth quarter. The introduction of new Middle Eastern sulphur capacity during the second half of the year will likely add to the softening trend, but the extent of the price reduction will be driven by the pace at which fresh Middle East supply will enter the market. The key projects impacting this balance are in Qatar, Saudi Arabia and Kuwait.

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The global sulphuric acid market has continued on a more stable footing compared to sulphur, albeit with prices stabilising at high levels in recent months. The NW European export benchmark has broadened slightly with the average price easing by \$5/t to a mid-point of \$230/t f.o.b in April. The benchmark has increased by 132% over the past year and has reached unprecedented levels since 2021. The tight supply/demand balance in the region has provided the support for prices to remain at a premium compared to export prices in other regions.

Direct impact from the Russia-Ukraine conflict remains limited but associated markets continue to be affected. NW European contracts for the second quarter settled in a range of €203-260/t c.fr for sulphur-based supply, representing an increase on the first quarter. The smelter price for second quarter contracts increased in a range of €20-30/t to €146-191/t c.fr. Tight molten sulphur supply fundamentals continue to drive the local market fundamentals. Logistics in the region

is hampering the short-term outlook. There has been a shortage of truck drivers on the continent since the start of the conflict in Russia/Ukraine. The increase in fuel prices has led to some sellers adding surcharges to deliveries. The Stolberg smelter in Germany had been expected to return to operations in the Spring but this has now been delayed to the summer. With heavy reliance on trucked transport at the plant concern is growing that there will be difficulty procuring trucks.

Meanwhile the Grillo Werke facility returned to operation following its maintenance in mid-April. The upcoming Aurubis Hamburg smelter maintenance is scheduled to last for 90 days. Contract commitments are expected to be covered during this period. On the buy-side there has been some demand destruction noted in NW Europe across both the fertilizer and non-fertilizer markets.

Over in Chile, acid shipments from Asia led to higher delivered prices at \$280-285/t c.fr in mid-April, representing an increase of around \$24/t on a month earlier. Spot demand is expected to increase for arrivals in the second half of the year. Some buyers took short positions for contract tonnage and will likely return to the market for spot volumes. Concern remains in the market following industrial action in Peru and Chile leading to supply worries. Congestion is likely at ports because of delays to cargoes and potentially arriving close together. Imports of acid in January-February 2022 totalled 514,000t, up by 25% on a year earlier. China was the leading supplier at 200,000t of supply.

In North America, Rio Tinto reached a new collective bargaining agreement

with Kennecott union workers at the end of March, averting a potential stoppage. The agreement lasts five years from April, was reached after seven weeks of negotiations. The unions involved represent about 1,300 of the more than 2,000 employees at the Kennecott copper mine operations near Salt Lake, Utah. The smelter has the capacity to produce around 1million t/a sulphuric acid. The domestic US market has been tight on the back of logistical challenges and plant turnarounds. Rising demand from the fertilizer sector has emerged ahead of the spring application season. Trucking and rail transport have seen delays with reports of difficulty in procuring trucks for spot volumes.

China remains a key acid exporter but the rise in Covid-19 cases has led to logistical challenges in transporting acid. Chinese exports are expected to rise in 2022 on 2021 levels, but short-term disruption may hamper availability. Prices in April were stable at \$135-150/t f.o.b., with the high end \$10/t above the Japan/South Korea export range. South Korean acid exports dropped in March, down by 26% on a year earlier to 182,000t, with fewer delivered to Chile, China and southeast Asia.

The short-term outlook is bullish because of rallying freight rates and strong demand from industries including metals. Short term supply is expected to be disrupted, likely leading to higher prices for spot out of Asia. The second half of the year is likely to see stretched spot demand, but much will hinge on when Chinese supply will rise for the export market.

Price Indications

| Table 1: Recent sulphur prices, major markets | | | | | |
|---|----------|----------|---------|----------|-------|
| Cash equivalent | November | December | January | February | March |
| Sulphur, bulk (\$/t) | | | | | |
| Adnoc monthly contract | 230 | 265 | 310 | 318 | 335 |
| China c.fr spot | 325 | 327 | 342 | 378 | 413 |
| Liquid sulphur (\$/t) | | | | | |
| Tampa f.o.b. contract | 183 | 183 | 282 | 282 | 282 |
| NW Europe c.fr | 228 | 228 | 327 | 327 | 362 |
| Sulphuric acid (\$/t) | | | | | |
| US Gulf spot | 228 | 238 | 238 | 238 | 238 |
| Source: various | | | | | |

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Market Outlook

Historical price trends \$/tonne



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- The ongoing conflict in Russia-Ukraine remains a key focus for the market in the months ahead. It is unclear whether buyers that are currently doing so will permanently choose non-Russian sulphur sources, but trade flow changes are expected to persist through the rest of 2022.
- Two-tier pricing will be a feature of the market with Russian sulphur expected to be priced at a heavy discount to other exportable supply in the outlook. Demand for sulphur from North America and the Middle East will continue to support the run-up in pricing for at least the next few months.
- The re-entrance of China to the fertilizer export market underpins the view for a price correction in both the DAP and sulphur markets. High raw material costs for processed phosphates producers will keep prices at elevated levels on the 2021 average.

- The progress of the Covid-19 outbreak in China is a risk to the sulphur market with new capacity expected to add considerable supply in the second half of the year. The reduction of crude runs may hamper short term output in some provinces but Chinese sulphur supply is forecast to rise to 9mn t for the first time in 2022.
- Outlook: Global sulphur prices are likely to see further increases in the short term through the month of May but a price correction is forecast in the latter part of the year. The last time prices were at these levels was in 2008 which was followed by a crash in pricing. Strong demand and support from high product prices in end user markets is expected to limit the extent of the downturn in sulphur in 2022.

SULPHURIC ACID

ISSUE 400

 Freight rates have been on the rise. The Asia-Chile freight increased in April to a range of \$115-130/t for a 20,000t

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vessel. This is supporting the view for firmer prices for acid.

- Chile's state copper mining agency, Cochilco has increase its copper price forecasts for 2022-23 amid a perceived scarcity of supply caused by the Russia-Ukraine conflict. Russia makes up about 4% of global refined copper. Higher copper prices are a supportive factor for acid consumption rates at mines and supports pricing.
- Moroccan acid imports totalled 199,000t in January 2022, up by 54% on a year earlier. Imports for the year are expected at 1.3 million t/a in 2022, down on 1.7 million t/a imported in 2021.
- Outlook: There is strong support for sulphuric acid prices in the short term with buying activity in major markets increasing. Second half demand for spot is expected to test prices further against a backdrop of tight supply. The spate of turnarounds in Europe as well as potential demand destruction remain key influences on the balance.

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Abu Dhabi Live in-Person

SOME OF THE TOPICS TO BE DISCUSSED AT SOGAT 2022

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- Enhancing HSE Practices in Sour Hydrocarbon Management through Digitisation
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SOME OF THE ORGANISATIONS PARTICIPATING IN SOGAT 2022



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Breakthrough in lithium-sulphur battery technology

Researchers from Australia's Monash University say that they have created a new generation of lithium-sulphur batteries which could provide a cheaper, cleaner and faster-charging energy storage solution that outlasts lithium-ion alternatives and is rechargeable hundreds of times without failing. The team has creating a new interlayer which allows for exceptionally fast lithium transfer, as well as an improvement in the performance and lifetime of the batteries.

"The interlayer stops polysulphides, a chemical that forms inside this type of battery, from moving across the battery; polysulphides interfere with the anode and shorten the battery life," said professor Matthew Hill, deputy head of the university's Department of Chemical and Biological Engineering. "The new interlayer overcomes the slower charge and discharge rates of previous generation lithium-sulphur batteries. It means the battery can be charged and discharged hundreds

of times without failing."

Lithium-sulphur batteries already offer higher energy density and reduced costs compared to lithium ion batteries and can store 2-5 times more energy per kg, but previously the electrodes in lithium-sulphur batteries have deteriorated rapidly during the recharge process. Hill said the development could be a 'gamechanger' for lithium-sulphur batteries. which do not rely on metals like cobalt, nickel and manganese, which are critical minerals for lithium-ion batteries.

Separately, scientists in the United States have announced that they have developed a lithium-sulphur battery using a commercially available carbonate electrolyte which retained more than 80% of its initial capacity after 4,000 cycles. The group used a vapor deposition process, which unexpectedly produced a form of sulphur that did not react with the electrolyte, overcoming one of the key challenges for this battery chemistry.



Monash University's lithium-sulphur battery prototype.

UNITED STATES

LyondellBasell to shut Houston refinery by 2024

LyondellBasell says that it will stop operations at its 268,000 bbl/d Houston refinery in Texas by 2024 unless it can find a buyer for the facility. The company has been trying to sell the complex since last year, but is also said to be evaluating other uses for the site as part of its goal to reach net zero emissions by 2050. LyondellBasell, which is based in the Netherlands and run from Houston, aims to produce 2 million t/a of recycled or renewable-based polymers by 2030.

"While this was a difficult decision, our exit of the refining business advances the company's decarbonisation goals." LyondellBasell interim chief executive officer Ken Lane said. "The site's prime location gives us more options for advancing our future strategic objectives, including circularity."

The refinery is designed to process heavy, high-sulphur crude grades, chiefly from Mexico - in 3Q 2021 it imported 5.6 million barrels of oil from Mexico. However, Mexico has declared its intention to halt crude oil exports in 2023, and US

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sanctions against Russian oil have also clouded the outlook for sour heavy crude supply in the US Gulf coast.

Sulphur fire on cargo barge

A sulphur fire broke out on the Alafia sulphur barge and its attendant tug the Kelly at the port of Tampa on April 22nd. The vessel, owned by Savage Marine Services, was evacuated and the fire brought under control. There were no reported injuries among the crew and minor injuries to one firefighter. The boat was docked at the International Ship Repair and Marine Services for repairs and the fire was reportedly started by welding sparks igniting sulphur dust in the cargo hold.

IRAN

New sulphur forming plants

Two new facilities have been inaugurated at the Shahid Soleimani Sulphur Complex at Sarakhs in the northeastern Khorasan Razavi province of Iran. close to the Turkmenistan border, to convert raw crushed lump sulphur into more valuable forms, according to Iranian Oil Ministry's news agency Shana. The facilities, built at a

cost of \$15 million, join two existing sulphur forming facilities at the site. One of the new plants will produce 72,000 t/a of sulphur bentonite for fertilizer use, and the other 150,000 t/a of granulated sulphur.

CANADA

Refuel Energy to use Topsoe technology at renewable fuel facility

Refuel Energy Inc has announced plans for the construction of a 3,000 bbl/d renewable fuel plant in southern Ontario. The proposed project, called Refuel YYZ, would supply the aviation and terrestrial fuel needs of the greater Toronto area, home to 6 million Canadians, while lowering the CO_2 emissions for the end users by up to 80%. The plant would utilize Haldor Topsoe's proprietary HydroFlex[™] and H2bridge[™] technologies for the production of renewable diesel and sustainable aviation fuel (SAF). Planned feedstocks include a mix of waste fats, oils and greases, such as regionally-sourced used cooking oil, animal fats and non-edible crop oils.

"We are very pleased that Refuel has selected our technologies for this state of the art, standalone renewable diesel and

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SAF facility. Our market-leading technologies are complementary and together they will produce some of the lowest carbon intensity renewable fuels in the world," said Henrik Rasmussen, managing director, The Americas at Topsoe.

Refuel expects to make a final investment decision in 2023. If approved, production at the new facility would start in 2025.

UNITED ARAB EMIRATES

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Bids submitted for Fujairah LNG project

Front end engineering and design (FEED) bits have reportedly been submitted for the Abu Dhabi National Oil Company's (ADNOC's) 10 million t/a Fujairah liquefied natural gas export terminal. Middle East Economic Digest reports that the bidders include KBR. Fluor and McDermott International of the US and French engineering company Technip Energies. Japan's JGC and Chiyoda are said to no be longer involved. The FEED study will be carried out later this year. The LNG project includes two 5 million t/a liquefaction trains, processing facilities and utilities, as well as an export jetty, and possibly a 2 bcf/d pipeline from Habshan to Fujairah. The project will be owned and operated by ADNOC LNG, in which ADNOC holds the controlling 70% stake, with other holdings from Mitsui, BP and Total.

The company is separately progressing with a revised FEED study on the Hail & Ghasha sour gas project to supply gas for the LNG and other projects. The UAE is aiming to reduce its dependence on gas imports from Qatar via the Dolphin pipeline and expand its existing 6 million t/a of LNG exports. Technip is said to be revising designs for Hail and Ghasha to reduce estimated \$15-20 billion construction costs, aiming to competed FEED work by the end of 2022. The development will now be phased to spread costs: first gas will come online in 2025 as originally planned but will then be ramped up in stages to the 1.5bn ft^3/d target plateau by end-decade.

MALAYSIA

Samsung tipped to win sour gas EPC contract

South Korea's Samsung Engineering looks set to be awarded the engineering, procurement and construction contract for Malaysia's new Rosmari-Marjoram onshore gas plant on Sarawak. The plant, to be built and operated by Petronas, will process highly sour gas from offshore sour gas fields operated by Royal Dutch Shell (75%), Brunei Energy Exploration and Petroliam Nasional. The project is expected to start commercial production in 2025 and is forecast to peak in 2028 at approximately 16,500 bbl/d of crude oil and condensate and 495 million scf/d of natural gas.

It is one of several sour gas developments in Sarawak, where gas fields include high levels of carbon dioxide (between 20-70%). However some fields, including PTTEP's Lang Lebah off Sarawak, also have high H_2S concentrations. Petronas is targeting reinjection as a way of dealing with the acidic component of the gas feed, but is pitching this as 'carbon capture and storage'; gas produced at Lang Lebah will flow to a platform on the Golok field and from there to a new 900 million scf/d onshore gas processing plant at Kasawari, where the H_2S and other contaminants will be removed before the CO_2 rich stream is sent back offshore via pipeline for injection into the designated storage site. Honeywell UOP is providing modular natural gas processing technology to the project, including MemGuard and Separex technologies and adsorbents, to remove contaminants such as carbon dioxide, hydrogen sulphide, and mercury.

RUSSIA

Halliburton says contracts will end in May

Halliburton says that sanctions imposed in the wake of Russia's invasion of Ukraine will require it to wind down several of its ongoing contracts in Russia by May 15th. On March 18th the company said that it was ending all future work in Russia, and that it would "prioritise safety and reliability" as it wound down existing operations in the country. Halliburton says that the total net book value of its assets in Russia is about \$340 million and warned that sanctions could cause the company to take a charge related to those assets. Trade restrictions are blocking Halliburton's ability to export, re-export and move some equipment within Russia, according to company filings.

The US government has tightened export controls on oil and gas equipment, including drilling rigs, hydraulic fracturing software, high-pressure pumps and drill pipes, and refinery technology including gas separation, hydrogen generation and sulphur recovery. Other major contractors including Schlumberger and Baker Hughes have agreed to halt future work in Russia.



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Sulphuric Acid News

JORDAN

Memorandum on new phosphoric acid plant

The Jordan Phosphate Mines Company (JPMC) has signed a supply agreement with Germany's LUMA-International Company. Under the terms of the agreement, JPMC will sell 850,000 t/a of phosphate rock to the German company at international market rates. The agreement was signed by JPMC CEO Abdulwahab Rawad and managing director of LUMA-International Ralf Keller, in the presence of JPMC Chairman Muhammad Thneibat. Thneibat expressed hope that the deal would open wider scopes of cooperation between the JPMC and German companies in the field of phosphate fertilizers, and Keller likewise said that his company was looking forward to more cooperation with the JPMC

and new partnerships to produce phosphoric acid and phosphate fertilizers.

Two days later, the parties signed a memorandum of understanding (MoU) to establish and operate a new phosphoric acid plant in southern Jordan. At the signing, LUMA's Keller praised the achievements of JPMC in production and exports, expressing appreciation for the JPMC's efforts in being open to global markets and diversifying partnerships in this field. JPMC will, under the MoU, provide the new plant with its needs of phosphate rock to produce phosphoric acid, while LUMA commits to buying the entire output of the plant.

UNITED STATES

Fox River phosphate project moving forward

Canadian fertilizer developer Fox River Resources Corporation says that it has received a positive preliminary economic assessment (PEA) study for its Martison phosphate project and, with no current domestic production of finished phosphate products in Canada, the company believes that now is the time to advance the project. The proposed project, located near Hearst, Ontario, will include an open pit phosphate mine, a phosphate beneficiation plant, slurry pipeline, road corridor, and a 'fertilizer conversion complex' near to existing rail, power, and natural gas infrastructure. The latter will include a phosphoric acid plant, a super phosphoric acid plant, a granulation plant, a sulphuric acid plant with co-generation capacity, a warehouse and loadout facility, and a rail yard.

The economic assessment was based on capacities of 221,000 t/a of superphosphoric acid, 474,000 t/a of granular monoammonium phosphate (MAP) and 247,000 t/a of granular nitrogen, phosphate, sulphur (NPS). The target market includes the Eastern Canadian provinces, Canadian Prairie provinces and US northern states, and the company says that the Martison facility will capture a freight advantage relative to US and offshore producers in this market, especially in nearby provinces where demand is projected to grow and where a larger share of output is forecast to ship over time.

Stephen Case, Fox River Resources Corporation CEO said: "Western Canadian phosphate market demand has doubled in the past decade and remains the fastest growing market in North America, a market which the Martison project is designed to serve. With no current domestic production of finished phosphate products in Canada and a competitive operating cost, Martison is uniquely positioned to capture these markets that are primarily served by producers in central Florida, Idaho and the Gulf Coast."

RUSSIA

Nornickel continues installation for Sulphur Programme

With the first batch of five multi-tonne heat exchangers for Nornickel's Sulphur Programme having arrived on-site at the Nadezhda Smelter, Nornickel has begun the next step – installation of the giant units in the factory's confined space. Preparatory work made it possible to coordinate the contractors, the transportation and installation, which the company says are proceeding on schedule. Five of the 15 units have been hauled from the Dudinka port to the smelter, and the first one has now been mounted. The weight of the first unit installed is 147 tonnes, the heaviest one is 230 tonnes. All 15 are scheduled to be installed over a three month period. Their task is to aid the exchange of heat between the layers in the contact apparatus, which are being installed in parallel. The first heat exchanger is the start-up unit, which will take part in the start-up of the catalyst in the sulphur dioxide contact tank and play its part in reducing emissions.

"We will have to deliver 15 unique installation operations. Their uniqueness is that the weight and dimensions of the heat exchangers are different," said Andrei Zhuravlev, project manager for the installation and assembly of the heat exchanger units.

"Construction of one of the biggest projects in the recent history of the Russian



The first of 15 heat exchangers for the Sulphur Programme is installed at Nadezhda Smelter.

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SULPHURIC ACID NEWS

mining and metallurgical industry is in full swing. Within the next few months we will already be entering start-up mode for the individual facilities. Therefore, we expect that in 2023 we will be able to deliver on the Sulphur Programme goals and targets that we have set for ourselves at the Nadezhda Smelter," said Sergey Dubovitsky, Nornickel Senior Vice President.

SOUTHEAST ASIA

Outotec awarded process technology contract

Metso Outotec says that it has been awarded a major order for key minerals processing technologies at a copper and gold plant at an undisclosed location in southeast Asia. The contract value of approximately €40 million has been credited to the firm's Minerals division Q1 2022 orders received. Metso Outotec has a strong presence in southeast Asia including a Service Centre, which is able to support local mining customers.

DENMARK

Haldor Topsoe is now Topsoe

At the company's annual general meeting on April 7th, the shareholders voted to change the name of Haldor Topsoe A/S to simply Topsoe A/S, as part of a rebranding strategy. Founded in 1940 by Dr Haldor Topsoe, Topsoe aims to become a global leader in developing solutions for a decarbonised world, supplying technology, catalysts, and services for the energy transition, including for challenging sectors such as aviation, shipping, and the production of crucial raw materials.

CHILE

Drought affects Antofagasta Q1 results

Antofagasta says that its financial performance in the first quarter was as weak as expected, as the Los Pelambres copper mine continues to be affected by the drought in Chile. Copper production in Q1 2022 was 138,800 tonnes, in line with guidance and is expected to increase quarter-on-quarter during the year. Production was 24.2% lower than in the same quarter in 2021 and 22.4% lower than in Q4 2021 mainly due to the expected temporary reduction in throughput at Los Pelambres because of the drought and lower grades at Centinela Concentrates. Higher input prices, particularly for diesel and sulphuric acid, and general inflation were largely offset by the weaker Chilean peso. Compared to the previous quarter, costs increased by 21.9% on lower copper production due to lower grades and throughput.

The company also said that the review of its Los Pelambres expansion project has been completed and group capital expenditure for the year is expected to be \$1.9 billion. The Los Pelambres expansion project was 73% complete as at the end of Q1 2022.

INDIA

Paradeep claims to be the largest single site producer of phosphoric acid

In the past year, the Indian Farmers Fertilizer Collective (IFFCO) Paradeep plant produced 805,000 tonnes P_2O_5 of phosphoric acid. The company says that this makes it the largest single site production plant for phosphoric acid in the world. IFFCO operates a single reactor plant with a daily production capacity of 2,650 t/d

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The Sterlite copper smelter in Tuticorin.

at Paradeep. The acid is used in the production of downstream phosphate-based fertilizers including DAP and NPS, and, the company says, reduces India's dependence on imported complex fertilizers.

Petition for destruction of copper smelter

The Madras High Court has granted four weeks for the Tamil Nadu Pollution Control Board (TNPCB) to respond to a petition filed by activist Fatima, seeking to demolish the Sterlite copper smelting plant at Thoothukudi and forcing the owner Vedanta to take remedial measures for soil contamination, allegedly caused by the dumping of copper slag. Chief Justice Munishwar Nath Bhandari and Justice D. Bharatha Chakravarthy adjourned the hearing on the case after Vedanta disputed the claim that the soil had been contaminated because of the copper slag, and contended that the slag was actually used for road fills and in the cement industry. The company's lawyer argued that the copper slag was not hazardous at all and stated that it was one of the prime grounds that Vedanta had taken before the Supreme Court, where its appeals against the factory's closure by the Tamil Nadu state government, on the basis of alleged environment pollution, were still pending at present. The case was adjourned until after the Supreme Court decision on the matter.

Extra subsidy for phosphates

The Indian government has approved an additional subsidy \$760 million for diammonium phosphate (DAP) fertilizers to keep a lid on prices for farmers. The subsidy had already been raised by 140% on March 1st for the 2022-23 financial year, but soaring

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global phosphate prices in the wake of the Russian invasion of Ukraine have necessitated additional support. Prices of phosphoric acid and rock phosphate increased by 92% and 99% respectively, over the 12-month period to March 2022. India's subsidy bill was originally budgeted for just over a trillion rupees (\$13.7 billion), but there are concerns that it could reach as high as \$21.5-\$25 billion.

TUNISIA

Tunisia doubles phosphate production in 10 2022

Tunisia's phosphate production doubled to 1.3 million tonnes in 1Q 2022, compared to the same period in 2021, according to Gafsa Phosphate. The company is targeting production of 5.5 million t/a of phosphate for 2022, a 50% increase on 2021's 3.7 million t/a, to take advantage of soaring phosphate prices due to the war in Ukraine. Tunisia has struggled to regain the major position it held as a phosphate exporter prior to the Arab Spring, when it averaged 8 million t/a of production. Strikes and other labour disputes cut output to around 3 million t/a for most of the 2010s.



Loading phosphate at the port of Sfax.

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AUSTRALIA

GM and Glencore enter multi-year cobalt supply agreement

Glencore and General Motors have announced a multi-year sourcing agreement in which Glencore will supply GM with cobalt from its Murrin Murrin operation in Australia. Cobalt is an important metal in the production of EV batteries, and the cobalt processed from Australia will be used in GM's Ultium battery cathodes, which will power electric vehicles such as the Chevrolet Silverado.

By the end of 2025, GM plans to have capacity to build 1 million electric vehicles in North America, and has announced a series of actions to create a new and more secure EV supply chain, including projects targeting key EV materials and components.

"We are delighted to announce this collaboration and support General Motors in delivering its electric vehicle strategy," said Ash Lazenby, Glencore US Cobalt Marketer and Trader. "Future facing commodities like cobalt play a pivotal role in decarbonising energy consumption and the electric vehicle revolution. Glencore is already a leading producer, recycler and supplier of these commodities, which underpin our own ambition of achieving net zero total emissions by 2050."

The agreement will support Glencore's Murrin Murrin high pressure acid leaching (HPAL) nickel and cobalt plant in Australia. In 2021, Murrin Murrin produced 30,100 t/a of nickel metal and 2,500 t/a of cobalt metal, down 17% and 14% respectively, year-on-year, reflecting a lengthy scheduled statutory shutdown in May/June and various maintenance issues earlier in the year.

INDONESIA

Loan secured for HPAL project

Indonesian nickel company PT Ceria Nugraha Indotama has secured a syndicated loan of \$277 million from a consortium of Indonesian banks to help finance \$2.2 billion worth of nickel processing projects. The loan was arranged via Bank Mandiri, Bank Jawa Barat Banten and Bank Sulawesi Selatan Barat to fund construction of a 23,000 t/a rotary kiln electric furnace (RKEF) plant in southeast Sulawesi province, the first of four that Ceria plans to build, with a total capacity of 252,000

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t/a of ferronickel, as well as a high pressure acid leach (HPAL) plant with capacity of 103,000 t/a of mixed hydroxide precipitate (MHP). The first train of the RKEF plant is due to start commercial production in 2023 and the HPAL plant in 2024.

Freeport issues bond to finance smelter project

Freeport Indonesia has announced an offering of \$3 billion in senior notes, as the company speeds up work on two copper smelters in the Southeast Asian country. Construction has already begun on the \$3 billion smelter, designed by Metso Outotec, in Gresik on East Java. On completion, the facility will produce 1.7 million t/a of copper concentrate, making it one of the largest in the world. Commissioning is planned for late 2023 or early 2024.

Meanwhile, Linde has signed a contract with PT Smelting, coowned by Freeport Indonesia and Mitsubishi, to supply additional oxygen to support the expansion of Smelting's copper smelter operations at Gresik. The plant will utilize Linde's vacuum pressure swing adsorption (VPSA) technology to produce oxygen using an adsorption process. The new plant is expected to be completed and go onstream by October 2023. PT Smelting is boosting copper cathode production to around 350,000 t/a.

"This new, long-term contract demonstrates the trust between Linde Indonesia and PT Smelting developed during our partnership spanning almost 25 years," President Director of Linde Indonesia and Cluster Head for Indonesia, the Philippines, and Vietnam Vinayak Kembhavi noted in a statement received in Jakarta on Friday.

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Nickel production up in spite of Ukraine crisis

Global nickel smelting activity climbed in March, including in major producer Russia, despite the Ukraine conflict, according to commodities broker Marex, which uses SAVANT, a satellite analytics service it launched in 2019 to monitor activity at nickel plants worldwide. SAVANT has picked up disruptions at Ukraine's only ferro-nickel producer, Pobuzhskiy, but not at Nornickel's Nadezhda plant in Russia, Marex said. Russia supplies about 10% of the world's nickel.

The company also noted that copper smelting activity was higher in March, despite problems at Chinese private copper smelter Yanggu Xiangguang that halted output.

UKRAINE

Metinvest to import sulphuric acid

Interfax Ukraine reports that Ukrainian steel producer the Metinvest Group is facing a deficit of sulphuric acid for its coke plants, and intends to import acid from the European Union. Metinvest has three coke plants which require acid for pig iron production. The company's blast furnaces were shut down in the early days of the Russian invasion, but reopened in early April. The company is now looking at new logistics chains for both raw materials and finished products.

In 2021, the company's Zaporizhstal subsidiary increased pig iron production by 0.1% to 4.5 million t/a. Steel production decreased by 0.1%, to 3.8 million t/a, while the production of steel rolled products remained at the same level as for 2020; 3.2 million t/a. In January-February 2022, the plant reduced its rolled products output by 8.7% to 502,400 tonnes.





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Itafos has announced the appointment of **Stephen Shapiro** and **Isaiah Toback** to its board of directors, effective from April 14, 2022. Toback replaces **Rory O'Neill** as a nominee by its principal shareholder, CL Fertilizers Holding LLC, pursuant to an investor rights agreement between the Company and CLF.

"We are pleased to welcome Stephen and Isaiah to our board. Both appointments add to the overall depth and skill set of the board and will be instrumental in providing oversight as the company continues to execute on of its strategic initiatives," said Anthony Cina, chairman of the company's board of directors. "On behalf of the board, I would also like to thank Rory for his leadership and contributions to the company."

Shapiro is also CFO at Cellview Imaging Inc., an emerging medical device company. Prior to joining Cellview, he had a 30 year career in investment banking, most recently leading the Canadian Industrials and Consumer Group for Wells Fargo Securities Canada. Prior to that, he spent 13 years with BMO Capital Markets, where he started and led the Agriculture and Fertilizer Group. He is a Chartered Financial Analyst and holds a bachelor of commerce from McGill University and an MBA from the University of Chicago.

Toback is a partner at Castlelake and deputy co-chief investment officer. He is responsible for guiding and executing the firm's global investment strategy across asset classes, overseeing the firm's value and income fund portfolios and supporting the growth and development of its investment teams. He is also a voting member of the firm's Investment Review Committee. He became a partner of the firm in 2020 and previously served in portfolio management and investment roles, with particular experience with investments in dislocated industries and corporate special situations. Prior to joining Castlelake, he was an investment banker with Goldman Sachs, where he was responsible for transportation structured financings, focusing on the aviation and shipping industries. He holds a bachelor of arts in economics from Vanderbilt University.

Berndorf Band Group has appointed a new management team. In an unusual dual appointment as CEOs, **Alexander Leutner** and **Gernot Binder** will replace long-standing managing director **Herbert Schweiger** at the market leading steel belts and steel belt systems company. Jointly developing corporate strategy within the Berndorf Band Group.

Leutner joined the company, based in Austria, in 2014, where he worked as

executive vice president of the International Commercial Division until the end of 2021, when he stepped up to be one part of the management duo. He has a master's degree in law, and brings a wealth of international experience to the role, having previously worked for global companies for many years. In 2008, he moved to Hungary with his family to run a business as general manager, returning five years later to join the Berndorf Band Group.

Gernot Binder, also CEO of the Berndorf Band Group, graduated in mechanical engineering and gained his first professional experience in a technical company in the Triesting valley, followed by a successful career within the Berndorf Band Group, where he started in 1996 as Service and Training Manager. After two multi-year terms in the management of Berndorf's overseas companies in the USA, he returned to Austria in 2014, heading Berndorf Band Engineering GmbH as president until the end of 2021.

Joint CEO Alexander Leutner said: "We achieve [success] through our qualified employees, a unified market presence, good leadership, technological progress, modern working methods, digital opportunities, efficiency and cost management, and attentive governance of the organisation."

Calendar 2022

JUNE

6-10

Sulphur Experts' Advanced Amine Treating & Sulphur Recovery Course, REDONDO BEACH, California, USA Contact: Derek Zaharko, Senior Manager Tel: +1 281 336 0848 Email: Derek.Zaharko@SulphurExperts.com Web: SulphurExperts.com

8-9

ESA Spring Meeting, LISBON, Portugal Contact: Francesca Ortolan, Sector Group Manager, Cefic Tel: +32 499 21 12 14 Email: for@cefic.be

10-11

AIChE Clearwater Convention, CLEARWATER, Florida, USA Contact: Michelle Navar, AIChE Central Florida Section Email: vicechair@aiche-cf.org Web: www.aiche-cf.org

20-22

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4th European Sustainable Phosphorus Conference, VIENNA, Austria

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The following events may be subject to postponement or cancellation due to the global coronavirus pandemic. Please check the status of individual events with organisers.

Contact: Chris Thornton, European Sustainable Phosphorus Platform (ESPP) secretariat Tel: +33 474 93 07 93 Email: info@phosphorusplatform.eu

20-24

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Amine Experts' Amine Treating & Sour Water Stripping Technical Training Course, KUALA LUMPUR, Malaysia Contact: Jan Kiebert, Senior Manager Tel: +31 71 408 8036 Email: Jan.Kiebert@SulphurExperts.com Web: AmineExperts.com

27-JULY 1

Amine Experts' Sulphur Recovery Technical Training Course, KUALA LUMPUR, Malaysia Contact: Jan Kiebert, Senior Manager Tel: +31 71 408 8036 Email: Jan.Kiebert@SulphurExperts.com Web: AmineExperts.com

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ASRL Chalk Talk, CALGARY, Alberta, Canada Contact: Alberta Sulphur Research Ltd

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SEPTEMBER

12-16

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

12-16

29th Annual Brimstone Sulphur Symposium, VAIL, Colorado, USA Contact: Mike Anderson, Brimstone STS Tel: +1 909 597 3249 Email: mike.anderson@brimstone-sts.com Web: www.brimstone-sts.com

15-16

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

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Russia's invasion of Ukraine has turned the sulphur market on its head, potentially removing several million tonnes of supply from Russia and Kazakhstan and sending prices skyrocketing. ulphur markets had already picked up in 2021 due to increasing demand from the phosphate sector, and tighter supply, but 2022 has seen prices soar, especially since the invasion of Ukraine and the imposition of stringent economic sanctions. Middle Eastern prices are now over \$450/tonne; levels not seen since 2008-9. While there are a number of new supply projects coming on-stream, demand has also been increasing rapidly, and the removal of Russian supply has had a major impact.

Demand – phosphates

The phosphate market continues to dominate demand for sulphur. About 60% of sulphur (in all forms) demand is provided by phosphate fertilizer production, usually to treat phosphate rock to make phosphoric acid, which is then converted into ammonium phosphate or triple superphosphate, but some is used directly to make single superphosphate (SSP).

Phosphate markets had already been tight going into the end of 2021 due to a variety of factors, and the situation in Ukraine

has only exacerbated this. Things influencing the high prices in 2021 included the imposition of countervailing duties by the US on imports of phosphate from Morocco and Russia in March 2021. This occurred at the same time as increasing grain prices and higher demand for phosphate fertilizer globally, as well as sharply increased costs for ammonia due to high gas prices, especially in Europe, which impacts MAP and DAP costs. This meant that prices for DAP rose from around \$500/t to \$800/t during the year, and that then had a knock-on effect on China, which decided to impose export restrictions in September and October 2021. China accounts for about 30% of the world's trade in phosphates, and said it would not export phosphate until at least June 2022 in order to assure domestic phosphate supplies during the peak application season because of the record fertilizer prices. The international prices had combined with high demand and high energy costs in China to reduce domestic production, as well as supply restrictions due to widespread flooding in Henan province, where the country's phosphate industry is concentrated.

Above: The Nordstream 2 gas pipeline to Europe.



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Finally, the already very tight market conditions were exacerbated in November 2021 by Russia's decision to impose quotas on exports of fertilizer. Prime Minister Mikhail Mishustin said that the Russian government would introduce quotas to run from December 1st 2021 to May 31st 2022 on the exports of nitrogen and complex fertilizers. The former, mainly urea and ammonium nitrate, would be limited to 5.9 million tonnes, and for MAP, DAP and NPKs the limit would be 5.35 million tonnes. According to Mishustin, from December 2020 to May 2021, Russia exported 6.8 million tonnes of nitrogen fertilizers and 5.7 million tonnes of NP and NPK fertilizers. Though the Russian export limitations have meant that the impact of the sanctions imposed in the wake of the Ukraine conflict have had a more limited effect, it has nevertheless meant that phosphate prices have been at their highest level since 2008.

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As far as the outlook for phosphate fertilizer demand goes, there is projected demand growth in two of the major enduse markets; Brazil and India. Brazil in particular is seeing rapid demand growth as the country's farmers seek to capitalise on the country's burgeoning agricultural export trade. In the other two major phosphate markets, US demand continues to be relatively stable, while China is expected to see a fall in demand as the government continues to tackle overapplication of fertilizer and consequent leaching into watercourses, as well as emissions and air pollution. Falling Chinese demand for phosphates is also leading to the domestic phosphate industry becoming more reliant upon export markets, but at the same time finds itself some of the highest cost capacity. In any event, the current ban on Chinese exports has shut off this source of demand and led to lower capacity utilisation in China. But while phosphate production in China continues to decrease, this is more than made up for elsewhere by new supply from Morocco and Saudi Arabia in particular. as well as India and Russia. Over the next few years, downstream phosphate expansions are expected at Ma'aden in Saudi Arabia, OCP in Morocco, WAHPCO in Egypt, Serra do Salitre in Brazil, Kazphosphate in Kazakhstan, and several smaller Indian projects, including Paradeep Phosphates Ltd, RCF at Maharashtra. Mangalore Chemicals and Fertilizers Ltd, and Madhya Bharat.

The overall trend is for an approximately 1.4% increase in phosphate demand over the period 2022-26, according to CRU,

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with total phosphate demand rising from 55 million t/a P_2O_5 in 2020 to 59 million $t/a P_2O_5$ in 2025. Between 2022 and 2026, inclusive, phosphate demand for sulphuric acid is thus expected to add the equivalent of 5 million t/a of additional demand for sulphur.

Metals – nickel

After phosphates, the metals sector represents the next major tranche of demand for sulphur. Copper leaching, in Chile, Peru, the US and central Africa has long been the largest slice of metal demand for sulphur. and there is also some significant demand for sulphuric acid for uranium leaching in Kazakhstan. But nickel is the most rapidly growing sector; the breakneck growth in demand for electric vehicles is boosting the requirement for high purity nickel sulphate, and this is leading to a step change in the nickel market. Nickel production for stainless steel has increasingly come to reply upon pyrometallurgical processes such as ferronickel and nickel pig iron manufacture. However, producing high purity nickel sulphates from cheaper laterite ore bodies requires strenuous condition, generally involving sulphuric acid. After some years in abeyance because of being a higher cost production route, high pressure acid leaching (HPAL) is in vogue again, with several Chinese battery makers setting up plants in Indonesia, which has a large amount of laterite nickel ore, and a government ban on its export unless it is upgraded to higher value products. Indonesia is far and away the largest miner of nickel ore, representing around one third of all production.

While there are also copper smelter projects in Indonesia which will generate some sulphuric acid for domestic use. Chinese HPAL projects in Indonesia are by and large relying on burning imported sulphur, leading to around 1 million t/a of additional sulphur demand over the next four years. There are also some projects under development in Australia, although it is not looking likely that any will be onstream before 2026.

Metals – lithium

Looking slightly further down the track, there is also huge interest in lithium mining, again for battery production for electric vehicles. Lithium occurs primarily in lithium pegmatites, found mainly in Australia, China, and Canada, as well as Brazil, Portugal and

Zimbabwe, or in the form of high-lithium brine deposits, which are mainly found in an area known as the "lithium triangle" in Argentina, Bolivia and Chile. While lithium is recovered from brines using sodium carbonate, for lithium ores it is generally leached using sulphuric acid. It ca also be recovered form lithium bearing clays, such as occur in the United States, with acid leaching again the main method of recovery.

Currently around 350,000 t/a of lithium is mined per year, but it is reckoned that some 3 million t/a will be required by 2030. Lithium prices doubled in 2021. Consequently, there is a rush to develop new lithium capacity worldwide. Chile's SQM and several Australian projects are all under development. In the United States, ioneer is looking to develop a 20,000 t/a lithium mine at Rhyolite Ridge, with production beginning in 2024, and in northern Nevada. Lithium Americas is pressing ahead with a project three times the size, the largest in the Americas, with up to 1.9 million t/a of sulphuric acid consumption at capacity. Overall, CRU estimates that these two projects alone could represent almost 1 million t/a of additional sulphur demand over the coming few years. By the end of the decade, lithium leaching could become a significant source of new sulphur demand.

Industrial demand

Sulphuric acid is also used in a wide variety of industrial processes, from caprolactam production for fibres to pulp and paper manufacture and one of the main routes to titanium dioxide. These uses tend to collectively grow at roughly equivalent rates to global GDP, and will add just under 2 million t/a of new sulphur demand by 2026. Overall, from 2022-2026, sulphur demand is estimated to increase by just over 8.5 million t/a.

Supply – refineries

In general the trend for sulphur supply from refineries has been a steady increase for several decades, as regulations on the permitted sulphur content of fuels tighten to reduce emissions of sulphur dioxide, especially from vehicles, to reduce the impact on public health. While most countries have now moved to a 50ppm or lower sulphur content in fuels (15ppm or less in most of the developed world) standard, and so the extra incremental amount of sulphur being produced to reached higher standards is relatively modest, refinery sulphur

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production saw another boost due to the International Maritime Organisation's move to a global 0.5% cap on sulphur in bunker fuels, and 0.1% in emissions control areas.

Vehicle use continues to rise, especially in Asia, though the rate of increase is slowing, and the covid pandemic saw a slump in demand in 2020, though this recovered by 4% to 80 million new vehicles sold in 2021. However, the move to electric vehicles and more fuel efficient gasoline powered cars, as well as impending bans or restrictions on diesel vehicles are likely to lead to stagnating demand for fuel and oil over the medium term. The International Energy Agency's most recent (March 2022) forecast puts global oil demand at 99.7 million bbl/d by the end of 2022, a downward revision of 1.3 million bbl/d from previous forecasts due to the supply shock caused by the Ukraine conflict and western sanctions on Russia. Global refinery throughput estimates for 2022 have been revised down by 860,000 bbl/d as a 1.1 million bbl/d reduction in Russian refinery output is not expected to be fully offset by increases elsewhere. In 2022, refinery intake globally is projected to rise by 2.9 million bbl/d year-on-year to 80.8 million bbl/d. Surging oil and commodity prices could lead to global recession however and lower demand.

As far as new sulphur output goes, Europe and North American refineries are likely to be relatively constant, with growth from oil sands production balancing falls in sulphur inputs into US refineries from increased shale oil use. New refining capacity will come from China, Kuwait, Saudi Arabia, Qatar, Malaysia and Nigeria.

Supply – sour gas

The other main source of sulphur is from processing of sour gas. Use of natural gas has been on a rising trend for many years, mainly for power production, as it is seen as cleaner than coal in terms of carbon emissions and gas-fired power stations are cheaper and easier to set up. The rapid growth of a global LNG market has made global access to natural gas relatively affordable. Nevertheless, as more renewable and nuclear power is installed, so the 'dash for gas' that characterised the previous three decades is slowing. Demand growth has been strong in North America as cheap shale gas displaces coal-fired power generation capacity, and also in the industrialising countries of Asia. It has also seen a surge in the Middle East, where

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rapidly rising populations and demand for electricity in fast-growing cities like Dubai and Abu Dhabi have pushed growth in power generation. Conversely, Europe has seen gas consumption fall because of falling domestic production and the higher cost of importing from Russia and the international LNG market. Lack of availability of sweet gas has led to an increasing focus on sour gas resources to meet demand.

Sour gas production continues to decline slowly in Germany and Alberta, though there is a small increase in neighbouring British Columbia. The era of major new projects in Central Asia is drawing to a close. Most new sour gas production continues to come from the Middle East, especially Abu Dhabi, Saudi Arabia and Qatar. Saudi Arabia has added 1.3 million t/a of sulphur capacity via the Fadhili gas plant, which began production in 2020 and which is continuing to ramp up. Qatar's longdelayed Barzan LNG project is also now commissioned. Abu Dhabi is expanding the already huge Shah sour gas project to add a potential 1.7 million t/a of sulphur from around 2023. There is also likely to be around 300,000 t/a of additional production from Chuangdongbei in China.

Major project delays

The covid pandemic and associated slump in economic activity managed to delay several of the major new sulphur producing projects, including Barzan and Kuwait's Mina Al Ahmadi and Mina Abdullah refinery projects. However, with many of these projects now commissioned or commissioning, 2021 and 2022 are seeing a surge in new sulphur production after a fall in 2020 caused by refinery shutdowns or reduced run rates. In theory this should lead to supply overtaking demand later this year and an easing of the high prices that have been seen. However, the situation in Ukraine has served to complicate matters considerably.

Ukraine

The war in Ukraine has led to an unprecedented range of sanctions on Russia. Some of the most important include its removal from the SWIFT inter-bank transfer system, making processing payments more difficult. Many companies have announced their withdrawal from Russia, including several oil and gas majors. For the time being, Europe continues to buy large quantities of natural gas from Russia, though Russia recently stopped shipments to Poland and Bulgaria because they were not willing to make payments in roubles, and the Nordstream 2 gas pipeline project to Germany now has had its certification removed and gone into liquidation.

Russia produced just over 6 million tonnes of sulphur in 2020, though the figure was only 5.3 million tonnes in 2021, and Russian exports fell even more dramatically that year to only 1.8 million t/a due to increased domestic demand, mainly for phosphate processing. About half of this was exported to Europe and North America, countries which have now imposed sanctions. In addition to this, Kazakhstan, which exported 3.4 million t/a of sulphur in 2021, also used to export most of its sulphur via the Black Sea. Though it can export by rail to China, this is a long and expensive process and the capacity of the rail network acts as a bottleneck.

Some of this 5.2 million t/a of sulphur will inevitably make its way to market. But the question is how much? In their absence, there are stockpiles of sulphur around the world which can be drawn upon, though melting down the blocks in northern Alberta could take time and expense. It seems that in the interim there will be a significant shortage of sulphur on the market, and prices have reacted accordingly. While there is new capacity commissioning, it will not be enough to prevent the shortfall in the market. China, which had been running down its pyrite-based acid capacity, may need to rely upon it for a while longer.

Longer term, everything depends upon how long the war and associated sanctions regime go on for. In spite of some abortive peace talks, Russia has not shown any sign of relenting in its attempt to capture at least a significant part of Ukraine, and the war could drag on for months or even years. In theory, projected new supply from refining and sour gas, taken together, adds about 9.3 million t/a of new sulphur production capacity out to 2026 - additions to refinery sulphur production continue to be larger than sour gas projects, a turnaround from the previous decade. Over the same period, new demand had been forecast to increase by 8.5 million t/a, most of it from the phosphate industry, and this surplus should have led to steadily falling sulphur prices. However, for the moment, the shortage in the market will lead to high prices and possibly even demand destruction in the phosphate sector.

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Oil markets face their most severe disruption since the 1970s.

Sulphur content of crude feeds

US refiners have upgraded to take advantage of generally cheaper, sourer crude feeds. However, a ban on oil imports from Russia may make that harder to come by.



United States: Mars is an offshore drilling site in the Gulf of Mexico. WTI = West Texas Intermediate; LLS = Louisiana Light Sweet; FSU = Former Soviet Union; UAE = United Arab Emirates. Source: US Energy Information Administration, based on Energy Intelligence Group – International Crude Oil Market Handbook.

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ne of the key determinants of refinery sulphur production is the sulphur content of the crude oil (and other components) that the refinery processes. Sulphur content of crude oil can very widely, from almost zero to as high as 15%, though the most common range is between 0.5 and 3% sulphur content (Figure 1). How sour a reservoir is can be hard to predict, as the souring of oil is a complex process caused by the decomposition of ancient organic matter into kerogen and its breakdown by heat below ground, coupled with the presence of hydrocarbondegrading bacteria known as obligate hydrocarbonoclastic bacteria (OHCB), which feed on hydrocarbons in the reservoir and increase the effective sulphur content. The latter is highly dependent on conditions being right for microbial growth, in terms of pH, temperature and pressure.

Higher sulphur content of crude oil, as well as higher viscosity and API gravity were historically regarded as undesirable qualities. Heavier, thicker oil is more difficult to pump, and higher sulphur content can lead to corrosion of plant and equipment. The two variables also tend to be correlated, as Figure 1 shows – heavier oils are often sourer, and lighter oils often sweeter. For this reason, light, sweet oil typically has a several dollar per barrel price premium over heavy, sour oil. Increasingly strict regulations on the final sulphur content of fuels means that simpler refineries also find it harder to achieve the desired sulphur content of fuel using heavier, sourer crude feeds. Conversely, however, it also means that more complex refineries can take advantage of cheaper, sour crudes. Refining margins are often quite thin, and a \$5/ barrel price advantage can sometimes make the difference between profit and loss.

Oil is also generally getting sourer. As the most favoured light, sweet reservoirs are depleted, so there has been proportionately greater exploitation of sourer sources. Figure 2 shows the increase in sulphur content of crude feed to refineries in the US since the mid-1980s. Sulphur content of crudes being processed increased by 50% from 1985 to 2005, at a time when sulphur content of refined products fell dramatically. In the 1980s and early 1990s, sulphur levels of up to 5,000 ppm were acceptable in gasoline and diesel. However, by 2017 this had fallen to 10 ppm, meaning that 99.8% of the sulphur had to be removed during processing, creating the boom in refinery sulphur processing which has seen refin-

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ing come to represent half of all elemental sulphur production. It has been a similar situation in most of the industrialised world: Europe, North America, China, India, Japan and South Korea all have 10 ppm sulphur standards for gasoline and diesel. South America and Southeast Asia allow up to 500 ppm (higher in Venezuela), while Africa and the Middle East remain the main holdouts against low sulphur fuel standards. This of course also means that countries hoping to export refined products to markets such as Europe and the Far East need to be capable of producing ultra-low sulphur (ULS) fuels.

Shale oil

Because of the tightening sulphur standards and rising sulphur content of crudes, US refiners, especially in the US Gulf Coast, spent many years and many dollars during the 1990s and 2000s optimising their refining operations to handle heavier, sourer - and of course cheaper - crude feeds. This provided a boom for Venezuela, Mexico, and Canada, all of whom had a surplus of heavy, sour crude grades - in Canada mainly from oil sands processing in Alberta, with the synthetic crude made from bitumen sometimes travelling long distances via pipeline or rail to reach the refiners. However, there has been a wrinkle in the past decade with the rapid expansion of US oil production from tight oil shales.

Using the horizontal drilling and hydraulic fracturing techniques pioneered in the gas industry, oil shale exploitation has rapidly boosted US domestic oil production, from just over 5 million bbl/d in 2010, to a peak of just under 13 million bbl/d in early 2020. The 'problem' for US refiners is that the oil coming from the shale deposits is mainly light and sweet, and often needs to be blended with heavy sour grades to be usable in US refineries. Geography is also a factor -US West Coast refiners often find it cheaper to import oil from overseas than source light sweet shale crude from the other side of the Rockies. The impact of the International Maritime Organisation's mandate of a 0.5% sulphur cap on marine fuels in 2020 has also meant that there is increasingly cheap high sulphur fuel oil (HSFO) available, which can also be blended to offset the light sweet US crude grades.

Hydrogen

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The other side of the refining equation is hydrogen. Hydrogen is required to break down heavy oil grades into lighter compo-



nents in refinery hydrocracking and hydroprocessing units, and most hydrogen is generated from the partial oxidation of natural gas in a steam methane reformer (SMR), either on-site at the refinery, or, in the case of the US Gulf Coast, often generated centrally in a large scale hydrogen manufacturing operation and piped to several refineries in the area. The cost of hydrogen depends on the cost of natural gas, and here the US refiners have an advantage courtesy of shale gas production, which has brought the cost of US natural gas down to some of the lowest levels in the world, certainly the lowest outside of countries where gas prices are controlled or subsidised by the government.

Market disruptions

Even before the present situation, the US oil market faced considerable disruptions. During 2021, the impact of Hurricane Ida on the US Gulf Coast temporarily shut down up to 85% of oil production in the region, leading to refiners turning to increased imports of Canadian sour crude, as well as Russian imports, and even a release of 18 million barrels from the US Strategic Petroleum Reserve. However, undoubtedly the greatest market disruption this year has come from the Russian invasion of Ukraine and the attendant slew of economic sanctions imposed on Russia and Russian companies. Russia is the world's second largest oil exporter after Saudi Arabia, with an average of more than 7.8 million bbl/d exported in 2021 according to IEA figures, representing about 8% of global demand. Of that, around 60% was sent to Europe, 20% to China, and

17% to North America. Oil prices spiked in early March, reaching \$130/bbl, and while they have since come back down to an average of around \$100 bbl/d, they remain extremely volatile as the market absorbs the continuing uncertainty. The question now is to what extent Europe and North America will try to ban imports of Russian oil.

The US has already banned the import of oil and refined products from Russia, leading to something of an upset for domestic refiners there. The US imported 685,000 bbl/d of crude and refined products combined from Russia in 2021, including 200,000 bbl/d of crude oil and 356,000 bbl/d of products such as topped crude oil, heavy vacuum gasoil and high sulphur fuel oil. HSFO alone represented about 160,000 bbl/d. Overall Russia was responsible for about 8% of US crude, intermediates and refined product imports, and Russian oil is predominantly sour - the very component US refiners require. The ban on Russian imports has thus forced US refiners to seek out alternative supplies, with additional volumes now coming from Canada, Algeria and Iraq. While the Biden administration has tried to press US shale producers to increase their output to assist with the shortfall, there are a number of factors which make this more difficult. The industry is still coping with the after-effects of the covid pandemic, which has led to shipping disruptions, labour shortages, and even a shortage of sand for fracking. Furthermore, after having been burned during the covid pandemic and losing an estimated \$76 billion, the shale oil industry is in no mood to suddenly boost output again only to find the

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crisis resolved and oil prices crashing again. And as discussed, the oil produced would mostly be for export, as US refiners would have trouble absorbing more sweet crude.

In the interim, president Biden has once again turned to the US Strategic Petroleum Reserve, releasing 180 million barrels of mostly sour crude, but longer term he has tried to put pressure on other suppliers to increase output. The problem is that OPEC has ruled out an increase in output to make up for any supply loss from Russia due to a boycott. In a move that looks a little like desperation, there were even US delegation sent to Venezuela and Iran to discuss a partial lifting of sanctions to allow their oil to start flowing to the US again. However, neither government is likely to do that without some quid pro quo, and Venezuela's ability in particular to lift output after decades of poor maintenance and declining production is very much open to question.

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The situation is even more difficult for Europe. Europe is the biggest purchaser of Russian crude, receiving 3.8 million

bbl/d of supply from before the conflict, representing around 25% of Europe's supply. Some countries, like the UK, have been more bullish on stopping Russian oil imports, with the government announcing a ban from December, and support for a phase-out of Russian supplies on that time scale is now gathering momentum in the EU. The EU is already increasingly turning to US production -US crude exports to Europe were around 1.5 million bbl/d in April, the highest level since the covid pandemic. Other supply could come from the Middle East, Latin America and Africa. Middle Eastern producers have tended to service Asian markets, but such a large scale reorientation of supply would take time. In the meantime, European countries may have to impose 1973-style restrictions on fuel use to eke out lower supplies. European refiners are also struggling with high natural gas prices - some of the highest ever seen in Europe, due to a combination of high demand and the restriction of supplies from Russia, which supplies half of Europe's natural gas, increasing the cost of processing sour crude.

A shortage of sweet?

Marginal demand in global refining tends to be for sweet rather than sour grades, to feed lower complexity refineries, and rising demand for sweet crude, for example for increasing gasoline demand and production in Europe and Asia, can be seen in increasing premiums for sweet oil over sour. Higher natural gas prices have also helped make processing sour crudes more expensive, encouraging more sweet demand. However, the largest sweet crude exporters, Nigeria and Angola, have struggled with raising production due to a combination of declining fields and infrastructure issues, and it is not certain if the US and Malaysia can make up for the shortfall. Although Russian exports are primarily sour, since the invasion of Ukraine sweet-sour price spreads have increased, up to \$10/bbl for Brent crude vs US Mars medium sour, indicating Russian oil is presumably still finding its way to market somehow, albeit not in the US, or perhaps is being forced to trade at a discount. For the time being, this bodes well for US refiners geared to run on sour crude feeds, provided they can find oil for sale.



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SULPHUR MAGAZINE







Sulphur 100, May/June 1972.

Sulphur 200, Jan/Feb 1989.

Sulphur at 400

This is the 400th issue of *Sulphur* magazine, now in its 69th year. From its beginnings as the Quarterly Bulletin of the Sulphur Exploration Syndicate, it remains the only magazine dedicated to both the sulphur and sulphuric acid industries.

ulphur began its existence in 1953 as the Quarterly Bulletin of the Sulphur Exploration Syndicate. The Syndicate represented nine chemical producers, mainly in Britain and the US, who were concerned about dwindling world supplies of sulphur; F.W. Berk and Co. Ltd, British Titan Products, Brotherton & Co., Courtaulds, Dunlop Rubber, Fisons, Laporte Chemicals, Monsanto Chemicals, and Charles Tenant & Sons Ltd. It was formed in the wake of a 'sulphur crisis' in 1950-51, when a global shortage of sulphur led to the setting up of the International Materials Conference, which instituted a world-wide system of sulphur 'rationing' in the western world that lasted into 1953.

The Syndicate aimed to provide "accurate technical, economic, statistical and price information" on the world sulphur industry as global sulphur consumption increased rapidly, and also to examine

new sources of sulphur. At that time, the global market for elemental sulphur only amounted to just under 13 million t/a, most of it (90%) produced in the United States and Gulf of Mexico from Frasch mining, and mostly destined for industrial sulphuric acid use. However, this figure was on the cusp of rapid expansion as the modern phosphate industry was created. At the same time, the use of pyrites to manufacture sulphuric acid, which had been the predominant method to that time, was also coming to be overtaken by the burning of sulphur via the Contact Process. But that led to concerns about whether there was enough sulphur identified in underground deposits to meet proiected future needs.

The Syndicate and the magazine were the brainchild of John Lancaster, the founder of the British Sulphur Corporation, which published the Bulletin, soon to be renamed Sulphur Magazine. Lancaster's

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Sulphur 300, Sep/Oct 2005.

name was an anglicisation of his birth name – he was a refugee from Czechoslovakia after its takeover by Nazi Germany in 1938, and had served with the British Army in WWII as an intelligence officer, charged with sourcing key raw materials for the war effort. This in turn led to his preoccupation with sulphur and where it might be found.

Sulphur 100

By the time it reached its 100th issue, in 1972, Sulphur was being produced at the British Sulphur Corporation's offices at Parnell House near London's Victoria Station. Fertilizer demand was growing rapidly as India and South America experienced their 'Green Revolution', and the sulphur industry was growing with it - fertilizer demand for sulphur tripled from 1952-72 from 5 million to 15 million t/a as the US phosphate industry boomed. However, production was now outpacing demand, as Canada's sour gas industry rapidly ramped up sulphur recovery, reaching 8 million t/a in 1972, and with the USA and France's own sour gas extraction not far behind. Controls on SO₂ emissions from smelters were also starting to see large volumes of excess acid being recovered, especially in Japan. With a surplus from involuntary production looming, it was slightly amusing for me to read an article in issue 100 on new uses for sulphur, which listed sulphur asphalt, concrete and sulphur polymers - a topic which seems to remain a perennial one

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even 50 years later, though now, as then, without every quite seeming to achieve a breakthrough.

Sulphur 200

Published in 1989, Sulphur's 200th edition, now with the familiar yellow cover, carried an editorial from John Lancaster himself (always referred to at British Sulphur as 'JML') reviewing the sulphur industry. Global demand for sulphur in 'all forms'(i.e. including smelter and pyrite acid) had now reached 60 million t/a, with sulphuric acid production reaching 155 million t/a. More sulphur from sour gas was now coming from the USSR with its Astrakhan and Tengiz plants, though the US continued to develop new Frasch mines. Sulphur prices at Vancouver - then exporting 5 million t/a via the Cansulex consortium - stood at around \$100/tonne.

Sulphur 300

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Sulphur's 300th edition came in 2005, its cover highlighting the Sulphur 2005 conference in Moscow, and this time carries a

guest editorial from its new publisher, John French. The British Sulphur Corporation had by then been bought up by CRU, though Lisa Connock then as now was Technical Editor and Tina Firman Advertisement Manager, and there were contributions from names which must surely be familiar to longer-term readers such as Mike Kitto, Peter Clark, Jim Hyne, Jerry D'Aquin and Lou Doerr. The increase in consumption of 'sulphur in all forms' had slowed from the heady days of the 1970s and 80s, but had still reached 70 million t/a, of which 46 million t/a was represented from elemental sulphur, now 98% produced from refineries and sour gas processing. The intervening years had seen the rise of premium sulphur forming techniques for better product quality, and a move away from the liquid sulphur transportation and trade that had characterised the 1970s and 80s, as well as increasingly stringent regulations on emissions of sulphur, especially from vehicles that had boosted the refinery component of recovered sulphur. Sulphuric acid consumption reached 190 million t/a, with the onset of demand from new high pressure acid leach plants for nickel recovery.

Sulphur 400

And so we come to today, with BCInsight having taken on the British Sulphur fertilizer titles - Nitrogen+Syngas, Fertilizer International, and of course Sulphur, though with most of the same team producing them. The sulphur industry continues to evolve, with sour gas from the Middle East now eclipsing the declining fields of Europe and Canada, and fuel regulations continuing to tighten as the refining industry shifts from North America and Europe to Asia and the Middle East. Sulphur production in all forms has now topped 80 million t/a, and the need for phosphate continues unabated, while metals like nickel and lithium are seeing a boost in demand from the world's move towards electrification and more use of batteries. We may be at nor near peak oil production, and more changes are doubtless ahead for the industry. It has been my own great privilege to be the magazine's editor for the past 13 years, and who knows, perhaps to be compos mentis enough to contribute to Sulphur's 500th edition, some time around 2039.



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OTO: POYLOCK19/SHUTTERSTOCK.COM

The Sulphur Community is set to reconvene in Abu Dhabi. CRU and UniverSUL Consulting, with the support of ADNOC, are hosting a new live event, Middle East Sulphur Conference (MEScon), which will take place at the Rosewood Abu Dhabi from 24-26 May 2022.

iddle East Sulphur Conference (MEScon), co-organised by CRU and UniverSUL Consulting, with the support of ADNOC, is a new live event for the global sulphur and sour gas community, which will take place at the Rosewood Abu Dhabi from 24-26 May 2022.

The Middle East, and Abu Dhabi in particular, is at the epicentre of global sulphur and sour hydrocarbon production, making it the ideal location to host this event that will gather representatives from along the entire sour gas/sulphur value chain to promote technology and innovation, lessons learned, best practices, knowledge transfer. and R&D.

Against a backdrop of record sulphur prices and considerations about the future role of the sulphur industry, this new event

aims to provide a forum to share knowledge and resources in support of continual improvements in HSE, reliability, efficiency and general best practices for the sulphur and sour gas industry.

Building on the legacies of MESPON and CRU Middle East Sulphur, the partnership of CRU and UniverSUL Consulting combines the respective strengths of market-leading analysis and technical expertise, which is reinforced by the support of host sponsor, ADNOC, a recognised leader in the production of sour gas and sulphur. Collectively, this partnership enables a unique event that incorporates the market dynamics and technical and operational aspects of the entire sulphur value chain from sour gas processing through sulphur recovery to transportation, marketing and end uses.

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MEScon is intended to 'connect the dots' - to maximise utilisation of current local experience and expertise via networking and to provide access to the knowledge and resources of the global sulphur community. The goal is to foster enduring, cooperative relationships between sour gas and sulphur plant operators across the UAE, the Middle East and the world. Delegates can look forward to an agenda with a strong technical focus, featuring 25 technical presentations and five highly interactive panel discussions, exploring new technologies and operational excellence across key elements of the sulphur value chain. The technical agenda will be supplemented by scene setting presentations led by CRU analysts and with industry thought-leaders covering sulphur market dynamics and the role of sulphur in the energy transition.

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Exploring the supply and demand dynamics of the sulphur market landscape

- MEScon sulphur value chain positioning and perspectives Angie Slavens, UniverSUL Consulting
- The CRU View on the sulphur market outlook Dr Peter Harrisson, CRU
- Sulphur as a strategic commodity and ADNOC as a Centre of Excellence

Presenters to be confirmed

Maximising sulphur product value

- Session overview and objectives Angle Slavens, UniverSUL Consulting
- What do sulphur specifications have to do with dust?
- Robert Marriott, Alberta Sulphur Research Limited (ASRL)
 Reliable, economical sulphur acidity control: New advances in technology

Jeff Cook; Tibor Horvath; Mark Greenberg, DuBois Chemicals Canada

- Wavelength dependent performance of Distributed Temperature Sensing (DTS) instruments on sulphur pipelines Kent Kalar, AKOS Energy Corp.
- Topic Spotlight: Liquid Sulphur recirculation through SEET pipelines during long term total shutdowns
- Cesar Zambrano; Mahmood Al Murid, ADNOC Sour Gas
- SG20 A new generation of drum granulation systems *Casey Metheral, IPCO*
- Granulator single pass header technology Mariam Banabeela, ADNOC Sour Gas
- Fire detection challenges in sulphur handling terminals Arivazhagan Rajendran, Saif Al Tenaiji, ADNOC Gas Processing
- Topic Spotlight: Preventing failures and eliminating HSE incidents from sulphur conveyors system by using innovative "Optic Fiber Sensing technique
- Rajeeva Kumar; Mohammed Tannaf, ADNOC Gas Processing
- Panel session: Maximising the value of sulphur product

WEDNESDAY 25 MAY

Sulphur plants in context and emerging new drivers

- Session overview and objectives Angie Slavens, UniverSUL Consulting
- Viable green strategies for energy transition in sulphur recovery Saqib Sajjad, ADNOC Gas Processing
- Recovery of CO₂ from sulphur plants
 Frank Scheel, Worley Comprimo
- How about capturing CO₂ and generating H₂ via advanced sulphur recovery technology in this energy transition era? Thomas Chow, Fluor Energy Solutions
- Multicomponent emission measurement from the sulphur recovery unit

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- New technologies to increase energy efficiency and reduce nonsulphur emissions (CO₂, CO, NOx) from tail gas incinerators *Ali Abdullah Alshimiri, Koch Engineered Solutions Middle East*
- A Pathway to Carbon Neutral LNG: Challenges, Opportunities, Costs and A Way Forward
- Nafisa Yousif; Happy Saini, ADNOC LNG Panel session: Sulphur plants in context and emerging new drivers

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Optimisation of sour gas plant process operation

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- Mercaptan closure around the gas sweetening unit Inshan Mohammed; Bob Veroba; Caleb Kuhn, Sulfur Recovery Engineering Inc.
- Mitigation of Sulphur Dioxide emissions in SRUs towards achieving sustainable development goals Ibrahim Khan; Dr. Falah O. Alhameli; Dheeraj Nagwani; Pramodh Kalampully; Dinesh Aggarwal; Sandeep Dhebar; Anand Singh; Afra Almansoori, ADNOC Gas Processing
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Satyadileep Dara; Ibrahim Khan; Eisa Al Jenaibi; Nawal Al Yahyaee; Vincent Goveas; Ponraj Ponnaiah; ADNOC Gas Processing

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Innovations in sulphur plant process, equipment, catalysts & instrumentation

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 Angie Slavens, UniverSUL Consulting
- Low CO₂ footprint and low sulphur emissions at high lean amine temperatures for SRU mega-projects in the Middle East *Andreas Kern, BASF Middle East Chemicals LLC*
 - Understanding unpurged thermocouples in sulphur recovery units

Matthew Coady, Delta Controls Corporation

• The ease and robustness of titania-based tail gas catalysts start-up

Mark van Hoeke; Bart Hereijgers, EuroSupport

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 Strategies to minimize the cost of a piping thermal maintenance system without compromising performance Justin Tucker, Ametek CSI
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Meeting oil and gas pipeline quality specifications

A new fully automated process has been developed that combines real time H_2S readings from an H_2S analyser and Q2 Technologies' proprietary scavenger chemistry to treat high H_2S crude oil on demand. The process provides an efficient and effective way to administer the chemical product to avoid overtreating or undertreating. In some cases, the end user is seeing greater than 50% savings. It is a unique confluence of technology including IoT, advanced chemistry, and oil and gas personnel incentivised to demonstrate continuous improvement.

eeting commercial oil and gas pipeline quality specifications with regards to hydrogen sulphide (H_2S) is of the utmost importance when it comes to the overall merchantability and safety of a barrel of crude oil. A new automated process for H_2S mitigation using a refiner-friendly H_2S scavenger chemistry is presented. Hydrogen sulphide is an extremely toxic and corrosive gas that can be present in all stages of development in oil and gas, originating deep in geologic formations, the noxious substance can be found in upstream to midstream as well as downstream infrastructure. To be safely managed, H_2S levels need to be lowered. Hydrogen sulphide can cause extensive corrosion and damage to equipment and even at low ppm levels it has the potential to cause death. By successfully treating H_2S and permanently removing this problematic compound, crude oil quality is elevated, which translates into higher netback prices of the barrel. Traditionally,



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the oil and gas industry has relied on testing methods designed for refined products that do not measure H_2S in crude oil reliably. New technology has emerged that allows for greater accuracy and repeatability that also opens the way for automated H_2S treatment.

Dealing with H₂S

Historically, if faced with H₂S in crude oil or liquid hydrocarbons, producers had limited options to mitigate the problem (Fig. 1). Both H_2S treatment and measurement options have proven to be a constant challenge. Mechanical H₂S removal solutions have limited scalability and economic feasibility at production sites, so chemical scavenging solutions have become prevalent. Triazine-based scavengers have traditionally been used since the late 1980s to remove H_2S from both natural gas and oil streams. However, using triazine-based compounds may lead to equipment fouling and corrosion. Refiners and consequently midstream companies have banned the use of amine/ triazine-based scavengers for these reasons. Alongside treatment, H₂S measurement is key for both quality and safety purposes. Traditionally, testing involves having field personnel responsible for pulling stain tubes on a nearly continuous basis which can be operationally burdensome and potentially exposes operators to the toxic gas. Test

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methods that have been adopted as industry standard for H_2S measurement in crude oil were first developed for refined products and offer limited accuracy and repeatability. Accuracy is fundamental in how a chemical programme is administered and negating human error and time variability is a critical notion for how Q2 Technologies strategically set a path to change this treatment and testing continuum.

Next generation analyser

Treating H_2S starts with accurate measurements. For field and certification tests in the oil and gas industry, the approved methods (Fig. 2) are ASTM-5705 (modified) and UOP 163. These methods not only offer limited repeatability and accuracy but are not suited for constant monitoring in the field. In addi-

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tion to testing H_2S , UOP 163 also determines total mercaptans present in a sample.

ASTM-5705 (modified) measures concentrations in the vapour space or ppm/v. UOP 163, alternatively, measures the liquid phase and gives a reading by total weight, or ppm/w. Unfortunately, there is no standard method for aligning the two readings, as they are registering the components of different states of matter, and the properties in one, do not always match the other. So how to determine which test is correct? It depends on what the commercial contract stipulates.

Next-generation H_2S analysers that offer companies the ability to constantly measure H_2S in pipelines on a real time basis, equating to thousands of readings per hour have been developed. Taking manual readings in the field is rife for quality control issues, inasmuch as the manual process cannot take account of the vast amount of variability when taking a stain tube sample. Variabilities include swings in ambient temperature, pipeline pressures, quality of the stain tubes, or the overall operator know-how on taking a sample. Inline H₂S analysers are now becoming more common as pipeline companies need sustainable solutions to continuously manage their crude quality as it pertains to H₂S. Several long-haul pipelines transporting millions of barrels of crude oil per day from West Texas to coastal markets have adopted this new methodology. The analyser works in a closed loop fashion, as the crude oil sweeps past a probe in the pipeline, where a small oil sample routes through an enclosure that analyses the crude for H₂S. Taking the best of both worlds: fresh samples, immediate readings, consistent amount of volume, with lab quality equipment in a temperature-controlled housing. The compact analyser can take up to 70 readings per minute and calculate a ppm/w measurement within 2% accuracy. The technology utilises a specialised membrane where the H₂S is stripped without letting the liquid pass through. With relatively few moving parts, the resulting reading is a continuous H₂S level. Comparing the two methods is one of extreme contrast: an inline analyser can give up to 400 high quality readings in the same time it takes one stain tube reading to be measured. Having access to annotated trends with maximum and minimum variability spread out over time versus a single data point is the equivalent to watching a 4k movie versus viewing a single photo.

Technologically advanced chemistries

Even though amine- and triazine-based scavengers have been widely used for H₂S removal in oil, refiners have been pressuring chemical producers for friendlier alternatives that are not corrosive to their equipment. This has led to commercial deducts placed on amine/triazine contaminated oil. Several midstream companies now monitor amine content in their crude quality assays to ensure oil marketers are not fined by their refining customers. To address the market need for non-amine and non-triazine chemistries, Q2 Technologies has engineered the Pro3® line which uses breakthrough non-amine/non-glyoxal H₂S and mercaptan removal technology. The Pro3[®] technology requires far less chemical use, up to 50-75% as compared to glyoxal and MEA-triazine. This innovative technology

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is currently used by producers, midstream companies, and commodity traders and it has been approved by major terminals and pipelines to treat millions of barrels of oil per month. The chemistry not only provides cost savings to producers needing to treat their oil to meet commercial requirements but allows midstream companies and traders to maximise market options for clean oil barrels. Refiners, in turn, reduce costly downtime brought by previously used amine/ triazine-based chemistries.

Some producers have invested in sulphur reduction treatment at the wellhead to reduce the fouling of gathering lines. Chemicals manufacturer Q2 Technologies is among the leading chemical suppliers partnered with E&P and midstream operators to clean up Permian barrels. In one case it helped bring more than 50,000 b/d of Permian production to mercaptan levels of less than 75ppm, compared with pretreatment levels of up to 600ppm.

What makes $Pro3^{\circ}$ so unique is its ability to chemically alter the base H_2S structure in a quick and scalable manner. The chemistry brings a proprietary blend of polymers that react with H_2S to form a nonhazardous sulphate molecule (Fig. 3). The efficient reaction allows for scalable treatment all the way from wellheads producing a few hundred barrels per day up to treating tens of thousands of barrels per hour when ships are being loaded. The chemistry is water based and oil dispersible which allows for easy separation in the desalting process at refineries.

Real time analyser + advanced chemistries

A fully integrated system has been developed to automate H₂S treatment in midstream applications that allows for costeffective and transparent treatment. Pairing the H₂S analyser with an accurate flow reading (reading from a flow meter) to a pump that has variability control, allows for a fully automatic system to respond accordingly in real time to throttle the appropriate chemical dosage on an on-demand basis. Due to the placement of the analyser upstream of the $\ensuremath{\mathsf{Pro3}}\xspace^{\ensuremath{\mathsf{@}}}$ injection point, if a spike of high H₂S is detected in the pipeline, the system can account for these surges and will treat accordingly. When the H₂S fluctuation drops back to normality, the pump will throttle down and back off the injection rate. Commercial and financial results are immediate: the resulting exact amount of chemical translates into not over treating or under treating, which in turn yields crude oil that meets pipeline specifications in an ongoing manner. With a hyper automated

ISSUE 400 SULPHUR MAY-JUNE 2022 process running in the background, producers and midstream clients are able to redeploy their field personnel back to their current job and manage the automated system on an exception-basis.

Clients gain valuable insight into meaningful KPIs such as \$/barrel treated or gallons/hour and can see in real time the effect the product is having on their bottom line.

An integrated solution

From a field personnel perspective, managing an H_2S programme can be a full-time job. Conceptually, it makes sense: ondemand treatment frees up field personnel to focus on their main asset objectives. But how does it work and is the technology compatible with current systems?

With a fully integrated H_2S treatment system, the sour crude is analysed and treated flawlessly as it flows through the pipeline. The flowmeter, the H_2S analyser, and the pump work together for appropriate dosage (Fig. 4).

For an effective measuring and dosing treatment solution, the programmable logic control or PLC, is another critical component for the combined system to run smoothly. The PLC runs a simple script that needs only a few inputs. First, as previously detailed, the H_2S analyser sends

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a signal to the PLC control via a variety of methods, be it a 4-20mA signal or via SCADA or other secure encrypted methods. Second, the operator will have a flow data meter near the analyser to give an accurate indication of how much volume is sweeping by at the point in time when the H_2S level is measured. There are a variety of ways flow is calculated and some of the units available today are quite sophisticated with the Coriolis and ultrasonic flow meters leading charge.

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The PLC then communicates these inputs to a variable rated pump that follows a logic table for dosing, simply put, at a certain H₂S level with a specific bbl/ hr, the PLC configures a resulting dosage that the pump will inject. This action is then repeated and adjusted accordingly every 15 seconds. The constant fine tune adjustments ensure that the crude oil is being dosed appropriately in an ongoing manner. Storing chemical products in ISO tanks offers the client ways of monitoring tank levels via satellite telemetry and potentially optimised resupply configuration that standard totes cannot provide. Offering these added ease-in-operations benefits ensures that there is never a gap in treatment. Lastly, as with any automated system, the team members monitoring the setup are essential for long-term success. Having a logistics team dedicated to monitor all of the ISOs deployed, making sure the logic displayed on mobile and control room dashboards is sound, and that the updated predictive usage calculations are being configured correctly is critical for a successful treatment solution.

Highly automated systems also need to account for troubleshooting and be capable of defaulting into a safe or manual mode. Prudent service providers recognise this aspect of the process. If the analyser registers anomalous readings, the unit has the programming to recalibrate itself if these outliers are detected. Further, the PLC can acknowledge when these trips occur and will send the last verified H₂S reading and appropriate dose to the pump. A redundant pump and dual head configuration are always recommended, this ensures that if a component of the pump fails, the unit will compensate to avoid any downtime. Lastly, being able to view the equipment on a mobile device is essential. Dashboards

provided on an encrypted web-based app, display visual representations of the current H_2S levels, injection rates of the pump, and allow for the operator's field personnel, control room technicians, and chemical provider to remotely monitor and bypass the system if needed.

In conclusion, providing alternatives to treating H₂S with improved technologies is a path producers, midstream companies, and commodity traders are currently seeking to reassess their assets in order to gain efficiencies and increase their overall value. By accurately measuring H₂S on a consistent and repeatable basis, dosing parameters can be fine tuned to account for fluctuations. Furthermore, when comparing this next generation of H₂S and mercaptan chemistries to that of previous generations, the results are in the form of immediate savings, and ultimately, a better netback price on the barrel. And finally, a total H₂S treatment solution for the client puts the technology provider in a category of trusted partnership - where open communication and responsiveness is key in keeping a highly automated solution up and running.

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MCS200HW: READY FOR STRICTER FLUE GAS MONITORING.

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Sensor Intelligence.

The MCS200HW is the answer to continuous monitoring of more stringent flue gas limit values in industrial combustion plants. The analyzer system monitors up to 10 infrared active components simultaneously such as HCl, SO_2 , NO and NH_3 and can be individually configured to your measurement tasks. The analyzer enables access irrespective of device and location with a web-based operating concept that is also convenient and secure to use. The need of only dry test gases and the wear-free gas transportation minimize operating costs while ensuring high availability of measurement results. MCS200HW: a cost-efficient emission monitoring solution that is quick to install. We think that's intelligent. www.sick.com/MCS200HW

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Enhanced emission monitoring from sulphur recovery units

The trend for multicomponent analysis of emissions from sulphur recovery units is becoming more widespread. David Inward of Sick reports on a recent field trial to test the suitability of a hot extractive infra-red analyser for this application. In addition to reliably measuring and reporting emissions to air, the analyser is also capable of contributing to reducing overall tail gas emissions by supporting enhanced optimisation of the thermal oxidiser.



Fig. 1: MCS 200 HW Multicomponent Analyser for SRU CEMS.

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ecent trends in reporting emissions to air from sulphur plants increasingly require additional components to be measured beyond just sulphur dioxide (SO₂). Emission limit values for both carbon monoxide (CO) and oxides of nitrogen (NOx) are now also defined for operators in the Middle East, following an equivalent trend in other parts of the world. Quantifying the mass emission of carbon dioxide (CO_2) as a greenhouse gas is also coming increasingly into focus across the globe.

Adding more components to the emission monitoring scope from the sulphur recovery unit raises demands for an application already known to be difficult due to the unique nature of the tail gas. The presence of traces of elemental sulphur coupled with that of acidic species (SO_2/SO_3) means that any cooling of the flue gas can result in severe blockages in the sample system or damage to sensitive optical parts.

Applying a hot extractive multi-component infra-red analyser avoids the need to cool the sample gas and so avoids these problems. The infra-red photometer is able to measure all the necessary components, even covering the new requirements.

Reporting requirements

Emission limit values are always referred to standard measurement conditions.

This requires correction to standard temperature and pressure, dry basis (i.e., at 0 vol-% water vapour) and to a defined oxygen concentration (typically 3 vol-% O₂ in the case of the sulphur recovery unit).

Therefore, as well as the pollutant concentrations CO, NO, NO₂, SO₂, and CO₂, the analyser must be also able to measure oxygen (O_2) and water vapour (H_2O) .

Monitoring the mass emission of gases such as SO_2 and CO_2 needs to be coupled with an in-situ flow measurement and so fits an analysis technique measuring in the natural raw tail gas condition, so without water vapour removed.

System design

The MCS200 HW analyser is based on a hot extractive design base, featuring only four elements (Fig. 1).

A sample probe with heated filter element connects to a heated sample line. The heated sample line connects directly with the hot extractive infra-red analyser. The sample is drawn through the analyser by means of a heated ejector pump. The entire sampling chain is maintained at 200°C. This avoids any cold spots, which would result in deposition of elemental sulphur or condensation of corrosive acidic aerosols in the sample system and analyser optics.

The system is fully certified according EN 15267 & is available in an Ex protected version according ATEX & IEC.

Hot wet extractive multicomponent IR analyser field trial

To prove the suitability of a hot extractive infra-red analyser, Sick AG commissioned a test system on an SRU tail gas stack at a European refinery.

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| Measured component | Measuring range |
|---------------------------|--------------------|
| SO ₂ high, ppm | 0-5,000 |
| SO ₂ low, ppm | 0-300 |
| CO, ppm | 0-500 |
| NO, ppm | 0-250 |
| NO ₂ , ppm | 0-25 |
| CO ₂ , vol-% | 0-25 |
| H ₂ O, vol-% | 0-40 |
| 0 ₂ , vol-% | 0-21 |

The trial analysis system was commissioned in February 2019 and operated for 11 months until January 2020 and was

Source: Sick

then replaced by a permanent installation. The original MCS 200 HW analyser configuration is shown in Table 1.

Based on experiences gained in the field trial, the SO_2 high range was increased from 0-5,000 ppm to 0-15,000 ppm. This was necessary to cover short term SO_2 spikes during process upset conditions.

Similarly, the CO range was increased from to 0-500 ppm to 0-1,000 ppm.

Interesting to observe was a clear relationship between high SO_2 events, triggered by a sudden increase in the H₂S concentration flowing to the thermal oxidiser, and the efficiency of CO oxidation in the thermal oxidiser.

It could be established that variability in the thermal oxidiser temperature, resulting from fluctuations in the H_2S feed concentration, created CO spikes at moments when the thermal oxidiser temperature was reduced.

Summary

The MCS 200 HW hot extractive infra-red analyser has proven itself to be a reliable, low maintenance solution capable of measuring all components needed as the basis for reporting emissions to air from the sulphur recovery unit.

Beyond the fundamental task to reliably measure and report emissions to air, it is also capable of contributing to reducing overall tail gas emissions by supporting enhanced optimisation of the thermal oxidiser.







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Design, safety and operational aspects of SRU analysers

Jochen Geiger of AMETEK Process Instruments reviews SRU process analyser standards, how to choose the right instruments, what to watch out for when selecting the point of installation, responsibilities for the analysers after installation, and how to make best use of the information provided by these analysers. Potential upset conditions and how analysers can help us to understand and mitigate them are also discussed.

hile all process control instruments are important, SRU analysers should be viewed as particularly important, and their reliability is paramount. Not only is there virtually no back-up for these instruments, but there are also very limited "process back-up" options available.

This article will discuss and review the design, safety, and operational aspects of SRU process analysers. Fig. 1 is a simplified process flow diagram of a Modified Claus process with tail gas treatment unit showing 7 analyser tags.

Step 1: Sample point selection

It is important is to choose the sample location as per the need of process control, but it is also important to take into account safety considerations. All measurements under review in this article are measuring a process gas which is toxic. Besides the question, "Is the instrument designed for this application?", the sampling point should be easily accessible (Fig. 2). It is recommended to have mechanical design engineering, process piping, and instrumentation engineering review the sample point layout in a team effort.

Step 2: Instrument selection

After the location of the instruments has been finalised, the right analyser for the application needs to be chosen. The first question to ask is whether the instrument is suitable for this application and is it safe under all possible process conditions?



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Fig. 2: Is this the best sample point location?

|--|

| Complexity factor | omplexity factor Analyser type | |
|-------------------------|--|-----|
| 1-5 (simple) | pH, conductivity, gas detection, O_2 | 2 |
| 6-8 (physical property) | boiling point, flash point, freeze point, RVP, viscosity | 3 |
| 9 (environment) | CEMS SO ₂ , CO, H_2S , opacity | 2.5 |
| 10-15 (complex) | tail gas, GC, mass spec., NIR, FTIR | 4 |
| | | |

Source: AMETEK

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| Category | Number of analysers | Estimated man-hours to perform the task | Total maintenance hours/week |
|-------------------|---------------------|---|---------------------------------|
| Simple | 20 | 2 | 40 |
| Complex | 14 | 4 | 64 |
| Physical property | 1 | 3 | 3 |
| Environmental | 2 | 2.5 | 5 |
| Total | 37 | | 112 |

Scheduled man-hour/week = 40.

Staffing required = 112/40 = 2.8 (3-4 personnel to allow for training and vacation). Source: AMETEK

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The second part of this article will focus on the specifics of each of the seven sample points.

Step 3: Installation and commissioning

Every process analyser installation consists of a sample take-off point (probes), sample transportation, the analyser itself and the infrastructure (shelter, platform etc.) From a cost perspective, roughly 30% of the total installation cost is analyser related and 70% of the cost is for the infrastructure, but more importantly, 70 to 80% of the total downtime of process analysers is related to failures in the sampling system and infrastructure such as heating, ventilation, and air conditioning (HVAC) units. It is therefore recommended to involve the instrument vendor and the maintenance group of the user in the installation planning/design process.

Step 4: Ownership and operational aspects

Any instrument requires service and maintenance, but how much? It very much depends on the application service and individual site conditions. It is recommended to create a "measurement matrix". To begin with, all analytical instruments should be classified into different categories:

- Category A: Simple (such as the pH meter or gas detector)
- Category B: Liquide applications (such as physical property)
- Category C: Standard applications (such as emission monitoring or IR/ TDLS Instruments)
- Category D: Complex analysers (such as process gas chromatograph and SRU analysers).

An hourly factor should be assigned to each of these categories, for example, four hours per week for Category D instruments and two hours for Category A instrument. Analyser vendors should be consulted to define the hourly factor. The rest is simple multiplication of instruments installed for each category; the result is a weekly estimated maintenance time demand sheet (see examples in Tables 1 and 2). The actual hours spent can then be compared to these theoretical numbers.

The outcome will provide a good base of information and help to identify root cause

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problems or help to understand if there is a requirement for technical training.

The next step to be considered is cross training between process engineers and maintenance engineers – it is not uncommon to hear, "These analyser readings cannot be correct, there must be something wrong today with the instrument!"

The following example is one of many; an air demand analyser suddenly moves to a full scale reading on the sulphur dioxide (SO₂) output and a zero reading on the hydrogen sulphide (H_2S) output. What was the reaction from Process Control? The analyser is down/the analyser is not working! In fact, the true story behind the picture in Fig. 3 which shows the digital output of the analyser in question is that both measurements of this analyser were working fine, but there was a significant process upset condition. The amine circulation pump had failed so the SRU reactor was no longer receiving acid gas, only sour water stripper gas. Consequently, far too much air was being supplied to the reaction furnace which was being shown by the analyser reading. It has been observed in many such cases that the process control staff have limited knowledge about analyser readings, and, on the other hand, the maintenance staff have limited knowledge about the SRU process, resulting in misinterpretation and misunderstandings about the analyser behaviour.

One way to improve this is to have joint training classes with Process Control & Maintenance and Process Engineering in order to achieve a common basic understanding about the following points:

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Claus process fundamentals

- basic Claus chemistry;
- a review of the capability of and limitations imposed on the process;
- the process vessels, reaction furnace, converters condensers;
- straight through, SWS burning and split flow reaction furnaces;
- tail gas treatment unit how it work what are the differences.

Sulphur plant process control analysers

- a review of the Claus chemistry as it pertains to control;
- feed forward control, advantages and limitations;
- feedback control, advantages and limitations;
- trim and main air control;
- related instrument topics (furnace temperature, emission, feed gas analysis);
- tail gas treatment units and their impact on the Claus process control.

Understanding Claus process upsets using your tail gas analyser

- different case studies of Claus process upsets and their effect on the process. The studies concentrate on initial control response, tail gas analyser response and other confirming process indicators. Note this information is sometimes site specific and it is recommended that a process engineer be present so the relevant details for that particular SRU are accurate.
 - delineating process upsets from analyser failure;

- verifying the analyser by "bumping" the process.
- analyser and sample system basics so process operators can aid the analyser technicians in trouble shooting problems.
- explaining the consequences of increased process temperatures, sulphur carryover and process upsets on the analyser.

All of these points will help to improve online instrumentation stability.

The following remarks refer to safety, design, and operational aspects for each of the sample/application points as shown in Fig. 1.

AT 1 – Feed gas analyser: to measure the acid feed and the sour water stripper gas: Most process engineers are interested in having this measurement as it sounds like a straightforward and simple task. However, the difficulty is the measurement has to be designed on a basically unknown process gas composition. The other factor is the measurement must be fast in terms of response time. Finally, it has to be considered that the sample gas can contain up to 90% H_2S , one of the most toxic gases in a refinery. So, whatever it takes, the measurement has to be designed in the safest way and should under no circumstances include a mechanical pump for sample transport. Safety as regards the sample system design, means keeping the sampling system simple. Something that is simple, easy to understand and operate eliminates "human errors".

AT 2 – Sulphur pit sweep gas: This measurement is there for plant safety – higher H_2S concentrations can cause an explosion in the sulphur pit, the sulphur dioxide (SO₂) measurement is there as an alarm for sulphur fires. From the design criteria the application has similarities to the air demand application.

AT 3 – Air demand: the most common, widely used and often discussed application: The main task for the air demand/tail gas analyser is to provide reliable measurement of the hydrogen sulphide (H_2S measured at 228 nm) and sulphur dioxide (SO_2 measured at 280 nm) concentration. The challenge is shown in the pictures in Fig. 4.

The process gas also contains elemental sulphur in vapour or aerosol form and has strong absorption of ultraviolet (UV) energy in the same spectral region as the measurement of the two components of interest.

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AT 4 – Reduction reactor off gas: This is a low-level sulphur dioxide measurement. What makes this application difficult is that the sample is hot and wet, plus the H_2S concentration is high (safety aspects) and the usual reading of the analyser is around zero, so there are trust issues when there is a sudden increase.

AT 5 – Quench tower outlet: This H_2 measurement is used as a standard but the additional measurement of H_2S should also be taken into consideration. Both measurements can be taken using a single instrument. The other use of the H_2S reading is during a plant shutdown – only when the H_2S is reading zero can you be sure that there is no elemental sulphur left in the Modified Claus unit.

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AT 6 – Absorber outlet: The H_2 measurement is standard but the additional measurement of H_2 will provide the recommended redundancy. In addition, COS and CS₂ can be measured by the same instrument.

Consider the combination of AT 5 and AT 6. First, a redundant measurement of H_2 will make the entire process control safer. Second, if H_2S is measured at the quench tower outlet and the absorber outlet it will be possible to control and measure the efficiency of the absorber online, on a 24/7 basis. A question for the future will be the energy consumption of the amine regenerator; an on-line efficiency measurement of the absorber can potentially reduce the energy put into the regeneration process

and help to reduce the overall emission of carbon dioxide (CO_2). Plus, closer control of the flowrate of recycled amine is becoming possible based on the H₂S IN and OUT measurement.

The COS and CS_2 measurement will provide information about the "status" of the catalyst in the reducing reactor.

AT 7 – Stack analyser: the final point of the SRU process control. Besides the emission monitoring aspects usually discussed in relation to this measurement, this can be also regarded as the final plant control analyser.

When the SO_2 is measured correctly, i.e., hot/wet without any dilution systems, the reading can be considered as the overall efficiency measurement, comparing the H₂S entering the reaction chamber vs. the SO₂ mass emission.

Another critical design aspect has to be considered if the SRU train includes a tail gas treatment unit (TGTU) which might be bypassed under process upset conditions. In such cases, the SO_2 concentration can be significantly higher than normal (factor 20+).

Conclusion

Sulphur recovery unit process analysers are essential for process control and operating within the environmental limits as required by law. In order to guarantee the best possible overall performance of such analysers the selection and thinking process need to start during the very early stage of the design phase (sample point location). Process and instrumentation engineers should be consulted at each step of the instrumentation selection phase. Guidance should be obtained from instrument vendors and safety aspects should be thoroughly considered. Maintenance and training should be regarded as essential for the smooth performance of the instruments over the instrument lifetime.

Beside a proven industrial track record, potential instrument (analyser) vendors should offer:

- support during the bidding phase of projects, data sheet review, installation and piping review;
- planning and design of tailor-made turnkey analyser packages;
- supervision and commissioning support;
- start-up services;
- side service training;
- SRU training covering chemical hardware and operational topics.

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Detecting waterrelated issues in sulphur recovery units

Most inspection personnel are familiar with the symptoms of process-related issues; however, they often lack an understanding of the root causes of water-related issues. In this article L. Huchler of MarTech Systems and E. Nasato of Nasato Consulting provide insight about early warning signs of common water-related failures in steam generators and sulphur condensers, proactive monitoring practices, practical operating strategies, options for corrective actions, reminders about robust water-side design and reminders about the challenges of prematurely destroying evidence by prioritising cleaning over diagnostic efforts during turnaround activities.

rocessing natural gas and refining sour crude creates a sulphideladen waste stream. The sulphur recovery unit (SRU) processes this waste stream, creating a commercially valuable commodity, sulphur, and allowing the plant to conform to environmental discharge regulations. In the past, operators of SRU systems focused on process-side improvements in energy efficiency and production capacity. The current focus is addressing water-related failures in the waste heat boiler (WHB) and the sulphur condensers with a goal of eliminating water-related failures. The objective of this article is to define the warning signs of water-related failures in steam generators and provide options for corrective actions. Many of the risks and warning signs of water-related failures described in this article are relevant to waste heat boilers and process condensers in other refining processes and other industries such as petrochemical, fertilizer and inorganic chemicals.

A particular concern is the increase in the frequency of failures of the sulphur condensers (low pressure steam generation ~50 psig (350 kPag)) as compared to the WHB (higher pressure steam generation of minimum 250 psig (1750 kPag)). This trend is consistent with the use of high purity reverse osmosis (RO) permeate or 100% condensate for make-up

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water. In theory, the use of RO permeate will increase the water-side efficiency of all of the high pressure steam generators; however, in practice, this change usually results in poorer control of the boiler water chemistry and a higher risk of corrosion and iron deposits. In the lower pressure sulphur condensers, this higher purity make-up water appears to correlate with chronic failures such as flow-accelerated corrosion (FAC) and/or dissolved oxygen corrosion.

The water-side related failures in both high pressure WHBs and low pressure sulphur condensers are each unique with regards to specific needs for water chemistry and flow related boiler feedwater distribution and steam removal. The high pressure WHB is more susceptible to water-side issues related to system fouling and thus failures related to high temperature sulphidation and high temperature metal failure. The low pressure sulphur condenser failures are not susceptible to high temperature process gas related issues since the typical process gas operating temperature is below the carbon steel limit of 650°F (343°C) but is a result of water quality issues related to items such as oxygen concentration, pH and/or FAC phenomena.

The greatest challenges for early detection of water-related issues are the lack of understanding of the warning signs and the lack of real-time operating data as compared to the process side. Often the first evidence of water-related issues is a failure or poor inspection results. As plants have increased throughput and upgraded water pretreatment systems, they have inadvertently increased the risk of lost production from water-related issues.

Early warning signs of waterrelated failures

Obtaining early warning signs of waterrelated failures requires effective monitoring practices. Most plants monitor several parameters in the boiler feedwater (conductivity, pH, total hardness) and the waste heat boiler and sulphur condenser water (conductivity, pH, alkalinity, concentrations of water treatment chemicals) at least once per day and measure a subset of these parameters on the other shifts. Based on these data, operators make adjustments to the chemical feed pumps and/or the blowdown flowrate. Boilers have long time constants; operators must learn the optimal frequency and degree of adjustments.

The chemical supplier routinely measures the same parameters as the plant and may routinely measure additional parameters such as silica and iron in the

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Fig. 1: FAC on condenser Inlets (high purity BFW)

boiler water. However, few plants, or water treatment specialists, routinely measure the boiler water in the condensers because most plants lack installed sample coolers on each condenser. And some plants will not allow the use a portable sample cooler, citing the safety issues of the cooling water flooding the area near the sample location. The minimum sampling frequency for condensers is annually to detect problems and after turnaround to properly reset the blowdown flowrate. Plants that have high purity feedwater may find that all of the blowdown control valves are oversized, either due to poor design or due to an upgrade of the water pretreatment system. Plants should consider requesting an exception for a temporary installation of a portable sample cooler to control the sample temperatures to 77°F (25°C) to protect the condensers from corrosion.

There is another, more common monitoring issue: poorly performing sample coolers. The higher the temperature of the water samples, the lower the accuracy of the test



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Fig. 2: Flow-accelerated corrosion caused by disturbance at the BFW Inlet

Transition from hermatite to magnetite away from BFW inlet disturbance. Half way down tube bundle.

Fig. 3: Transition from hematite (left side) and magnetite (right side) downstream of the BFW inlet

result. Water temperatures that are high enough to "flash" (evaporate a portion of the sample) will have even lower accuracy. SRU systems that use high purity make-up usually have rather small specification ranges for boiler water parameters, increasing the risk of flow-accelerated corrosion (FAC).

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Practical operating strategies

High purity make-up water

Plants that use 100% condensate or have replaced sodium zeolite softeners with reverse osmosis units create a risk of FAC. FAC requires three conditions: high purity water (i.e. low alkalinity and/or reducing conditions), high local velocity (e.g. turbulence), and high temperature.

Fig. 1 shows the inlet tubesheet of a 50 psig (345 kPag) horizontal sulphur condenser. The semi-circular pattern of corrosion is FAC damage due to high turbulence, low OH alkalinity and locally higher heat flux than the original equipment manufacturer (OEM) specifications for this SRU.

High concentrations of the oxygen scavenger chemical create a reducing environment, increasing the risk of single-phase FAC. Feedwater inlet piping and areas



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Fig. 6: Blowdown collection lateral

adjacent to internal baffle supports are especially vulnerable to dissolution of the magnetite layer and erosion of the carbon steel substrate that eventually leads to a localised failure. Fig. 2 shows the effect of a rudimentary boiler feedwater (BFW) inlet deflector (first tube on the right-hand side, with holes) that compromised the circulation pattern, creating a highly turbulent stream of low alkalinity BFW that caused corrosion of the top row of adjacent tubes.

Downstream of the BFW inlet, as the low alkalinity BFW mixed with the boiler water; Fig. 3 shows the impact of lower localised turbulence and higher alkalinity: the metal surface transitions from red-coloured hematite (damage from FAC) to gray, protective magnetite. Replacing softened water with RO permeate as make-up always creates a risk of corrosion. These risks include failure to accurately feed caustic and/or phosphate to compensate for the low alkalinity (low pH) and buffering of RO permeate, and poor modulation of the blowdown flowrate due to oversized control valves.

Research confirms that there are three conditions that determine the rate of iron dissolution (i. e. generalised corrosion): reducing water chemistry, aqueous pH and the temperature of the tube surface. Fig. 4 shows that the maximum solubility of

the protective magnetite, Fe_3O_4 , peaks at 300°F (149°C) and a pH of 8.75. In other words, the maximum magnetite solubility is the minimum stability of the protective oxide layer. Consequently, SRU sulphur condensers that operate at a nominal pressure of 50 psig (350 kPag) with a saturated steam temperature of 298°F (148°C), are highly susceptible to FAC failures. SRU sulphur condensers that have BFW with low alkalinity (i.e. low pH - "off the graph in Fig. 4") are especially vulnerable to FAC.

Water treatment experts often cite ASME Guidelines as a source of specification limits for boiler feedwater and boiler water chemistry. However, while ASME Guidelines show specifications for total alkalinity, there are no specification limits for OH alkalinity (the only kind of alkalinity in high purity water).

For SRU systems that have high-purity BFW, the assumption that the specification limits for total alkalinity are suitable is incorrect. The footnote for the specification limits for total alkalinity for steam generators operating at or below 600 psig (4,200 kPag) drum pressure assumes the use of high-alkalinity BFW:

"Maximum total alkalinity consistent with acceptable steam purity. If necessary. should override conductance as blowdown control parameter. If makeup is demineralised quality water and boiler operates at less than 1,000 psig (6,900 kPag) drum pressure, the boiler water conductance should be that in table for 1,001-1,500 psig (6,900-10,300 kPag) range. In this case, the necessary continuous blowdown will usually keep these parameters below the tabulated maximum values. Alkalinity values in excess of 10% of specific conductance values may cause foaming."

This footnote focuses on the risks of excessively high alkalinity. A review of

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the historical alkalinity in condenser FAC failures (Fig. 5) shows that the problem is exceedingly low OH alkalinity. The challenge is to determine the minimum safe specification limit for OH alkalinity in SRU systems using high purity make-up.

One approach to determine a safe minimum specification limit is to review the ASME guidelines for total alkalinity for "moderately high pressure" steam generators 600 to 1,000 psig (4,200 to 6,900 kPag) because the total alkalinity in steam generators that use high purity make-up is OH alkalinity. These "moderately high pressure" steam generators often have high purity make-up but, unlike higher pressure steam generators, do not require sophisticated water treatment programs (coordinated or congruent pH-phosphate, oxygenated treatment or AVT). Experience has shown that moderately high pressure steam generators with high purity make-up water can operate reliably with a free OH alkalinity water treatment program. A conservative recommendation for OH alkalinity specification limits for SRU systems is 75 to 150 mg/L as $CaCO_3$.

Poor control of condenser water level

The proper water level in the condenser is above the top row of tubes just above the elevation of the blowdown collection lateral (Fig. 6); this operating condition maximises heat transfer and system reliability. Close inspection of the tubesheet in Fig. 6 show three horizontal marks, indicating three historical water levels.

The water level near the top of the tubesheet is too high; it is likely that carryover occurred due to the small steam-disengagement space. The middle water level is the correct elevation that allows the blowdown collection lateral to collect a sample of the most-highly concentrated boiler water:





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Fig. 10: Level control system

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Fig. 11: Historical boiler water temperature



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just below the interface of the steam and boiler water. The lowest water level is the setpoint required to provide a sufficient amount of space for steam disengagement to avoid carryover. Obviously, this setpoint required that the plant disconnect the blowdown collection lateral, resulting in a nonrepresentative boiler water sample.

Fig. 7 shows that at this low water level setpoint, the tubes were, for the most part, below the steam-water interface, but significantly below the elevation of the (disconnected) blowdown collection lateral. The optimal water level is at the top of the (disconnected) blowdown collection lateral, approximately six inches (15 cm) above the top of the tubes.

Fig. 8 shows the results of the eddy current inspection that detected thinning, generalised corrosion, in all of the tubes in the top eight rows. The reason that there was corrosion on these tubes is likely due to the process design. Sulphur condensers operate as waste heat boilers, transferring heat from the process side to generate steam. Condensers generate steam using natural circulation; the concentration of steam bubbles is the lowest at the 6 o'clock position and the highest at the water-steam interface. Consequently, the heat transfer rate, or cooling effect, of water is much more efficient than a mixture of water and steam. In other words, the lower water level changed the "steam concentration gradient" and compromised the heat transfer efficiency and accelerated the process-side corrosion in these top rows of tubes. Note that the purple colour indicates tubes with the thinnest walls and the orange colour indicates tubes with least corrosion. The white colour indicates tubes with the thickest walls.

Solving the control issues for condenser water level are difficult and usually require an outage. This plant reviewed the design basis for steam disengagement space and determined that, even with low-alkalinity boiler water, the OEM design was not consistent with typical condenser configurations. At the next turnaround, the plant installed external steam separators and reconnected the blowdown collection laterals (Fig. 9).

The accuracy of the level control system may be a contributing factor for poor level control. Fig. 10 shows a highly instrumented system.

Poor shutdown procedures

Shutdown and start-up activities have much greater temperature and other excursions than steady state operation for all process

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Fig. 12: Corrosion at 6 o'clock on condenser inlet tubesheet.

units, but especially for waste heat steam generators. Fig. 11 shows the temperature of the process side for a 45-day period that included an outage. The plant replaced the petroleum feedstock with natural gas to condense the residual sulphur on the process side, especially in the catalyst bed. However, the plant had no defined procedure for the water-side operation. When the plant stopped the boiler feedwater pumps, the temperature increased to approximately 1,000°F (540°C) as seen in Fig. 11. Figs. 12, 13 and 14 shows circular marks around an area of localised corrosion at the 6 o'clock location of the tubesheet. The mass of the tubesheet retained heat for a longer time than the thinner condenser tubes and transferred that heat to the portion of the tubes adjacent to the tubesheet. There was no natural circulation in the stagnant boiler water, trapping steam at the 6 o'clock position at the tubesheet. Steam has a lower thermal conductivity than water, resulting in very high metal temperatures that caused rapid corrosion ("steam-side burning").

The plant may have delayed draining the water from the condensers or close the vents after shutdown, allowing atmospheric oxygen to saturate the boiler



Fig. 13: Oxygen pitting on condenser inlet tubesheet.

water. The tubes cooled more quickly than the tubesheet; the residual heat in the tubesheet resulted in oxygen pitting (Fig. 13). Oxygen pitting can also occur on the tubes (Fig. 14) during shutdown.

The obvious solution is to develop, and implement, an effective shutdown procedure. This shutdown procedure uses a powdered volatile corrosion inhibitor (VCI). There are several different VCI liquid and powder products. All of the VCI products use amines that have a very low toxicity and have no restrictions for discharge to the POTW (sewage treatment plant). There is no need to rinse the WHB and condensers before returning the units to service. Like neutralising amines, VCI amines are compatible with boiler water chemicals and will be present in the steam. The volatile components are amines that are compatible with neutralising amines for corrosion control in steam/condensate systems.

Powdered VCI amines control corrosion in two ways: first, the powder dissolves in any liquid water, reacting with the dissolved oxygen and preventing the water from corroding the carbon steel surface. Second, the powder sublimes, becomes a vapour, and reacts with the water vapour.

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Fig. 15: Proper design of BFW inlet.

HOTO:



Fig. 14: Oxygen pitting on condenser tubes.

The feed rate of VCI powdered products depends on the volume of the vessel.

This basic framework of a shutdown procedure is:

- 1. Replace the acid gas with natural gas or hydrogen to reduce the temperature on the process side and precipitate the sulphur, especially in the catalyst bed.
- 2. When the process side temperature decreases below 300°F (207°C), open the vents on the waterside of the WHB and condensers. Immediately open the drains to remove as much water as possible and allow the residual heat to "dry out" the water side.
- 3. As soon as practical, or when the process side temperature is below approximately 100°F (38°C), lay-up the water side by feeding a powdered volatile corrosion inhibitor (VCI product) into the drains and/or the vents. After completing the VCI application, close all of the vents and drains.

Robust water-side design

The proper design and location of the boiler feedwater (BFW) inlet and the continuous blowdown system can have a dramatic effect on the circulation in both the boiler and the condensers. Take for example the most rudimentary design of a BFW inlet, where a transfer pipe ends a few inches beyond the penetration of the wall of the pressure vessel, with a 90 degree turn to direct water along the longitudinal axis.

If the location of the boiler water sample is very close to the BFW inlet, the BFW will "short-circuit", and the blowdown will not be representative of the boiler water quality. The consequence of this design error is that the plant will not be able to properly control the chemistry of the boiler water, increasing the risk of corrosion.

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Fig. 15 shows the proper design of a BFW inlet lateral; this BFW inlet lateral is in a coal-fired boiler. However, the design of this BFW lateral is appropriate for the bottom of the kettle-style waste heat boiler. waste heat boilers and condensers. A properly designed BFW inlet distributor reduces the risk of localised areas of inadequate water circulation, off-spec water chemistry and steam blanketing in both the WHB and the condensers.

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Fig. 16 shows a computational fluid dynamics (CFD) model showing the impact of a mis-aligned BFW inlet distributor in a condenser: the velocity profile and the circulation pattern compromises the heat transfer efficiency. SRU condensers are designed to operate with natural circulation that allows the steam bubbles to rise and disengage at the water-steam interface. Introducing the colder BFW at the wrong location compromises the circulation, the heat transfer efficiency, and the steam generation rate.

Fig. 17 shows a CFD model showing the velocity profile of a properly aligned BFW inlet distributor in a condenser. Proper disengagement of steam bubbles is critical to optimise the steam production rate and minimise carrvover.

Confirming the process capability for blowdown based on the feedwater quality and ensuring consistent and accurate level control can reduce the risk of corrosion and fouling of heat transfer surfaces and steam blanketing, tube-thinning, carry-over and compromised continuous blowdown flow.

Priorities during turnaround

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The industry continues to expand the timeframe between scheduled turnarounds. Historically, it was common to have annual turnarounds and thus known

design or systemic problems were fixed in-kind. However, the modern trend is to expand the timeframe and thus reliability has become paramount. The design and operation of the process side appears to be better understood than the utility side and in particular water-side chemistry, operating practices, and good design practice. Turnaround intervals now vary between four and six years. Inspections during turnaround are important for all boilers; however, they are especially valuable for waste heat steam generators because they provide diagnostic information about the operation and integrity of the water side. Typically, the priority for inspection of the water side is much lower than the process side, creating a risk that the plant will reduce the scope or eliminate inspections of the water side.

A borescope can provide qualitative visual information about the condition of the heat transfer surfaces, the location(s) of the steam-water interface, and integrity of the inlet distributor and the blowdown collection laterals in the WHB and condensers. The water-side borescope inspections of the WHB and the sulphur condenser should be a critical turnaround activity.

Eddy current testing is especially important for "up-rated" SRU systems (i.e. operating at higher than OEM throughputs) and SRU systems that have high purity feedwater because eddy current test results provide information about tube thinning and pitting corrosion. The most important eddy current inspection is the top two rows of tubes (first 6 inches/15 cm) at the inlet of the low steam pressure generating sulphur condensers to confirm the condition of the heat transfer surfaces (e.g. presence of corrosion) and the tubesheet (e.g. off-line dissolved oxygen pitting).

Conclusion

Detecting water-related issues in the SRU requires understanding the warning signs during operation and the options for corrective actions. Reducing the risk of waterrelated issues requires a multi-faceted approach. The foundation of risk management is operational:

- implementing proactive monitoring practices (gathering the right kind of data, at the right frequency, properly interpreting the data, and implementing the right corrective actions to ensure consistent compliance to the specification limits for water chemistry)
- following practical operating strategies such as strict control of the water level. A third aspect to manage risk is to advocate for a high priority for waterside inspections during turnarounds.

The most challenging to minimise risk is to ensure robust water-side design, especially in operating units, to ensure that components such as inlet distributors, blowdown collection laterals, and blowdown control valve sizes are consistent with current best engineering practice and are matched to the BFW and boiler water quality.

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Phosphogypsum use in a circular economy

The economic conversion of phosphogypsum waste into a valuable product has been pursued for decades. Although phosphogypsum is still generally disposed of as waste, industry attitudes are changing and greater use of phosphogypsum will be expected in a circular economy.

he global expansion of phosphate fertilizer manufacturing is generating ever larger volumes of phosphogypsum waste. The conventional manufacturing route for phosphate fertilizers involves treating phosphate rock with sulphuric acid to make phosphoric acid. This intermediate is then used to produce a range of finished fertilizers (e.g., MAP, DAP, TSP). But although commercial fertilizer is the primary objective, a gypsum-rich

Table 1: Impacts of phosphogypsum impurities on plaster and cement quality

waste known as phosphogypsum is the most abundant material produced by this wet process route. About 4-6 tonnes of phosphogypsum are generated as a waste by-product for every tonne of phosphoric acid produced. This corresponds to annual phosphogypsum production of around 250 million tonnes globally.

Billions of tonnes of this material are currently being managed at great cost within giant waste stacks. Although gypsum is the main constituent of phosphogypsum, a range of other impurities can also be present, including residual phosphate, fluoride, organic matter, iron, aluminium, heavy metals, and radionuclides. Certain countries have placed legal restrictions on the disposal and use of phosphogypsum due to the presence of these impurities.

Table 1 shows the impact of phosphogypsum impurities on plaster and cement quality1.

| Type of impurities | Contaminant | Impact on product quality | Action required |
|---------------------------------------|--|---|---|
| Plaster and wallboard | | | |
| Water soluble acidic impurities | Water soluble P ₂ O ₅ , water soluble fluorine, sodium, potassium | Unwanted acidity, blistering | Need to be removed or neutralised |
| Potentially acidic compounds | Precipitated F, Al, SiO ₂ , Na ₂ SiF ₆ , K ₂ SiF ₆ , Co-crystallised P_2O_5 | Unwanted acidity, blistering | Must be controlled and reduced to acceptable levels |
| Radioactive elements | Radium, thorium | Generate radioactivity | May need to be controlled and reduced to acceptable levels, depending on regulations and recommendations |
| Organics | | Result in unwanted coloration at the surface of wallboard due to diffusion of water-soluble organics during painting | Need to be controlled and reduced. Water-soluble organics need to be removed |
| Inerts | Silica, unreacted P ₂ 0 ₅ | Coarse particles affect the quality of final product in those applications requiring fine and homogeneous products | Coarse particles need to be removed for some applications |
| Others (iron, other metals) | | Might lead to unwanted coloration of the product | Needs to be controlled |
| Cement additives | · | | |
| Soluble P ₂ O ₅ | Water soluble P_2O_5 and co-crystallised P_2O_5 | May affect settling time and mechanical resistance of the product | Need to be controlled and neutralised. Water soluble P_2O_5 + co-crystallised P_2O_5 <0.5% |
| Soluble fluorine | | | Needs to be controlled and neutralised. Water-soluble F <0.1% |

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This raises two fundamental questions: How is phosphogypsum best managed and to what extent can it be transformed from waste into a valuable resource?

Impact of the phosphate rock

The phosphate rock used in phosphoric acid production is the main source of residual impurities present in the phosphogypsum generated. For this reason, the composition and purity of phosphate rock raw materials have an important impact on the quality of the phosphogypsum.

Igneous phosphate rock types, such as apatite ore from Kola, Russia, and Phalaborwa, South Africa, and calcined rock have lower impurity levels and organic content compared to sedimentary rocks.

The phosphogypsum produced from these rock types, depending on the phosphoric acid production technology used, can be sufficiently pure to avoid further treatment, or only require simple washing of the repulped gypsum to reach the required purity. However, these phosphate rock types only represent 15-20% of overall world production and are generally more expensive compared to sedimentary phosphates.

Sedimentary phosphate rocks, in contrast, generally contain higher levels of mineral and organic impurities relative to their igneous counterparts. Consequently, when sedimentary rocks are consumed as raw materials for phosphoric acid – as is the case in most plants globally – the amounts of impurities remaining in the phosphogypsum are correspondingly higher, and a purification step is therefore generally necessary.

Regardless of the technology used for phosphoric acid production, some contaminants, such as soluble impurities and organics, will still affect the quality of phosphogypsum and therefore need to be removed prior to reuse.

Processing phosphate rock

There are several options for producing phosphoric acid from phosphate rock via the wet process route. Differences between these process options are mainly determined by calcium sulphate (gypsum) crystallisation conditions. Generally, gypsum is either precipitated in di-hydrate (DH) or hemihydrate (HH) form, or as a combination of both in successive steps. Crystallisation is a particularly important

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parameter when selecting a process technology that generates 'clean' gypsum as the desired by-product.

Standard single step DH process

The single-step DH process is widely used to produce phosphoric acid. The phosphate rock is treated with sulphuric acid to precipitate calcium sulphate as DH in one step in a reactor under agitation. A large recycling flow is achieved by agitation and/ or by external circulation associated with a flash cooling system.

The single-step DH process is a longstanding and mature industrial-scale technology that has been implemented since the 1950s. This process is by far the most flexible, compared to other phosphoric acid production routes, especially in terms of tolerance to phosphate rock impurities. Because of this, the DH process can handle a wide range of phosphate rock types. Its flexibility, together with low capex and high operability, are probably the main reasons why a large majority of the world's phosphoric acid plants utilise the DH route.

It is generally accepted that the standard DH process achieves recovery yields of approximately 95-96% – this corresponding to typical reaction yields of 96-97% P_2O_5 . If left untreated, with no removal of soluble impurities, this leaves approximately 0.8-1.1% residual P_2O_5 remaining in the gypsum, unfortunately exceeding the quality standards for plaster or cement production.

The hemihydrate (HH) process

The single-step HH process has been successfully implemented in different countries around the world as an alternative to the DH route. The HH route presents several advantages, such as the production of higher strength acid (39-42%) containing less impurities. But the process does have a lower P_2O_5 recovery (typically around 92%) compared to the DH route.

The PG produced from the HH route also contains more P_2O_5 and more impurities, compared to phosphogypsum produced via the DH route. The fact that HH gypsum reverts to the DH form, at a certain point post-production, is another constraint limiting the purification of phosphogypsum. For these reasons, the HH route is generally not an option when there is a need to recover phosphogypsum for industrial applications.

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Recrystallisation processes: DH-HH and HDH

Those technologies based on recrystallisation – either Hemihydrate to Di-Hydrate (HDH) or Dihydrate to Hemihydrate (DHH) – offer the highest P_2O_5 recovery. This is due to the liberation of the co-crystallised P_2O_5 during recrystallisation. These processes can also produce acid at higher strength compared to DH.

These advantages are offset by other factors, particularly the lack of flexibility of recrystallisation processes towards impurities. Because of this, their performance can depend strongly on the nature of the phosphate rock used as a raw material. Plants based on recrystallisation processes, being more complex and requiring more equipment, have lower plant availability, higher capex, and higher maintenance costs, compared to DH plants. Neither do recrystallisation processes provide significant advantages in terms of contaminant levels in phosphogypsum (fluorine, sodium, organic matter etc.). This makes additional treatment of phosphogypsum necessary before further use.

The two-stage Diplo process

In the 1980s and 1990s, a new approach to the DH method was developed by the French company Rhône Poulenc, the phosphoric acid technology predecessor to Technip Energies. The main purpose of this evolution in DH technology was twofold: firstly, to obtain higher P_2O_5 yields and, secondly, to increase the concentration of the dilute acid produced at filtration.

This new approach successfully generated both higher P_2O_5 yields and acid concentration, while keeping the original operational advantages of the DH route. This was of particular interest to producers in Europe who were sourcing from the merchant rock market and facing strong economic pressure to reduce their operating costs.

In the Diplo process, phosphate rock is digested using two reactors in series, with each reactor being fed phosphate rock, sulphuric acid and recycled phosphoric acid in set proportions (Fig. 1). The conditions of the reaction – including temperature, P_2O_5 concentration, and concentration of free sulphate in the acid – are optimised at each stage. In doing so, the Diplo process allows overall process performance to be optimised, according to the

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requirements of the producer, while still retaining most of the advantages of the traditional DH process.

Diplo process for high P₂O₅ recovery

When targeting high P_2O_5 yields, 70-90% of the phosphate rock is reacted in the first reactor. The first reactor is operated at lower P_2O_5 concentration, higher temperature and with higher excess sulphuric acid. Combined, these conditions tend to reduce co-crystallised losses in gypsum.

The remaining phosphate rock is reacted in the second reactor, increasing the P_2O_5 concentration of the acid. Excess sulphuric acid in the second reactor slurry is typically regulated close to 25-28g/l. This limits unreacted P_2O_5 losses and avoid excess sulphate in the phosphoric acid produced.

From waste into valuable product

It is estimated that some 50-60 million tonnes of phosphogypsum is now being utilised worldwide². A recently published study by the International Fertilizer Association (IFA) reveals that up to 25% of phosphogypsum produced annually is now reused for a range of applications, such as mine restoration, agriculture, plaster, and cement manufacture³.

While other usage estimates are less optimistic, there remains a clear upward trend with more phosphogypsum recycling over the last decade. This trend is expected to continue in the 2020s, along with new regulations and industrial

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technologies promoting more sustainable resource use.

Notable examples of commercial phosphogypsum use include:

- In Belgium, phosphates producer Prayon sells high-quality phosphogypsum for the cement and plaster market.
- In Brazil, most phosphogypsum now goes to agriculture (5 million t/a) following its reclassification.
- In Canada, Nutrien uses phosphogypsum for agriculture and, working with forestry service, afforestation using man-made 'anthrosols' phosphogypsum mixed with soil in a 9:1 ratio.
- In China, Wengfu Group uses more than half of phosphogypsum output in agriculture and construction or recycles it as ammonium sulphate/calcium carbonate.
- In Kazakhstan, phosphogypsum is use in the large-scale remediation of saline/sodic soils.
- In India, phosphogypsum was reclassified as a co-product, not waste, in 2008 and is widely sold for construction, agriculture, soil additive, cement and as bagged fertilizer (Paradeep). Examples include afforestation for green energy (Coromandel) and road construction (Paradeep).
- In Russia, PhosAgro uses phosphogypsum in agriculture, construction, and road building.
- In Tunisia, phosphogypsum is used for remediation and to return land to productive use in Sfax, brickmaking, road construction and housing.

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Phosphogypsum in construction

Phosphogypsum for cement and plaster in Belgium

Prayon provides a leading example of a successful circular economy approach to phosphogypsum use. The leading technology licensor, phosphates producer and equipment manufacturer has actually been selling gypsum as a co-product for more than forty years⁴.

The company sells virtually all of the phosphogypsum it produces at its phosphoric acid plant in Engis, Belgium, compared with 80-90% 5-6 years ago⁵. In 2018, for example, Prayon sold 708,000 tonnes of phosphogypsum for plaster and cement manufacture, with a further 60,000 tonnes sold for agronomic use, from output total-ling 790,000 tonnes.

When it comes to selling phosphogypsum, Prayon attributes its successful track record to several factors: notably the quality of its product, which in turn is attributable to the Central Prayon Process (CPP) used at its Engis plant, and the company's long-term partnerships with its gypsum customers.

The CPP, with its double crystallisation and two filtration steps, is exceptionally efficient. The process is, however, only responsible for about 1% of total phosphoric acid production globally. Key features of the CPP include:

- Flexibility: process can accommodate a wide range of phosphate rock types.
- High recovery: reduces phosphate rock consumption and generates a saleable gypsum co-product.
- High P₂O₅ content in the filtered acid: reduces steam and therefore energy consumption.
- Self-drying gypsum: phosphogypsum from the CPP process naturally cures from wet hemihydrate (HH) to dry dihydrate (DH), meaning less fuel oil is required to process gypsum.
- Environmentally friendly interim storage: neutralised phosphogypsum with a low P₂O₅ content is stored as a temporary 'gypsum quarry' rather than a waste stack.

Prayon's commercial customer Knauf established a plaster production plant close to Engis in Belgium on the opposite bank of the River Meuse. Phosphogypsum from Prayon's production plant istransported by conveyor belt across the river to a discharge point where it is temporarily stored.

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Over a period of several weeks, the phosphogypsum cures naturally in-situ, reverting from wet hemihydrate (HH) cake (18% free water, 6% crystalline water) to rehydrated dry dihydrate (DH, 5% free water, 19% crystalline water). The resulting gypsum product requires no further treatment prior to its shipment down river by barge to Knauf's stucco plaster factory.

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In 2018, some 90 percent of phosphogypsum generated by Prayon at Engis met Knauf's HH feedstock specifications, while eight percent was used in agriculture, leaving just a minor volume in the interim storage area.

Prayon is currently collaborating with the British company Carbon Cycle on the innovative PureGYP process. This novel purification technology is designed to clean phosphogypsum so that it can be sold, rather than stacked, and offers the following advantages:

- Extracts fluoride and phosphate making phosphogypsum suitable for cement and plasterboard manufacture
- Typically removes 96% fluoride and 99% phosphate
- Widens the range of usable phosphate rock sources
- Has the potential to convert phosphogypsum stacks into valuable raw material quarries.

Phosphogypsum for cement in Senegal

Industries Chimiques du Senegal (ICS) is the largest producer of phosphate fertilizer products in sub-Saharan Africa and the third largest producer on the continent. The company began mining phosphate rock in 1960 and later started producing phosphoric acid in 1984.

Following the acquisition of ICS by Indorama in 2014, a rehabilitation programme has improved phosphoric acid output with levels expected to recover to 600,000 t/a P₂O₅. ICS Indorama currently operates two phosphoric acid trains - Darou 1 and Darou 2 – both based on Technip Energies' technology.

Darou 2, the second train, was started in 2002 with a nameplate production capacity of 1,200 t/d (reaction-filtration), and a nominal capacity for 53% phosphoric acid of 1,015 t/d. This unit, which is based on Technip Energies' two-stage Diplo technology, is designed to consume a blend of Taiba rock phosphate concentrate and slimes. This allows Darou 2 to achieve a reaction yield of 97.7-98 percent P_2O_5 recovery. The corresponding 2-2.3%

Table 2: Average composition of phosphogypsum sampled from old parts of the stack, ICS Indorama, Senegal

| | Weight %* |
|---|-----------------|
| H ₂ 0 | 21-25 |
| P ₂ O ₅ Total | <0.6 |
| P_2O_5 water soluble | <0.1 |
| P_2O_5 water un-soluble | <0.5 |
| P ₂ O ₅ co-crystallised | 0.29-0.40 |
| P ₂ O ₅ unreacted | 0.16-0.36 |
| SiO ₂ | 6-14.5 |
| Fe ₂ O ₃ | 0.10-0.35 |
| Al ₂ O ₃ | 0.1-0.55 |
| FeO | 0.20-0.90 |
| CaO | 37.5-38 |
| SO ₃ | 31.5- 52 |
| Organic C | 0.45-0.56 |
| C0 ₂ | 0.00 |
| Fluorine | 0.12-0.4 |
| *Dry basis (120°C) Sour | a: ICS Indorama |

reaction losses represent insoluble P₂O₅, this consisting of a 50:50 mixture of unreacted P₂O₅ and co-crystallised P₂O₅ locked in the gypsum. The total insoluble P_2O_5 remaining in the gypsum is below 0.5%. At ICS Indorama, the phosphogypsum produced by the phosphoric acid plant is discharged dry and stacked, where it is then exposed to the prevailing weather including both rain and sun. Under these repeated wetting and drying conditions, a decrease in mainly soluble P_2O_5 and fluorine occurs. The residual humidity - an important factor for the economics of phosphogypsum reuse - is also reduced below 10% free water due to natural drying.

Aged phosphogypsum is reclaimed and directly used as an additive for clinker production without further treatment. An analysis of ICS phosphogypsum sampled from various depth in the stack is provided in Table 2.

ICS Indorama is exploring other potential markets for phosphogypsum, including use as an agricultural soil amendment and use in the remediation of saline soils. The company has developed a new phosphogypsum formulation for soil amendment purposes. This granulated product functions as a calcium source and contains residual P_2O_5 and useful secondary elements such as magnesium and sulphur, all of which contribute to soil fertilisation.

This use of phosphogypsum as a constituent in roadbed construction is another potential application being targeted by ICS Indorama. As a result of these efforts, industrial and agricultural sales of phosphogypsum have increased substantially in recent years, generating additional revenues for the company.

Phosphogypsum treatment processes

The OSW-Krupp process

The OSW-Krupp phosphogypsum process was responsible for some promising early examples of commercial phosphogypsum use. This process combined phosphogypsum with additional clay, sand, coke, and natural gypsum to generate equal amounts of sulphuric acid and Portland cement.

A number of OSW-Krupp plants were built between 1956 and 1980 in South Africa, Poland, Austria, and Germany. Although their main purpose was to recover sulphuric acid from phosphogypsum via thermal decomposition, valuable clinker for the cement industry was also produced. Cement clinker is an intermediary in the manufacture of Portland cement and is conventionally produced by sintering limestone and clay in a cement kiln.

The OSW-Krupp plant in Phalaborwa, South Africa, is a typical example (Fig. 2). This conversion plant, which had a design capacity of 105,000 t/a each for sulphuric acid and cement, was commissioned in 1972 and subsequently operated for 15 vears.

The OSW-Krupp plants were eventually closed for economic reasons - with access to lower cost sulphuric acid being



Fig. 2: The Phalaborwa OSW-Krupp conversion plant in South Africa. Operating between 1972 and 1987, this had the capacity to produce 105,000 t/a of both sulphuric acid and cement.

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a deciding factor – although meeting cement quality and environmental standards were also issues.

New tkIS phosphogypsum treatment process

thyssenkrupp Industrial Solutions (tkIS) has conducted intensive research with the aim of developing a technology to convert phosphogypsum into a valuable product for the circular economy⁶.

The latest phosphogypsum treatment process from tkIS is based on the original conversion process for the OSW-Krupp plants. An investigation of the performance of these plants revealed that pre-treatment is required before phosphogypsum is suitable for downstream production of high-quality clinker/cement or other building materials. The literature on other approaches to phosphogypsum treatment were also reviewed^{7,8}.

Phosphogypsum from various phosphoric acid plants was chemically and mineralogically analysed prior to developing the treatment process. Additionally, information was also gathered on the specifications and quality requirements for cement and other building raw materials. Once this data had been collated, a laboratory-scale phosphogypsum treatment process was developed and tested using a step-by-step approach.

Once the laboratory tests were completed, results were transferred into a kinetic process model. This model was then used to predict the treatment process parameters needed to achieve the necessary phosphogypsum quality. In this way,



only a few laboratory tests are required to confirm a suitable process design for the new PG treatment method.

Treatment process results

The new phosphogypsum treatment process consists of two main steps in sequence. Each step involves a chemical reaction followed by liquid-solid separation (Fig. 3).

In the first treatment step, chemical impurities (P_2O_5 , fluorides and others) are separated from the phosphogypsum and removed in the liquid phase. This can, if required, be recycled to the phosphoric acid plant. After this step, the quality of

the treated phosphogypsum obtained should meet clinker/cement production requirements.

The aim of the second treatment step is to reduce radioactive components, especially radium, so the quality of the resulting phosphogypsum meets building materials requirements. This treatment step is optional, depending on the composition and quality of the untreated phosphogypsum.

The first treatment step performs well, being very effective at P_2O_5 reduction (see Fig. 4). A typical recovery rate of significantly more than 90% of P_2O_5 is possible, the exact reduction depending on the



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Fig. 3: tkIS PG treatment flow sheet

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process regime. Importantly, the liquid phase containing the dissolved P_2O_5 is fully reusable in the phosphoric acid plant – and therefore contributes to the overall P_2O_5 efficiency of the production complex. The first treatment step has also been shown to be equally effective at reducing the fluoride content of phosphogypsum.

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Generally, understanding the reaction kinetics of P_2O_5 recovery is critical, as this holds the key to optimising the whole process. Reaction conditions have a large impact on the recovery rate, with harsh reaction conditions, for example, typically leading to shorter release periods compared to mild conditions.

The overall reduction in phosphogypsum impurities achieved by both treatment steps is shown in Fig. 5 (first treatment step in blue, second treatment step in red).

In the first treatment step (Fig. 5, blue colour), P_2O_5 and fluoride are removed at efficiencies of up to 98% and 96%, respectively. In parallel with this, significant reductions in other elements (Cu, Mg, Fe, Mn etc.) are also achieved. This is highly beneficial for the potential use of phosphogypsum as a plaster industry raw material. The efficacy of this first treatment step has also been tested and confirmed on phosphogypsum

generated by both sedimentary and igneous phosphate rock types.

The main aim of the second treatment step is radium removal (Fig. 5, red colour). Treatment was found to reduce radium activity by approximately 40%, down from 570 Bq/kg originally to an eventual value of 330 Bq /kg. Typically, this would be expected to reduce the ACI of phosphogypsum from 1.4 to 0.9 approximately. Further studies are nevertheless underway to improve and optimise the removal of radioactive elements, particularly for more radioactive types of phosphogypsum.

With regard to radioactivity, and despite what is achievable technically, decisions on the ultimate usage of treated phosphogypsum will still require discussions between manufacturers, users and authorities.

Outlook

Building on these positive lab-scale results, the next step of process development will scale-up capacity and optimise energy consumption. A strategy for achieving full integration of the phosphogypsum treatment process within existing production plants will also be pursued. The opportunities for plant integration will be evaluated in cooperation and partnership with interested phosphate producers.

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Using phosphogypsum to create soil and combat climate change

The conventional way of reclaiming phosphogypsum stacks is to cover their surface with a thick layer of soil. When Nutrien began researching alternative methods of phosphogypsum stack reclamation in Alberta, Canada, in 2005, the company discovered that reclamation could be improved by mixing small amounts of soil directly into weathered phosphogypsum. This created a man-made soil known as an 'anthrosol'.

Creating healthy soils for trees

It was found that any amount of soil mixed into weathered phosphogypsum grew larger, healthier biomass than plants grown in soil alone. Nutrien then investigated the possibility of growing trees in the phosphogypsum mix to reduce long term maintenance costs and increase sustainability – while also creating value and sequestering carbon.

Approximately a thousand hybrid poplar (Populus spp) and hybrid willow (Salix spp) cuttings were planted into a phosphogypsum/soil mix in 2015 and found to grow extremely well. Based on this success, approximately twenty hectares of phosphogypsum stacks were reclaimed and planted to high yield afforestation plantations in 2016 and 2017 following the protocols developed by the Canadian Wood Fiber Center, Natural Resources Canada.

The tree plantations established at Nutrien are predicted to sequester 30 tonnes $\rm CO_2$ equivalents per hectare per year.

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Thus, in 20 years, the gypsum stack area reclaimed to date will sequester 12,000 tonnes of CO_2 equivalents. This same area is also predicted to produce 10 oven dry tonnes/ha/year of above ground woody biomass.

Food production

The phosphogypsum/soil (anthrosol) can also be used to grow many other types of high value crops. Nutrien has established a small research garden on top of the phosphogypsum stack and has tested various flowers, fruits and vegetables such as raspberries, potatoes, tomatoes and pumpkins.

Analytical results indicate that the quality of the vegetables is the same or better than plants grown on regular soil. Future research will include expanding pollinator habitat and working with local beekeepers to investigate other opportunities to create value in situ.

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