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SULPHUR

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Lithium sulphur batteries

Sulphuric acid demand for leaching

BTX destruction

Reducing soot formation in SRUs

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44
45
46

SULPHUR

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NUMBER 361 **NOVEMBER | DECEMBER 2015**

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CONTENTS

19 **Lithium sulphur batteries**
There is great excitement in the power industry about the potential for lithium sulphur batteries to take up where lithium-ion and nickel-cadmium batteries left off. What might it mean for sulphur?

22 **Sulphur storage**
As the sulphur industry faces more years of excess, the short, medium and even long-term storage of sulphur is returning to the fore as an issue.

24 **Acid leaching for metal extraction**
The slowdown in the Chinese economy has had a negative impact on metals markets, a major source of sulphuric acid demand for metal leaching.

28 **Managing the risk of H_2S**
Craig Jorgenson, Director of Transportation and Regulatory Affairs for The Sulphur Institute (TSI), describes the effects of hydrogen sulphide and TSI's work with attempting to help mitigate its risks.

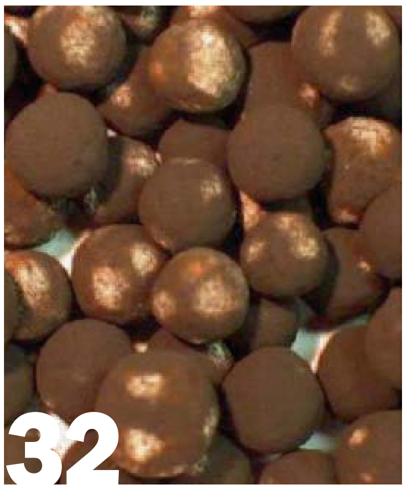
30 **MESPON 2015**
The 2nd Annual Middle East Sulphur Plant Operations Network Forum, MESPON 2015, organised by UniverSUL Consulting, took place in Abu Dhabi at the Sofitel Abu Dhabi Corniche from October 18-20, 2015.

32 **Soot formation on Claus catalyst**
It is common for SRU operators to soot up the first catalytic bed during start-up, shutdown or low turndown operation. In this article we discuss the causes and effects of soot fouling in SRUs, how it can be prevented and how it can be treated if it does happen.

46 **How to avoid problems with BTX**
Incomplete destruction of BTX in the Claus reaction furnace can lead to degradation of the Claus catalyst and reduced sulphur recovery. In this article we describe how BTX reaches the sulphur plant, how to minimise the amount of BTX in the acid gas feed to the SRU, and how best to deal with benzene toluene and xylene when present in the sulphur plant.

Managing H_2S risk

Mitigating the threat posed by hydrogen sulphide.



Soot formation

Fouling of SRU catalysts and how to avoid it.

REGULARS

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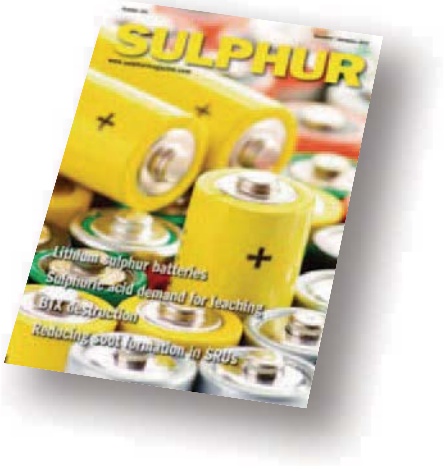
Acid – make or buy?



> **An increasing number of merchant acid consumers have started to look towards producing their own acid.**

Whether to manufacture sulphuric acid on-site or purchase it on the open market is a decision that all acid consumers around the world must make. Clearly, most choose to produce acid via burning sulphur – sulphur is a widely traded international commodity, and much more easily transported and stored than sulphuric acid. Those consumers who do use metallurgical acid are generally close to a source of acid; while one third of all acid production comes from smelters, only about 10% of all acid – or less than one third of metallurgical acid – is traded over longer distances. Nevertheless, this still represents a good number of consumers who have tended to buy smelter acid produced elsewhere.

The decision can be a finely balanced one – both sulphur and sulphuric acid markets can be volatile, and there are spells when sulphuric acid is cheaper than the equivalent amount of sulphur. Of course, if you have a sulphur burning plant, you can at least take if off-line and buy merchant acid at such times, as happened in India and some other parts of Asia during 2014, taking advantage of the price differential between the two markets. Of course there are other considerations, such as credits from power production, tanking, logistics and regularity of delivery, contract break clauses etc etc, but it does provide at least a partial hedge against periods of high sulphur prices.

It is interesting, then, that in recent years an increasing number of merchant acid consumers have started to look towards producing their own acid. Morocco's OCP started operations of a 1.2 million t/a acid plant in the first quarter of 2015, halving its acid import requirements for the year and expected to reduce that still further in 2016. Toros in Turkey is building a 726,000 t/a acid plant which will likewise replace imports of acid. In the case of Chile, where Noracid built a 720,000 t/a acid plant at Mejillones in 2012, the impetus was purely commercial. Like many sulphur-burning acid plants, Noracid gains valuable credit by producing and exporting power, in this case 26MW.

And Sherritt International has been a major buyer of mainly European sulphuric acid for its Moa nickel leaching joint venture in Cuba, which consumes around 500,000 t/a of acid, but is now building a new acid plant which is expected to come on-stream in the second half of 2016. Sherritt has said that it believes that it can reduce the cost of producing nickel at Moa by $0.50-0.60/lb – equivalent to about 12-15% – once the plant is up and running. This is important in a nickel market which has fallen to seven year lows on the back of reduced buying from China for stainless steel production. Sherritt says that its production costs at Moa are $4.07/lb – down from $5.25/lb from a year ago, taking it below prevailing nickel prices of $4.25/lb, but still a very thin margin, and one that integrating of acid production should help by a considerable margin.

Building a sulphur-burning plant looks like a safe bet in the prevailing sulphur market climate, with large sour gas projects starting to deliver large volumes of sulphur to global markets. But it is also notable that at the same time that sources of merchant acid demand are being choked off, acid consumption is also falling in some areas as cuts are made in copper and nickel leaching operations. Freeport McMoRan, for example, is cutting copper leaching operations in Chile and the United States, with the loss of an estimated 400-500,000 t/a of acid demand. Under such circumstances, the acid market might find itself in for a spell of lower prices as well.

Richard Hands, Editor

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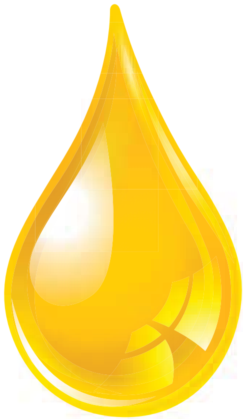

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Price trends

MARKET INSIGHT

Meena Chauhan, Research Manager, Integer Research (in partnership with ICIS) assesses price trends and the market outlook for sulphur.

SULPHUR

Turning point?

The bearish mood in the global sulphur market started to ease at the end of October. All eyes were turned to China, with hopes of demand there stabilising the sharp drop in pricing. Market confidence suffered this year through the weaker macro economic conditions, with key commodity prices continuing on a negative run. Fourth quarter contract discussions for sulphur have been protracted in some regions as decreases in the Middle East and China benchmarks led to pressure in other key markets. Some of the first contract prices to be settled included the Tampa price in the US, reflecting a 20% reduction, down by $27/long ton to $110/long ton delivered. This has come on the back of slow processed phosphates demand in the US and Brazil, resulting in cuts in production from Mosaic in the US and OCP in Morocco.

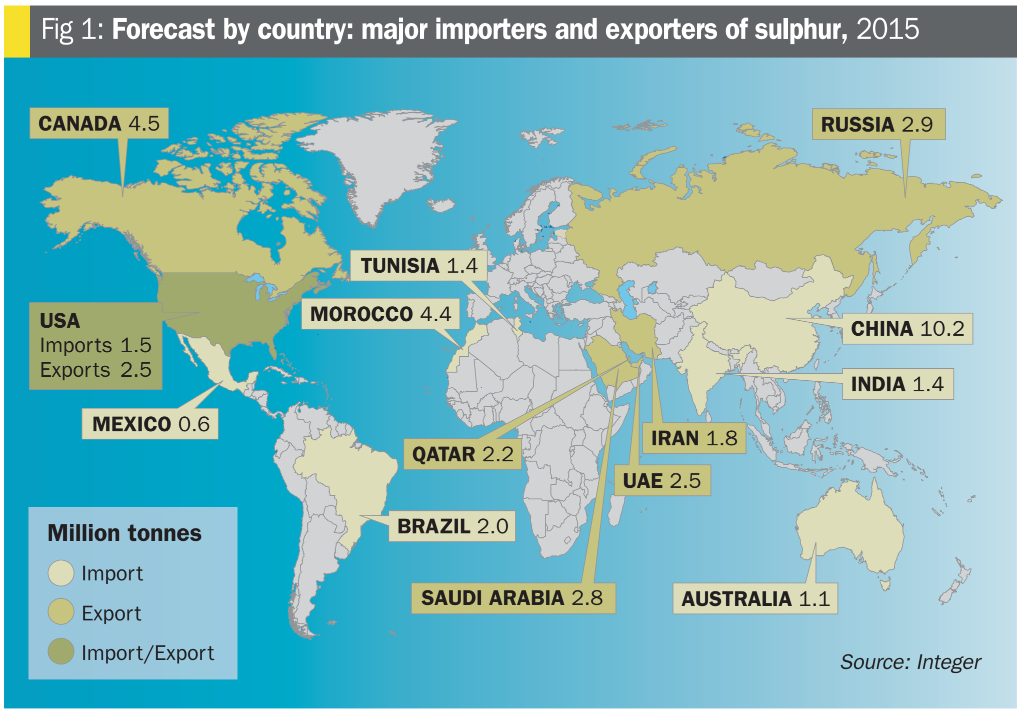
At the start of November, the market appeared to reach a floor, at least temporarily. Producers in the Middle East indicated minimal stock levels and being sold out in the near term, adding to the more stable outlook. Aramco Trading said it had no surplus for the spot market through the end of the year. In Qatar, Tasweeq increased its November monthly price by $21/tonne to $124/tonne f.o.b. Ras Laffan, on the heels of its spot tender, which was awarded in the low-$120s/tonne f.o.b. Meanwhile, Adnoc also increased its price for November, by $10/tonne to $125/tonne f.o.b. Ruwais, for shipments to the Indian market. The price increases from producers have set the tone for a firmer month ahead, despite the recent lull in end user interest. Producers are still looking to China, with reports of increased enquiries for spot cargoes for November and December, which could buoy the market. The outlook for Middle East pricing for the balance of the year remains stable, with potential for improvements if demand picks up in earnest.

Spot prices in China ticked up at the start of November, as buyers accepted a floor in pricing had been reached. The boost in Middle East producer pricing has also pushed the spot market up, with traders looking to place cargoes at prices in the $140s/tonne c.fr range. Spot prices are likely to remain stable to firm in the short term, although any meaningful recovery is likely to be mooted by the commodity price drop and weak processed phosphate market.

The Indian spot market also saw a rebound, with seasonal sulphur demand emerging during the sugar season from October. Prices at the start of November were pegged in the $140s/tonne c.fr India. Domestic sulphur supply has been ample however, with availability from local refiners a potential bearish factor. Sulphur from the new Paradip refinery is expected to be available for local buyers in the new year. End user FACT entered the market with a tender for November, but subsequently scrapped it, given the range of offers as high as $147/tonne c.fr Kochi. A new tender has been issued, which will test the spot market. This is likely to attract prices in a similar price range however, due to the recent stabilisation and uptick. Iffco, another major end user in India, remains out of the spot market due to adequate coverage from its contract commitments.

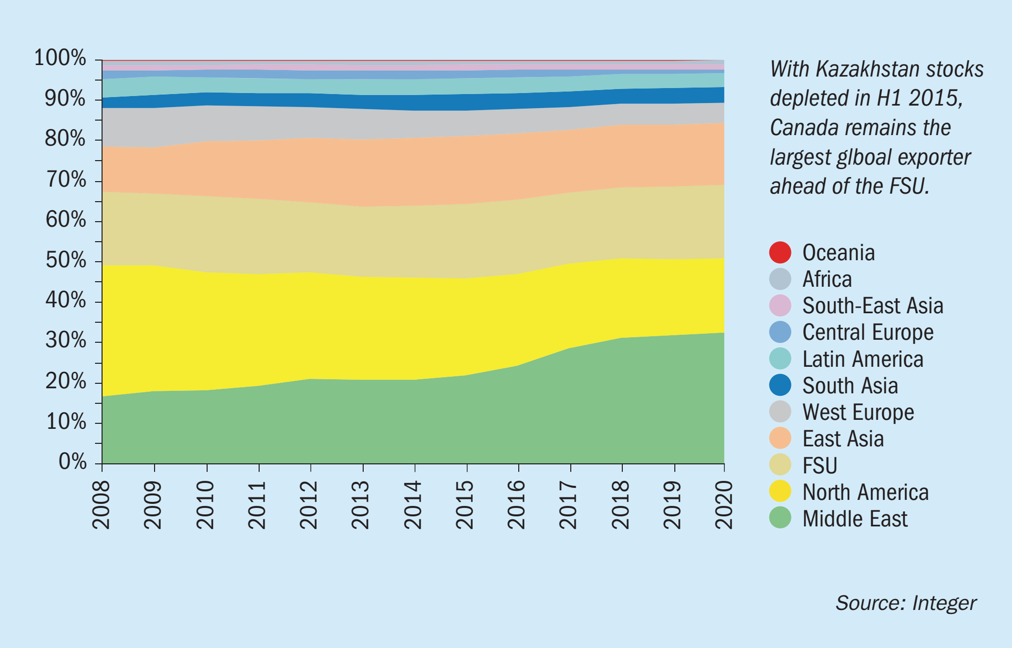
Contracts between North African buyers and a major FSU supplier were agreed

Fig 1: **Forecast by country: major importers and exporters of sulphur,** 2015



Source: Integer

Fig 2: **Global sulphur production by region** 2008-2020



With Kazakhstan stocks depleted in H1 2015, Canada remains the largest glboal exporter ahead of the FSU.

Source: Integer


DU PONT ®

at $115/tonne c.fr, for the fourth quarter. GCT/Tunisia's processed phosphates production is running at 50-60% capacity due to the downward pressure from the weak phosphates market. In the months ahead, sulphur imports into North Africa are expected to gain ground, with expansion projects in processed phosphates in Morocco and Tunisia impacting trade flows. OCP's Jorf Lasfar expansion is expected to be a key outlet for increased volumes coming out of Ruwais in 2016.

In North America, Vancouver spot prices increased to $115-120/tonne f.o.b., based on deals to China. Mosaic's 1 million tonne per year remelter is in on schedule for its start up in Q4 2015, and remains a focus for the outlook for North American trade dynamics. Integer expects to see the remelter utilised in 2016, leading to shifts in local balances. Solid cargoes from Kazakhstan have already been imported as part of the testing process. Canadian rail shipments showed a 1% decline in Q3 compared to a year ago, due to the uptick in offshore exports. Rail shipments will likely decline further in 2016, with increased availability from Vancouver expected.

The Latin American markets are expected to remain stable through the end of the year, although Vale in Brazil is covered by its contract volumes and does not expect to have any need for additional spot volumes during November and December. Anglo American is understood to have secured 37,000 tonnes of sulphur for January delivery at $124/tonne c.fr. Sulphur imports will increase in the outlook in Cuba, once Sherritt's new sulphur burner comes online. This will offset current trade of direct sulphuric acid from suppliers such as Europe.

SULPHURIC ACID

Bearish outlook

Global sulphuric acid prices came under pressure in September, with limited enquiries in the market as buyers appeared to be comfortable with contract volumes and scheduled arrivals. The NW European export price dipped through October and November, dropping down to $3/tonne f.o.b. on the low end of the range. The lower prices and length in the market stimulated interest in the spot market in various regions, leading to an uptick in fresh enquiries. In India, Iffco purchased around four cargoes of acid from a mixture of sources, heard to be priced in the high $40s/low $50s/t c.fr range. Meanwhile, PPL/Paradip is due to begin testing its sulphur burner in November, with ramp up in December, reducing the buyer's spot acid requirements going forward. OCP/Morocco also entered the spot market, purchasing cargoes at below $30/tonne c.fr. While sulphur imports are set to rise to Morocco going forward, acid imports are likely to remain a key part of OCP's procurement strategy, particularly looking at the price differential between sulphur and acid. However, it remains to be seen if record acid imports seen in 2014 will be matched.

In Japan, Pan Pacific Copper entered into a maintenance turnaround at its Saganoseki smelter. Sumitomo was also expected to enter a maintenance at its Toyo smelter at the start of November. Despite the turnarounds, prices are not expected to be supported due to ongoing length in the market.

Spot business in Brazil in the low $40s/tonne c.fr range in Mosaic's tender has contributed to the price erosion in NW Europe. The cargo will be delivered in December. Ongoing competition for supply into Brazil from Mexico has dampened spot prices recently. Tonnes are still thought to be available for export in the coming weeks.

The focus in Chile is on 2016 acid contract negotiations, with a number of suppliers expected to visit the country through November. A reduction in pricing is expected on 2015, due to the weaker outlook and recent downturn in commodity pricing and lower netbacks in key export regions such as Europe. Exact price ideas have been mixed, but levels around the low $50s/tonne c.fr were reported to be targeted on the buyer side. This is around $10-20/tonne lower than target prices expected from suppliers and traders. January – August acid imports to Chile have totalled 1.5 million tonnes. Import requirements for 2016 will likely be a talking point during the contract negotiations. The forward trend in Chile is expected to be a decline in acid import requirements, a bearish factor in the long term outlook for the market. ■

Price indications

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

Cash equivalent	**May**	**June**	**July**	**August**	**September**
Sulphur, bulk ($/t)					
Vancouver f.o.b. spot	135	145-155	145-155	144	115
Adnoc monthly contract	150	150	155	135	115
China c.fr spot	155	150-168	150-168	140	118
Liquid sulphur ($/t)					
Tampa f.o.b. contract	132	137	137	137	137
NW Europe c.fr	185	170-200	170-200	185	185
Sulphuric acid ($/t)					
US Gulf spot	75	70-80	70-80	68	60

Source: CRU

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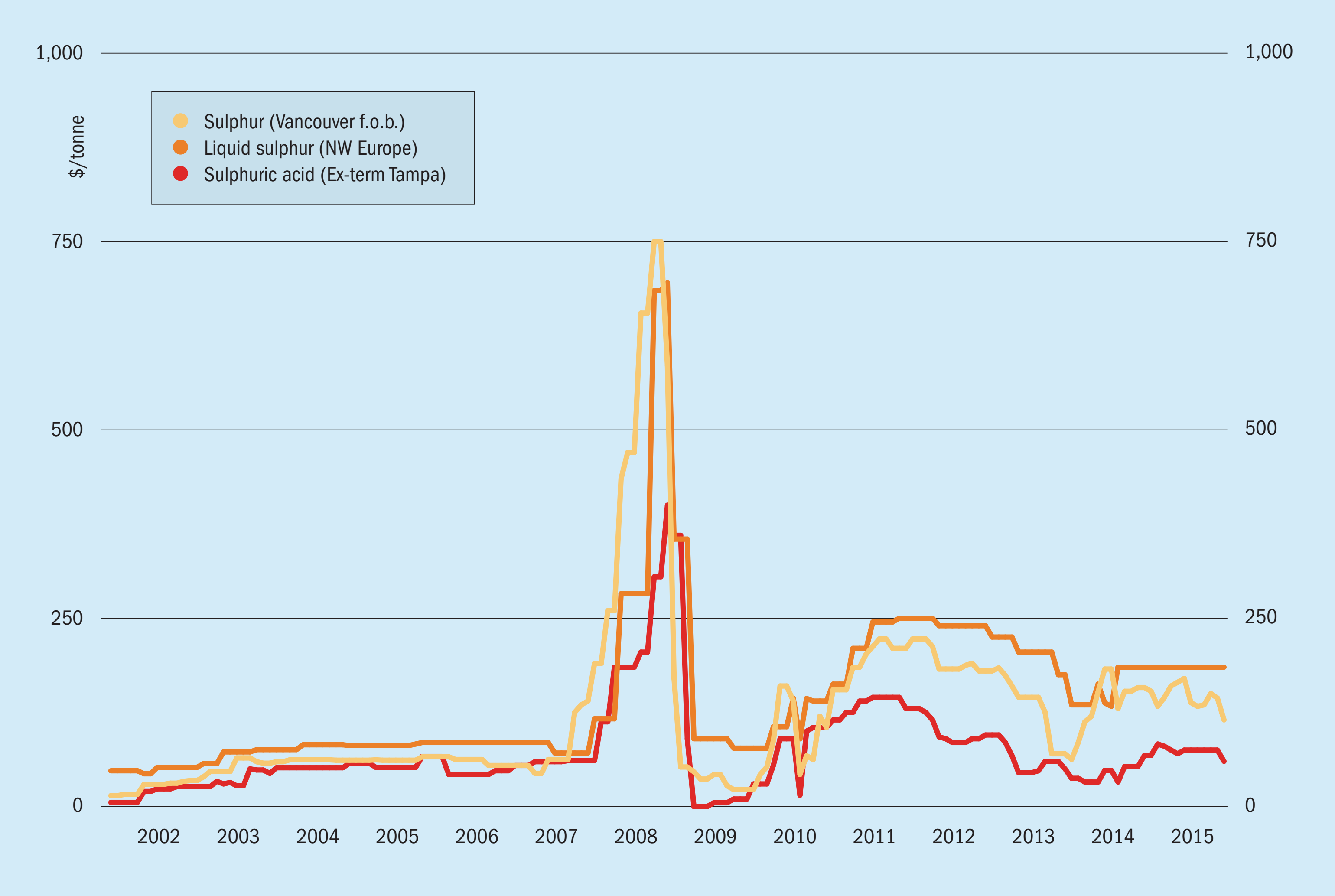
Market outlook

Historical price trends $/tonne



Source: BCInsight

SULPHUR

- Prices are expected to stabilise and improve during the remainder of the year, although upward momentum likely to reach a ceiling unless the phosphates market also improves significantly.
- China will be a key stabilising factor, with the entrance of market players to the import market for spot volumes. Imports for 2015 likely to be on a par with 2014 levels.
- Middle East producers to support the upward direction of prices, with increases or stable price postings likely in the coming months.
- Shell will not continue construction of its 80,000 bbl/day Carmon Creek thermal in-situ oil sands project in Alberta, Canada, because of low oil prices and a lack of pipeline capacity to ship the oil to market.
- Middle East sour gas and oil refinery projects to add export availability and put downward pressure in pricing in the long term. Al Hosn's Shah gas project will likely see a significant volume increase in 2016.
- Morocco, Turkey and Cuba to increase sulphur imports in the outlook in line with new sulphur burners.
- Latin American markets are expected to remain stable through the end of the year, although Vale in Brazil is covered by its contract volumes and does not expect to have any need for additional volumes during November and December.
- **Outlook:** Prices to remain stable to firm in the short term, although a significant increase is likely to be limited by a weak downstream processed phosphates market. Prices in 2016 are likely remain at similar levels to those achieved in 2015.

SULPHURIC ACID

- Chile contracts will likely settle at decreases for 2016, reflecting the weaker tone in demand and length in the acid market.
- The NW European export market is likely to remain under pressure in the coming weeks, despite the uptick in interest in spot cargoes, due to availability from other supply regions providing buyers with options for sourcing.
- Domestic acid production in China is expected to continue to rise, putting pressure on import requirements going forward.
- Weak macro economic conditions will likely dampen the outlook for acid, any rebound in commodity markets could help to recover demand and pricing.
- European contract price discussions are expected to begin in late November for 1H 2016.
- **Outlook:** Weaker pricing is expected to hold in the coming weeks, due to ample supply in the market. Any unplanned outages could help to stabilise the market. The upturn in global sulphur prices could also lead some buyers to purchasing acid instead of sulphur, providing further support to the market. ■

Sulphur Industry News

CANADA

Fire takes Syncrude upgrader off-line

A fire at Syncrude's Mildred Lake upgrader near Fort McMurray, Alberta, has damaged production of syncrude and forced the company to take the upgrader itself down for a month for repairs. The fire, on August 29th, damaged pipes, power and communication lines between two units of the upgrader. Syncrude production for September was estimated by the company to be 63,000 bbl/d, 80% down from its July average of 326,000 bbl/d, and the company said that it expected output for the year to come in at the low end of its estimate of 96-107 million barrels. The downtime will also affect monthly sulphur production of 60,000 tonnes. Syncrude is 37% owned by Canadian Oil Sands Limited, and 25% by Imperial Oil Resources. Other minority partners include Suncor, Sinopec, Nexen, Mocal and the Murphy Oil Company Ltd.

In other news, Canadian Oil Sands Ltd faces a hostile bid from its Syncrude joint venture partner Suncor. Suncor's offer of C$4.5 billion has been rejected by the Canadian Oil Sands' management. The bid – of 0.25 shares of Suncor for every COS share – would value COS at C$9.25/share at current prices, below the market value of C$9.92, and well below the $11.82/share that Suncor offered COS management in April, although falling world oil prices have pushed Canadian oil sands producers to the marginal end of the cost curve since then.

The move would give Suncor a 49% stake in Syncrude, which has been plagued by outages and downtime, and which Suncor claims it can run more efficiently than COS. Suncor produces 400,000 bbl/d of oil sands syncrude from its own mines in addition to its stake in Syncrude. ■

VMG and OGT announce alliance

Virtual Materials Group (VMG), a technology company which develops process simulation software and solutions for the oil and gas industry, has agreed to an alliance with Optimized Gas Treating, Inc., specialising in mass transfer rate-based process simulation software for gas treating. The alliance will link OGT's proprietary gas treating software, ProTreat® with VMG's proprietary process flowsheet software, VMGSim to help solve some of the most challenging process problems. OGT says that ProTreat's proven predictive models are backed by a database of exceptional quality for important reaction and mass transfer parameters for a wide range of column internals types and brands. VMG has focused on increased accuracy of fluid property predictions and the ability to solve complex problems with increased flexibility.

Ralph Weiland, Optimized Gas Treating's president and founder said: "we look forward to working closely with VMG to provide full service software solutions to the oil and gas industry. With the integrated power of VMGSim and ProTreat, engineers will have access to best-in-class tools for all their process simulation needs – the highest quality thermodynamics, impeccable flowsheet capabilities, and the predictive ability of mass transfer rate based tower simulation".

Construction complete on CCS project

Fluor Corp. has completed the construction of Shell's Quest carbon capture and storage (CCS) project near Fort Saskatchewan, Alberta. Responsible for the EPC contract on the CCS project, Fluor designed and built the facility using a modular system which it calls 3rd Generation Modular Execution, involving 69 separate interlocking modules that were assembled at site. Fluor says that the design approach compresses the space requirements of a typical plant, reduced material quantities and construction labour hours required in the field, as well as delivering capital efficiencies to the project and shortening time to completion.

The Quest CCS project will capture approximately one million metric tons of carbon dioxide per year from the Scotford Upgrader in the Athabasca oil sands and store it deep underground. The project was delivered under budget and on schedule with an exemplary construction safety record.

"The successful completion of the Shell Quest CCS project demonstrates the value of Fluor's 3rd Gen Modular Execution, an innovative project execution delivery that lowers costs and improves schedule predictability for our clients," said Jim Brittain, president of Fluor's Energy & Chemicals business in the Americas region. "By implementing this technology in the early phases and delivering it throughout the full project

The CCS project at Shell's Scotford Upgrader, Alberta.

execution, we were able to reduce the plot space of the facility by approximately 20 percent and eliminate material and labor costs from the project. This brought additional value to our client and enabled us to complete construction on schedule."

UNITED ARAB EMIRATES

Shah reaches full capacity

The Shah gas project reached full production capacity of 1 billion scf/d at the start of October, according to operator Al Hosn Gas. Al Hosn Gas and the Shah gas development joint venture is 60% owned by the Abu Dhabi National Oil Co (Adnoc) and 40% by US-based Occidental Petroleum. The project will produce 0.5 bcf/d of sales gas to reduce the UAE's increasing imports of gas, as well as producing up to 3 million t/a of formed sulphur.

ITALY

Diesel solutions highlighted at European refining technology meeting

The international refining industry will meet in Rome from 17-19 November for the 20th European Refining Technology Conference (ERTC). Amongst the presentations at the meeting, DuPont Clean Technologies will present its approach to meeting modern diesel specifications in a panel on November 19th focused on innovations for margin improvements.

Presenter Dr. Matthew Clingerman, EMEA Regional Engineering Manager for DuPont Clean Technologies, commented; "Refiners are challenged to meet increasingly stringent fuel specifications, even as the slate of available feedstocks becomes more difficult to process. Significant upgrades to existing facilities are often difficult to justify in an era of heavy capital restraint and must meet specific targets for long-term return on capital and product quality from cost-advantaged feedstocks for any investment to be attractive. One solution to reducing sulphur in finished products to ultra-low levels while minimising capital investment and operating costs is *IsoTherming®* hydroprocessing technology. Via case studies showing existing grassroots and revamp applications, I hope to demonstrate how this technology has been successfully implemented on a commercial scale in a number of applications, including ULSD, VGO hydrotreating and mild hydrocracking, to meet clean fuels specifications and ensure a safe and sustainable operating environment."

The ERTC Annual Meeting is a leading refining technology conference, attended by international petrochemical and chemical companies, as well as regulators and traders. From strategic planners to project and technical managers, they come together to network and hear of the latest technology developments that can further their industry.

SAUDI ARABIA

PetroRabigh tenders for SRU

Saudi Arabia's PetroRabigh has launched a bidding process for the construction of several new units at its refining complex in Rabigh. The tender is for engineering, procurement and construction (EPC) contracts for a polyether polyols plant with a capacity of 220,000 t/a, a 17,000 bbl/d naphtha treating unit to produce clean fuel, and a 106,000 t/a sulphur recovery unit (SRU). Work would start in the second half of 2016, according to PetroRabigh, which is a joint venture between Saudi Aramco and Japan's Sumitomo Chemical.

Wasit not yet processing sour gas

Saudi Aramco has almost finished construction of its giant Wasit gas project, but the plant is not yet processing non-associated sour gas from the offshore Arabiyah and Hasbah sour gas fields, according to press reports. Aramco began testing the facility in April using sweet gas from the Master Gas Gathering System (MGGS), but the sour gas processing section, removing hydrogen sulphide and carbon dioxide from the gas feed, is not yet fully up and running. It is expected to be on-stream before the end of the year, however. The issue is not seen as a critical one for Aramco as the peak summer gas demand season is over and the country still has huge reserves of stored gas to draw upon. Wasit is designed to process 2.5 billion scf/d of sour gas, 1.3 billion scf/d from Hasbah and 1.2 billion scf/d from Arabiyah, with H_2S content varying from 4-8%.

Contracts awarded for Fadhili gas plant

Spain's Tecnicas Reunidas and UK-based Petrofac have been selected by state oil company Saudi Aramco for contracts worth up to $4.7 billion to build the Fadhili gas plant in Saudi Arabia. Although Aramco has slowed down investments in some areas due to the collapse in oil prices, moving ahead with Fadhili shows the urgency with which the company regards getting non-associated sour gas processing capacity on-stream to boost the country's gas production. Fadhili will have a capacity of 2.5 billion scf/d of sour gas from the onshore Khursaniyah and offshore Hasbah fields.

Tecnicas Reunidas won the two packages in which it bid; the $2 billion gas processing unit and the $2 billion utilities and offsites, contract, while Petrofac won the $1.7 billion sulphur recovery package. The plant is due to come on-stream by 2019.

FRANCE

FMC and PROSERNAT in technology alliance

FMC Technologies, Inc. and PROSERNAT have signed an alliance agreement to become a single source supplier of integrated modular systems and solutions for the processing, separation and treatment of oil, water, gas and solids. The two companies bring together expertise in the areas of oil and gas separation, produced water, solids handling and gas treatment, such as mono ethylene glycol regeneration and reclamation, natural gas dehydration and sweetening, natural gas liquids extraction and sulphur recovery, which under the terms of the alliance, will be integrated into complete packages.

Axens to install HDS technology in Donges refinery

Axens says that its vacuum gasoil (VGO) hydrodesulphurisation (HDS) technology has been selected by Total for a new VGO HDS unit at the Donges refinery in France. The unit is designed to process around 40,000 bbl/d of VGO, and will allow Total to produce low sulphur fuels to meet evolving EU fuel specifications. Axens will supply the technology license, basic engineering, proprietary catalysts and equipment as well as related services for training, unit start-up and follow-up.

POLAND

Tecnimont to modernise Gdansk refinery

Italy's Maire Tecnimont SpA. Has been awarded a euro 36 million contract for licensing, engineering, procurement and

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construction services by Poland's Grupa Lotos for the execution of a hydrowax vacuum distillation (HVD) unit which will be integrated into the Gdanksk refinery, on the Poland Baltic coast. Project completion is expected by January 2018, according to Tecnimont. The award is part of the Gdansk's EFRA (effective refining) capital project, aimed at improving output efficiency of the complex. Grupa Lotos is one of the largest refining companies in Poland, engaged in the extraction and processing of crude oil, as well as in the wholesale and retail of refined petroleum products.

UNITED STATES

Keystone XL pipeline rejected

President Obama announced in early November that he was vetoing the construction of the 1,180 mile cross-border section of the Keystone XL pipeline. Then decision ends seven years of uncertainty over the pipeline's construction, which would have taken 800,000 bbl/d of Canadian oil sands syncrude through an environmentally sensitive area of Nebraska to a junction with existing pipelines in Kansas. US Gulf Coast refineries have adapted to handle heavier, sourer feeds in recent years, in anticipation of using oil sands syncrude. The pipeline had become a talisman for environmental protestors, and the president made the largely symbolic decision to supposedly bolster America's green credentials ahead of a UN climate change summit in Paris in December. However, around 500,000 bbl/d of syncrude is already crossing the border via existing pipelines, and in the absence of Keystone XL, several hundred thousand bbl/d of Canadian syncrude has also been heading south by rail, with an additional 180,000 bbl/d carried in 2015 as compared to 2014.

EIA revises down expected RFO demand

The US Energy Information Authority (EIA) has revised down its projections for consumption of high sulphur residual fuel oil (RFO). While some of this is in the light of changes to maritime fuel regulations, the EIA says that large reductions in RFO demand will come from decreased use for power generation and space heating. "In the power sector, the cost of pollution controls, maintenance, and RFO heating often offset the lower cost of RFO when compared to natural gas and other more expensive fuels. Consequently, power sector demand for RFO, especially in industrialized countries, is expected to decrease." However, it may still serve as a transitional fuel in developing countries that may be more sensitive to price and less sensitive to environmental and health implications.

As far as the MARPOL maritime fuel regulations are concerned, EIA notes that because "few refineries are capable of removing sulphur from RFO, MARPOL compliance will likely be achieved using two approaches: using fuels with lower sulphur content such as marine gasoil or intermediate fuel oil, or removing sulphur post-combustion, using scrubbers or other technologies… some operators are considering the use of liquefied natural gas (LNG) as an alternate fuel for ships operating along routes where LNG is available." ■

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Sulphuric Acid News

WORLD

Copper majors cut production, jobs

The slowdown in Chinese growth and copper consumption has led to a wave of industry cutbacks around the world, as copper prices languish at six-year lows. Freeport-McMoRan set the ball rolling with the announcement of cuts in copper output from operations in the US and Chile. It has cut production at Tyrone, New Mexico by 50% and mothballed its Miami, Arizona operation. Copper output from the large El Abra mine in Chile will also be cut by 50%. Around 10% of staff positions in the US will be cut, and capital expenditure will fall by 25%. Exploration costs will be halved. The company expects to produce 70,000 tonnes less copper in 2016 and 2017. CRU estimates that the impact on sulphuric acid demand could be around 40-50,000 t/a at Miami, 70,000 t/a at Tyrone,a nd 200-400,000 t/a at El Abra.

Glencore, saddled with $30 billion of debt, has slashed dividends, announced a major equity sale, and begun a fire sale of assets. Recently the company announced the sale of its Cobar copper mine in New South Wales, Australia and the Lomas Bayas mine in Chile after receiving "unsolicited expressions of interest for these mines from various potential buyers". Cobar is an underground copper mine and concentrate plant producing about 50,000 tonnes of copper concentrate a year. Lomas Bayas is a low-cost, open pit copper mine in the Atacama desert, 120 km northeast of Antofagasta, Chile. The ore is processed by heap leaching, producing about 75,000 t/a.

Chile's second-biggest copper mine Collahuasi, owned by Anglo American and Glencore, is planning to cut copper output from its leaching plant by 30,000 t/a as part of a restructuring of operations at the site, which produces 470,000 t/a of copper. Job loss estimates were between 110-200 positions, with mining unions likely to protest.

US copper producer Asarco plans to reduce copper production by 30,000 t/a by cutting back on leaching operations at its Ray mine in Arizona. The company also said that it will "indefinitely" close its copper concentrator at Hayden, New Mexico. ■

UNITED STATES

Mosaic settles over waste allegations

Mosaic Fertilizer has reached a settlement with the US Department of Justice and Environmental Protection Agency (EPA) after alleged violations of the federal Resource Conservation and Recovery Act (RCRA) regarding the storage, handling and future disposal of waste deemed to be 'hazardous'. The settlement covers the treatment, storage and disposal of an estimated 30 million short tons (27 million metric tonnes) of waste at six Mosaic facilities in Florida and two in Louisiana, including phosphogypsum stacks, and acidified water in tanks, ditches and ponds.

Under the settlement, Mosaic will establish a $630 million trust fund, which will be invested until it reaches full funding of $1.8 billion. These funds will cover the future closure of four Mosaic facilities; the Bartow, New Wales and Riverview plants in Florida and the Uncle Sam plant in Louisiana, and also be put toward the treatment of hazardous wastewater at and long-term care of those facilities and two additional facilities which are already undergoing closure. Mosaic will also spend $170 million on projects to reduce the environmental impact of manufacturing and waste management programs at its facilities and $2.2 million on two local environmental projects. Mosaic will also pay a $5 million civil penalty to the United States and $1.55 million to the State of Louisiana and $1.45 million to the State of Florida, who joined the Department of Justice and EPA as plaintiffs in this case.

As part of EPA's National Enforcement Initiative for mining and mineral processing, the agency has required phosphate fertilizer production facilities to reduce the storage volumes of waste water, ensure that waste piles and ponds have environmentally-protective barriers installed and verify the structural stability of waste piles and ponds.

Fibreglass acid tank trailer

Wabash National Corp and Poly-Coat Systems have launched a new fiberglass reinforced plastic (FRP) tank trailer designed to transport sulphuric acid in concentrations up to 98%. Previously, FRP tank inner surfaces were only qualified to handle dilute sulphuric acid at concentrations below 93%. The companies say that the lightweight FRP design provides a competitive alternative to traditional stainless steel tank trailers, allowing for increased payload and an extended asset lifecycle. The companies have previously worked together to develop FRP tank trailers for the transport of bleach, hydrochloric acid, ferric chloride, oilfield chemicals, corrosive wastes, and other hazardous cargoes.

ASARCO required to remediate SO_2 emissions

The US Environmental Protection Agency (EPA) has reached agreement with ASARCO over environmental remediation work which will be required at the Hayden smelter in Arizona to allow it to continue operation. The works, estimated to cost $150 million, will reduce airborne emissions of toxic heavy metals including lead and arsenic by 8.5 tonnes per year, particulate matter (PM) emissions by 3,500 t/a, and sulphur dioxide (SO_2) emissions by 19,000 t/a – a reduction of 90% of the latter. ASARCO will install new and upgraded ventilation hoods to capture hot flue gases from its furnaces to better capture the particulate matter. The company will also replace an aging electrostatic precipitator with a new, cleaner bag house and inject high performance lime to reduce SO_2 emissions.

The settlement also requires ASARCO to spend $8 million to fund two environmental mitigation projects to reduce dust pollution on local dirt roads close to the towns and residents exposed to PM emissions and assist the Gila County Environmental Health Services to conduct lead-based paint testing and abatement in homes, schools and other public buildings in the towns of Hayden and Winkelman.

ASARCO's Hayden site, owned by Grupa Mexico, opened in 1912 to process, concentrate and smelt copper ore. It includes a crusher, concentrator, smelter and tailings areas and produces 150-180,000 t/a of copper and over 450,000 t/a of sulphuric acid.

CHINA

ICL in Chinese joint venture

Israel Chemicals Ltd (ICL) says that it has completed the formation of joint venture company YPH with Chinese phosphate producer Yunnan Phosphate Chemicals Group Corporation Ltd. ICL has paid $180 million for its share in the venture, and

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the partners indicated that they will invest another $340 million over the next five years on a 50-50 basis. YPH is developing a world-scale phosphate rock mine producing approximately 2.5 million t/a of rock, as well as 700,000 t/a of downstream phosphoric acid and 60,000 t/a of purified or 'white' phosphoric acid (WPA), 850,000 t/a of ammonium phosphate, and 115,000 t/a of speciality fertilizers. The parties have also agreed to produce and sell WPA in China exclusively through the JV within five years following the deal.

In a press statement, ICL said: "The YPH JV represents a key milestone in ICL's "Next Step Forward" strategy by increasing ICL's phosphate platform by more than 50%, securing its long-term reserves and expanding its phosphate end-to-end business model focusing on Asia. The partnership is expected to transform ICL into the world's leading specialty phosphate player and to nearly double its global phosphate market share. The YPH JV is also expected to improve the cost competitiveness of ICL's phosphate operations by providing ICL with access to a low-cost phosphate rock operation with vast reserves, as well as with low-cost phosphoric acid. ICL also sees major potential for phosphates specialties in China, and through the YPH JV it will be well-positioned to capture this opportunity. The YPH JV further adds ammonia-based fertilizers to ICL's portfolio which will enable ICL to serve its customers with a broader suite of solutions."

JORDAN

JIFCO plant inaugurated

At a ceremony in Eshidya, 325km south of Amman, attended by Indian President Pranab Mukherjee and Jordan's King Abdullah, the Jordan India Fertilizer Company (JIFCO) officially inaugurated its new phosphate complex, including a 4,500 t/d (1.5 million t/a) sulphuric acid plant, one of the largest in the world. The $860 million phosphoric acid development at Edhidya is a 50-50 collaboration between joint venture partners the Indian Farmers Fertiliser Cooperative Ltd (Iffco), and the Jordanian Phosphate Mines Co. (JPMC). The plant, constructed by Jordanian-based Mid Contracting, was completed at the end of 2014 and came on-stream earlier this year.

JIFCO deputy chairman and Iffco India managing director U.S. Awasthi said: "Setting up the project in the deserts of Eshidiya, Jordan had great challenges for construction and commissioning. The JIFCO team, with the support of its promoters, JPMC and IFFCO, have been able to successfully commission the plant and continue its effort to stabilise the operations for greater capacity utilisations and efficiencies. Yet, during the first year of commissioning in 2015, JIFCO is expected to operate the plant above 80% capacity… a land mark in phosphoric acid industry worldwide."

Phosphoric acid produced at the plant will be exported to the Kandla port in Gujarat from Jordan's Aqaba port, which is close to the location of the plant.

KAZAKHSTAN

First phosphate delivery from EuroChem phosphate mine

Fertilizer manufacturer EuroChem says that it has completed its first delivery of phosphate rock from its new Kon-Jok mine in Kazakhstan. The shipment, of 11,000 tonnes of ground rock with an average 30.5% P_2O_5 content, was to EuroChem subsidiary Belorechenskie Minudobrenia (BMU) in southern Russia, where EuroChem produces phosphate and compound fertilisers. The company says that it expects to ship more than 50,000 tonnes to its phosphate plants in Russia and Belgium by the end of 2015, and next year the mine will be operating at its Phase 1 capacity of 650,000 t/a.

EuroChem CEO Dmitry Strezhnev said: "With this first intra-group shipment, EuroChem moves closer to being self-sufficient in the production of phosphate rock. We plan to further strengthen our presence in Kazakhstan with the construction of a fertiliser complex in close proximity to our mining facilities."

In addition to phosphate fertilizer production in Kazakhstan, EuroChem is looking to boost phos rock output to 1.5 million tonnes per year in the second phase of the project.

SAUDI ARABIA

Rail wagons contract signed for Ma'aden

Saudi Arabian mining company Ma'aden has placed an order for 1,200 rail wagons with US-based Greenbrier for its new Wa'ad al Shamal phosphate project. The wagons will be built by Greenbrier's Wagony Swidnica subsidiary in Poland, to US standards, with delivery from 2016-2018. The wagons, of three types, will be used to carry molten sulphur and phosphoric acid on the North–South Railway to the Wa'ad al Shamal Industrial City.

AUSTRALIA

Progress on phosphate mine

Junior miner Korab Resources says that it is making progress on its Geolsec phosphate project in Australia's Northern Territory. It has now secured an agreement in principle with a fertilizer distributor in the east of the country, and has had positive talks with a New Zealand-based company which Korab says is interested in an equity investment in the Geolsec mine and a distribution agreement for direct application phosphate in New Zealand. There have also been expressions of interest from Greenstar Fertilizer in India and PT Petrokimia Gresik in Indonesia. Geolsec, sited just south of Darwin, is ideally situated for export to south and southeast Asia, the company says, and should benefit from relatively low extraction costs.

SENEGAL

Minemakers buys Baobab phosphate project

Australian phosphate mining development company Minemakers says that it has completed the acquisition of Baobab Mining and Chemicals Corporation SA, which owns the Baobab phosphate project in Senegal, from Agrifos subsidiary Baobab Partners. Part of the deal is contingent on achievement by Minemakers of a board-approved preliminary feasibility study, a decision to proceed with construction of a phosphate rock mine; or first commercial production of phosphate rock – whichever is earlier. "We are pleased that completion of the transaction has been achieved and would like to welcome Cotton to the board and look forward to his contribution to the exciting future of Minemakers," said Minemakers managing director and CEO Cliff Lawrenson.

NAMIBIA

Tanker order for Tsumeb

Namibian rail company TransNamib has signed a deal to purchase 90 sulphuric acid rail tank cars for $10 million from China Railway Materials (CRM) Hong Kong. The tankers will be used to fulfil TransNamib's 10-year agreement with Dundee Precious Metals to transport acid from its new Tsumeb plant. The tank cars will be built to the specifications of the Tsumeb acid plant and delivered in July 2016. The new acid plant at the Tsumeb smelter is forecast to produce 300,000 t/a of sulphuric acid.

ZAMBIA

CCM forced to stop production over pollution

In September the Zambian Environmental Management Agency (ZEMA) has ordered China Copper Mines Ltd (CCM) to cease operations at its Chingola copper leaching and solvent extraction facility. In the order, ZEMA cited pollution of the Fitula and Muntimpa streams and surrounding area. As well as making good the damage, CCM has been told to build a new leach pond lined with high density polythene downstream of the current leach ponds to act as a pollution control dam, and "immediately" provide an alternative source of clean and safe drinking water to the communities of Kifisali and Kankomo and their livestock until remediation of contamination is complete.

A subsequent environmental audit cleared the company of some of the breaches and allowed the restoration of production on October 2nd subject to meeting 12 mine management conditions, but local farmers and landowners obtained a restraining injunction and the facilities remained closed. Around 200 copper miners protested the decision at local government offices at loss of livelihood. A $50 million investment by the company has also been postponed.

FINLAND

Partnership for slurry pumps in metals processing

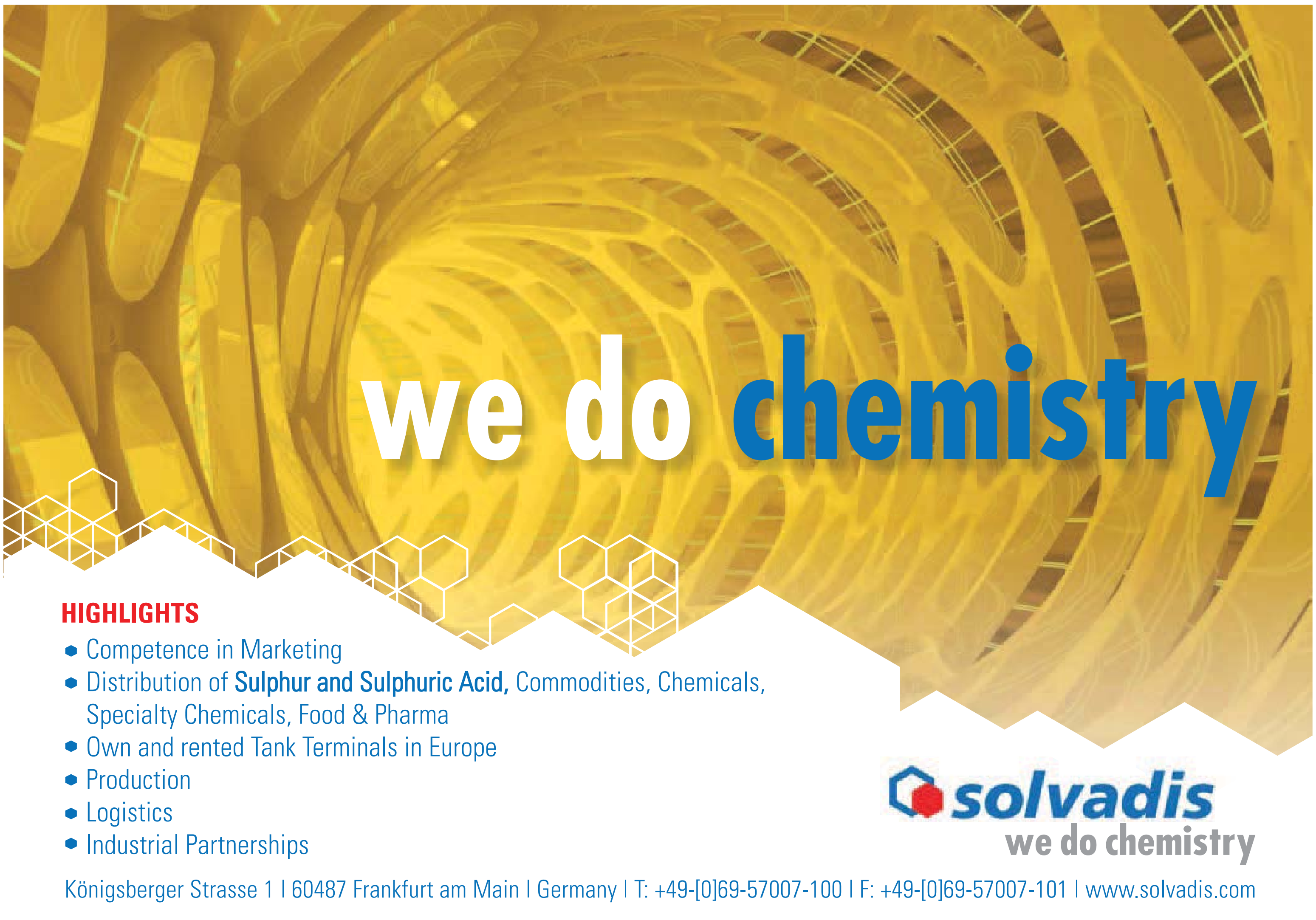
Outotec has agreed with GIW Industries, Inc., a subsidiary of KSB Partners, to enter into partnership for the sales and marketing of *GIW®* slurry pumps and related services to metal mining customers globally. GIW Industries is a leader in the design of high performance slurry pumps, used in minerals processing for grinding, flotation and dewatering circuits. The global market for high performance slurry pumps in metal mining applications is estimated to be around euro 1.3 billion.

"GIW Minerals products and services fit extremely well into our portfolio," said Kalle Härkki, president of Outotec's Minerals Processing business unit. "Together with GIW we are able to offer more complete solutions and expanded services to our customers, based on our joint technological breadth of experience and applications, extensive research and development capabilities together with life-cycle services."

RUSSIA

Acid plant commissioned at uranium mine

Atomredmetzoloto (ARMZ), the uranium mining arm of state nuclear corporation Rosatom, has officially commissioned a new sulphuric acid plant at its JSC Khiagda subsidiary in the Bauntovskiy region of Buryatia, in Russia's eastern Irkutsk region. ARMZ has an estimated 350,000 tonnes of uranium in the local deposits, of which 250,000 tonnes are amenable to in situ leaching. The plant was completed last year and began trial operations, with commercial production beginning in May 2015. Construction was carried out by Russia's Interest together with Italian engineering firm Desmet Ballestra. ARMZ says that the new acid plant will allow it to expand uranium production from the 440 tU produced in 2014 to 1,000 tU by 2018. A second stage and another acid plant could ultimately take output to 2,000 tU per year. ■



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People

SNC-Lavalin is pleased to announce that, **Neil Bruce** (above) has become president and CEO of the company, as well as a member of the Board of Directors, effective from October 5th. He succeeds Robert G. Card.

"The upcoming handover and smooth transition from Bob Card to Neil Bruce, previously COO, comes at an important stage in SNC-Lavalin's development," said Lawrence Stevenson, chairman of the Board of Directors. "Bob's tenure left a strong legacy during a critical time for the company, with a far-reaching transformation that changed the face of the executive team, repositioned the company strategically through the sale of AltaLink and the acquisition of Kentz among others, as well as turned its ethics and compliance system into a benchmark for the industry. We are in the right position to become a Tier-1 engineering & construction firm going forward and on behalf of the Board, I thank Bob for his leadership and tireless dedication. He will remain as an advisor to the Board and CEO.

"Neil has over 30 years of extensive experience in the engineering and construction industry and a comprehensive understanding of the four sectors in which SNC-Lavalin operates. Since joining the company in January 2013, he has transformed the Oil & Gas business from a niche 3,000-employee player into a 20,000-strong world-class organisation – before being named COO in April 2015. Since then, he oversaw the company's engineering and construction operations to make them more efficient and effective, and deliver global-calibre expertise in local markets, to better serve clients."

Before joining SNC-Lavalin, Neil held a variety of leadership roles, including executive director and COO at AMEC, where he directed the company's international expansion and high-value consultancy, engineering and project management services.

Neil commented: "I am proud to have been selected by the Board as President and CEO of SNC-Lavalin, a company with a strong balance sheet, so much growth potential and a bright future ahead. We have some of the best leaders in our industry and a highly capable workforce of 40,000 employees that our global clients count on every day. Together, we will deliver improved results and returns as we continue to improve operational efficiency, while managing the remaining legacy issues. I have already met many employees, clients and partners around the world and look forward to meeting many more over the weeks and months to share further details on the next phase of our strategic plan. On a personal note, while I will continue to travel around the world, my family and I are happy to have moved to Montreal, Canada, earlier this year."

The position of COO will not be refilled and the presidents of the company's four business sectors will continue to report to Neil Bruce.

Canadian fertilizer producer MBAC says that **Rodrigo Pinto** has tendered his resignation as Chief Financial Officer, vice-president of finance and corporate secretary of the company, effective from October 23rd, following a month long transition period. The board of directors has thanked and acknowledged Mr Pinto for his dedicated contribution to the company over the last six years.

Calendar 2015/2016

NOVEMBER

9-12

Sulphur 2015, TORONTO, Canada.
Contact: CRU Events
Chancery House, 53-64 Chancery Lane,
London WC2A 1QS, UK.
Tel: +44 20 7903 2167
Email: conferences@crugroup.com

17-19

European Refining Technology Conference,
ROME, Italy.
Contact: Eliot Morton, GT Forum.
Tel: +44 20 7316 9832
Email: eliot.morton@gtforum.com

26

European Sulphuric Acid Association meeting, ANTWERP, Belgium.
Contact: Patricia de Herthogh, Cefic.
Tel: + 32 2676 7253
Email: pdh@cefic.org

JANUARY 2016

27

ASRL Chalk Talks and Poster Session,
CALGARY, Canada
Contact: ASRL, University of Calgary,
Alberta T2L 2K8 Canada.
Tel: +1 403 220 5346
Fax: +1 403 284 2054
Email: asrinfo@ucalgary.ca

FEBRUARY

21-24

66th Laurance Reid Annual Gas Conditioning Conference, NORMAN, Oklahoma, USA.
Contact: Betty Kettman, University of Oklahoma
Tel: +1 403 325 3136 Email: bettyk@ou.edu

MARCH

13-15

Phosphates 2016, PARIS, France.
Contact: CRU Events
Tel: +44 20 7903 2167
Email: conferences@crugroup.com

20-22

AFPM Annual Meeting,
DALLAS, Texas, USA.
Contact: Yvette Brooks
Email: ybrooks@afpm.org
Web: www.afpm.org

20-24

SOGAT 2016,
ABU DHABI, UAE.
Contact: Dr Nick Coles, Dome Exhibitions.
Tel: +971 2 674 4040
Email: nick@domeexhibitions.com
Web: www.sogat.org

APRIL

11-13

TSI World Sulphur Symposium,
VANCOUVER, Canada.
Tel: +1 202 331 9660
Email: sulphur@sulphurinstitute.org
Web: www.tsi.org

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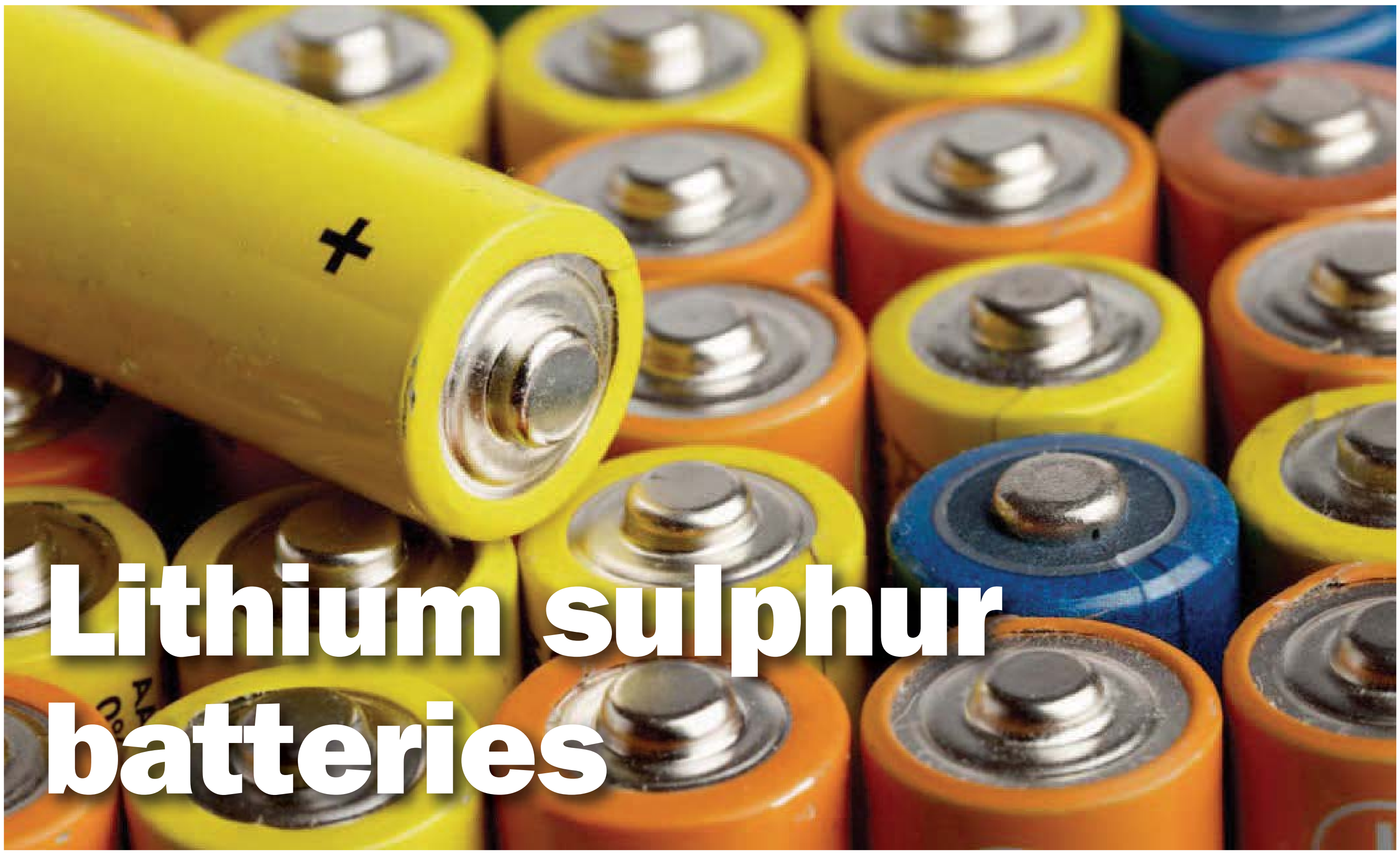

Lithium sulphur batteries

PHOTO: ROLAND MAGNUSSON / ISTOCKPHOTO.COM

There is great excitement in the power industry about the potential for lithium sulphur batteries to take up where lithium-ion and nickel-cadmium batteries left off. What might it mean for sulphur?

The world is hungry for energy. In particular, it is hungry for mobile energy, in the form of rechargeable batteries, for smartphones, tablets and laptop computers, and increasingly also for battery-powered vehicles. More advanced mobile devices, with wi-fi connections streaming large file such as movies, place greater demand upon batteries, resulting in shorter battery lifetimes between charges. Electric vehicle performance is similarly limited in terms of vehicle range by their batteries' capacity, and providing power via conventional lead-acid cells imposes a significant weight penalty.

Batteries convert chemical energy into electrical energy, and the chemistry of batteries has been changing as the years go by in order to try and squeeze greater energy density out of every cubic centimetre. The lead-acid battery dates back to the 1860s, using a lead anode and a lead oxide cathode submerged in a solution of sulphuric acid. Both electrodes react to produce lead sulphate, but the reaction at the lead cathode releases electrons while the anode reaction consumes them, creating a current when connected. In spite of the weight of the lead, the lead-acid battery generates around 25-45 Watt-hours per kilogram.

While the acid solution of the early lead acid cells was replaced by a gel in later portable cells, the first 'dry cell' was the zinc-carbon cell, developed in the 1880s. Carbon is the conductor, but the battery actually uses zinc and manganese separated by ammonium chloride. Zinc-carbon batteries enabled the development of portable electrical items like flashlights and radios, but suffered form low battery life. The next step forward came from nickel-iron batteries in the early 20th century, and then nickel-cadmium cells – developed around the same time but too expensive for everyday use until the 1950s. Using potassium hydroxide as the electrolyte, this was the first alkaline battery. Power density for NiCd batteries is around 40-60 W.h/kg.

Nickel-cadmium batteries had most of the market for rechargeable batteries into the 1990s, but were quickly replaced by nickel metal hydride cells (NiMH), where the 'metal' is usually mixture of a rare earth with nickel, cobalt, manganese, or aluminium. The electrode is again an alkali, often potassium hydroxide. Now specific energies of up to 75 W.h/kg could be achieved, but NiMH batteries have themselves been superseded in recent years by lithium ion batteries. Lithium is the metal with the lowest weight and highest power density and hence with the greatest electrochemical potential and energy-to-weight ratio. First commercialised by Sony in the 1990s, lithium ion batteries have become the new standard for consumer electronics, with specific energy up to 250 W.h/kg. Lithium-based batteries now represent 80% of the market for rechargeable batteries. Even so, while it has allowed manufacturers to make your laptop, tablet or smartphone smaller and lighter, few of us are, I imagine, particularly impressed with the battery life we get between charges; usually only a few hours of continuous use. And while lithium itself is light, lithium-ion batteries typically require bulky cathodes, typically

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made from ceramic oxides like cobalt oxide, to house the ions, which limits the battery's energy density. This precludes their use for more power-intensive applications like long-range electric vehicles. The race is still on to find a better battery.

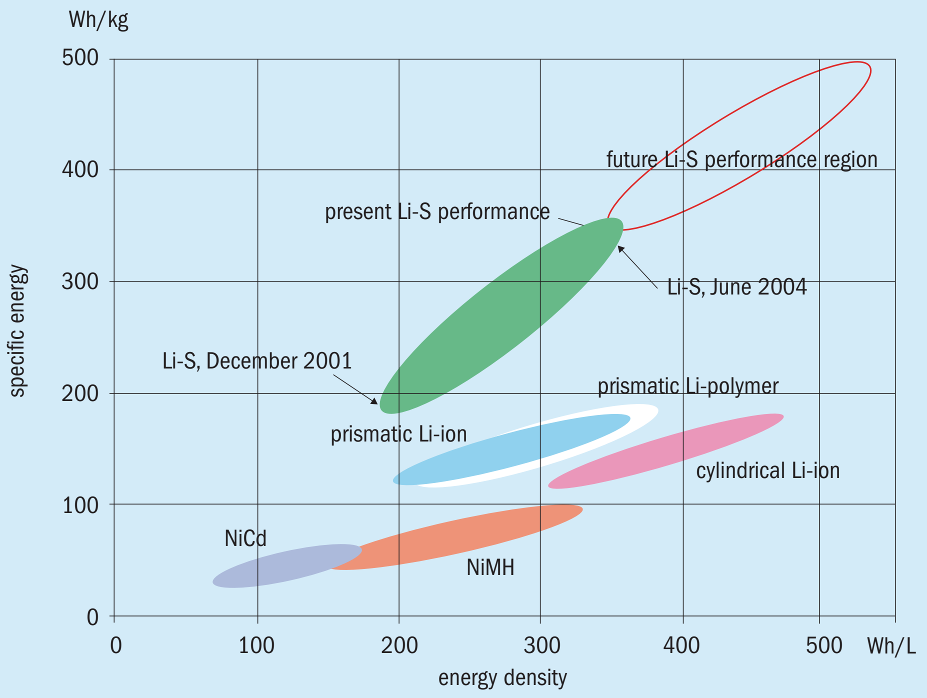
Enter sulphur

Sulphur has been used in battery technology before via the sodium-sulphur battery, developed in the 1960s and commercialised mainly by Japan's TEPCO (Tokyo Electric Power Co). However, the battery operates with the sodium and sulphur both molten, at 300-350°C, and hence has been used only for some specialist stationary power storage applications. However, over the past decade, research has been under way in a variety of institutes and universities on combining lithium with sulphur instead. Sulphur has only half the atomic weight of cobalt and can pack more than twice as many lithium ions into a given volume as can cobalt oxide, theoretically giving lithium-sulphur batteries several times the energy density of lithium-ion batteries. In theory they are also cheaper, as sulphur starts with a lower base material cost than lithium-ion or lithium-polymer batteries, while manufacturing techniques for Li-S batteries are generally similar to those used in other battery chemistries.

Lithium and sulphur can also form a wider variety of lithium polysulphide compounds with differing oxidation states than can be formed with other lithium compounds, from Li_2S through Li_2S_2, Li_2S_3, Li_2S_4 etc, all the way up to Li_2S_8. These form at the cathode as lithium migrates from the anode. However, problems also come with the switch to sulphur; higher lithium polysulphides tend to be soluble in the electrolyte, and over time this can destroy the structure of the cathode, leading to the formation of dentrite structures of polysulphide and cracks in the sulphur cathode with repeated cycling, making them relatively useless as rechargeable batteries.

Working out a way around this issue has been the main focus of Li-S battery research, and different teams have come up with different solutions. Sion Power, spun off from research conducted at Brookhaven National Laboratories in the US around 10 years ago, uses nitrate additives in the electrolyte to control the dendrite formation. It claims 99.5% charge efficiency and specific energy density of 350-400 Wh/kg, and new collaboration with BASF may take this to 550 Wh/kg.

Fig 1: **Li-S versus other cell chemistry, energy density comparisons**



Source: Sion Power

Separating the sulphur from the lithium with a thin carbon film is the major technology under development. Researchers from the UK's University of Cambridge and the Bejing Institute of Technology have used graphene as a way of keeping the sulphur at the cathode in a "carbonised metal-organic framework" which confines the active materials within its porous structure. This leads to improved cycling stability and high efficiency. Researchers from the Lawrence Berkeley National Laboratory have also announced the development of a Li-S battery based on a material they're calling a "sulphur-graphene oxide."

Elsewhere, scientists from the National Institute of Standards and Technology (NIST), the University of Arizona in Tucson and Seoul National University in Korea have used a 10-20% addition of carbon to the sulphur to create a co-polymer with sulphur at 185C in a process that they term 'inverse vulcanisation', as the carbon is linking long sulphur chains together rather than the other way round, as in traditional vulcanisation. These carbon bridges stabilise the sulphur cathode, preventing it from cracking as easily and keeping lithium-sulphur compounds from crystallising. The resulting battery has retained 50% charge through 500 recharge cycles. While this is not as good performance as other Li-S batteries, the researchers argue that the relative simplicity, cheapness and ease of manufacturing of this process outweighs other factors.

An Italian-Korean collaboration led by Hanyang University has instead used a dual sulphur cathode containing solid sulphur electrode and polysulphide catholyte with a lithiated Si/SiOx nanosphere anode. Results have been impressive, maintaining 85% of original charge over 500 charging cycles, with an average specific energy density of 500 Wh/kg, although commercial scale-up of such a complex construction remains an open question.

Oxis

However, the closest to commercialisation seems to be UK-based Oxis Energy, which says that it is gearing up to sell its first Li-S cells in March 2016. Oxis claims its batteries will be nearly five times as powerful as their Li-ion counterparts, in addition to being lighter weight, safer and maintenance free. The first product is a pouch cell which can produce 2.1 V, with a typical capacity of 10-35 Ampere hours, and a specific energy of 300 Wh/kg – already significantly better than commercially available Li-ion cells. Oxis says that it expects to achieve 400 Wh/kg in 2017 and 500 Wh/kg by 2019. As far as recharge rates go, the company expects to achieve 2,000 cycles before the battery reduces to 80% of its beginning of life charge. The company has set itself the ambitious goal of capturing 10% of the Li-ion market in the next 5-10 years.

While the company is coy about the technology used and the pricing level, the applications that it is looking towards suggest that there will be a significant cost increase on Li-ion in the short term, but the company says that once they move into high volume production, the projected battery price will drop to $250/kWh in 2020. Initially, however the company is looking towards space and defence applications, offering mobile power for the sophisticated electronic equipment that troops carry onto the modern battlefield, with battery weight only 20% of a comparable lithium ion cell. The lower weight also makes the technology more suitable for electric vehicle applications, and Oxis is working in collaboration with Lotus Engineering, Imperial College London and Cranfield University to develop a lithium sulphur vehicle battery and energy system controller. The Revolutionary Electric Vehicle Battery (REVB) project began in November 2013 is running until late 2016. The last application Oxis is looking towards is power storage for renewable, especially solar energy.

The impact on sulphur

Lithium-sulphur batteries are on the cusp, then, of commercialisation, with a variety of rival technologies under development, and the power densities achieved even by prototypes has been in excess of the best lithium-iion batteries, with theoretical maximum specific energy as high as 2,700 Wh/kg. It is in fact possible – in theory – to generate even higher specific power density via a lithium-oxygen combination. The problem lies in preventing the lithium from simply burning instead, and while Li-O_2 has been touted as an "ultimate battery", many in the industry see it as having too many practical problems to be overcome. Hydrogen-oxygen fuel cells can likewise generate very high power densities, but the difficulty of storing and transporting hydrogen is a strong factor counting against them. If Li-S batteries do become commonplace, then, it does not look as though there is a rival technology breathing down their necks.

Once Li-S batteries are commercially available then, many believe that their uptake may be as fast as that for Li-ion, with 80% of the market cornered in a decade. There are many ifs and buts with this forecast, but it is interesting to think about what that might mean for sulphur. In spite of it being an incredibly versatile material, new uses for sulphur have tended to be few and far between, after all.

The European Union calculates that the sale of batteries in the EU totals around 1.2 million tonnes per year. Automotive batteries, mainly lead-acid, represent about 800,000 t/a of this, or around two thirds of the market, with very approximately 200,000 t/a representing personal electronics and 200,000 t/a other uses. While Li-S batteries are lighter than their competitors, assuming for sake of argument 80% penetration into the personal electronics market, that might represent an upper limit of 160,000 t/a of batteries in the EU by say 2025-30, a major proportion of which would be sulphur – not a massive market then, but not an insignificant one either.

However, if Li-S batteries were to break into the automotive market, as their proponents hope, things might change radically, especially if there was a wide-scale switch towards electrically-powered vehicles. At the moment every gasoline and diesel vehicle carries an average of one lead-acid battery each for use as a starter motor, and there are a billion vehicles on the world's roads at present. Globally automotive battery sales total around 8 million t/a – sufficient, in fact, to be a the primary use for lead and a significant market for sulphuric acid. Electric vehicles, only 1 million of which are currently in use – 0.1% of the global total – might need many more batteries per vehicle than just one, and increased capability for electric vehicles would assist their market penetration. Tesla is aiming to be producing 500,000 vehicles per year by 2020. Increased demand for sulphur would of course be offset at least to an extent by reduced demand for sulphuric acid.

Likewise there is great potential for use as storage capacity for off-grid renewable power generation, which currently faces the problem that electricity is not always required when the sun is shining or the wind blowing, and vice versa. Taking these applications into account, the market might just potentially be looking towards millions of tonnes per year of sulphur in the very long term.

Is there enough lithium?

The cost and availability of sulphur is not a factor for Li-S batteries, indeed, relying on such a cheap and abundant material is one of their major selling points. Lithium is a different story, however, and may be the key constraint in the production of Li-S batteries. In fact, concerns about the availability of lithium have already been raised in the context of lithium-ion batteries. World production of lithium was 37,000 t/a in 2014, according to the US Geological Survey. Total proved reserves are 13.5 million tonnes globally, with 'identified resources' up to 40 million tonnes.

Producing Tesla's 500,000 electric vehicles annually would consume an estimated 5,000 t/a of lithium using current lithium-ion technology, well within the bounds of current reserves. However, if all of the 80 million vehicles sold per year were electric, and consumed a similar amount per vehicle, that might be 800,000 t/a – sufficient to deplete current proved reserves in 16 years without even taking into account other uses, and if global vehicle production doubles as it is projected to over the next 35 years, that figure becomes smaller still. Although lithium-sulphur batteries are lower in weight, that weight reduction comes from the use of sulphur, and the amount of lithium is likely to be comparable as for lithium-ion batteries.

However, a recent study by Argonne National Laboratory for the US Department of Energy took a much more conservative view of electric vehicle penetration of 10% of global sales by 2050 (the International Energy Authority has posited 20%) for pure electric vehicles, as opposed to hybrids. It also assumed that there would be a widespread recycling scheme for automotive batteries which was able to reclaim 90% of the lithium after a 10-year battery life, and hence indicated only a relatively modest increase in world demand, peaking at 100,000 t/a in 2050, and noted that there might well be a considerable degree of transport switching to smaller vehicles or electric bikes, buses, trams, trains etc, which would bring this down still further. The answer seems to be that there is enough lithium provided that it is used wisely.

Sulphur in batteries

All of the foregoing is, of course, somewhat speculative. At the moment there are no lithium-sulphur batteries on sale, and it is not yet known how much they will cost compared to lithium-ion. This time next year we may have a better idea. But if the excitement in the battery industry turns out to be justified, in a decade's time sulphur may have grown a new use – not one to compete with phosphate fertilizer or acid metal leaching, but a significant one nonetheless. ■

Sulphur storage

As the sulphur industry faces more years of excess, the short, medium and even long-term storage of sulphur is returning to the fore as an issue.

The sulphur blocks at Fort MacMurray have become in many ways emblematic of the sulphur industry. Over 9 million tonnes of sulphur from oil sands processing is currently stored there in block form; it has been calculated that the largest block (technically two blocks with a joining section) is bigger in volume terms – at 2.8 million m^3 – than the Great Pyramid of Giza (2.58 million m^3). The blocks are symptomatic of the difficulty in moving sulphur from remote areas to market when cheaper sources can be found more readily elsewhere, and as the sulphur market moves back into surplus, it seems inevitable that the industry will see stock building and more blocking of sulphur.

Sulphur is a relatively inert substance, and perfectly safe if handled correctly, but longer term storage – years and even decades – may risk the degradation of the outer surface of a block, from weathering and bacterial attack, leading to fugitive sulphur dust, and acidification of run-off water. While the latter can be controlled by properly constructed base pads and rain gulleys that lead to treatment facilities for run-off water, in the very long term, there is a risk of acidification of soils from acid contamination. Low pH in soils or ground water can also lead to leaching of metal ions that are stable at high pH.

Long term safe and environmentally sound storage of sulphur has been a concern for various companies in charge of large stockpiles, but may become a concern for new players in an oversupplied market.

Kazakhstan

The perils of large scale sulphur storage were illustrated a few years ago by the experience of TengizChevroil (TCO) in Kazakhstan. The TCO joint venture produced large volumes of sulphur from processing of sour oil and gas from the Tengiz field – about 1.6 million t/a at capacity in the first phase – and the relatively remote nature of the site, on the east side of the Caspian Sea, meant that opportunities for sale of the sulphur were relatively limited. This led to a steady build-up of inventory at TCO, reaching 9.2 million t/a in 2005, according to the company. However, complaints from local residents about fugitive sulphur dust and associated 'health problems' led to government intervention in 2006, forcing the company to come up with a plan for dealing with the sulphur. As a result of this, the legal status of Kazakhstan's sulphur storage changed in 2007, with sulphur's designation according to the Kazakh Ministry of Environmental Protection changing from a 'hazardous' product to a 'waste' product. Being defined as a waste product meant that the sulphur could now only be stored for three years until it was either recovered or processed, or no longer than one year if its fate was disposal in an approved landfill.

Fortunately for TCO, Kazakhstan's rapidly growing uranium mining industry led to a growth in local demand for sulphur, and the company also managed to sell some sulphur outside the region, and by 2013 it had reduced its stockpile to just over 1 million tonnes, and by the first half of 2015 had essentially cleared this to zero. Nevertheless, under the agreed management plan for sulphur storage, TCO is conducting monitoring and sampling studies which run to 2016 on five smaller, experimental sulphur blocks, four of which have different coatings to try and prevent emissions – the fifth is a control. The government has also said that it would like future sulphur storage to be covered, although this has not been a preferred option in most parts of the world because it allows the build-up of potentially flammable or explosive sulphur dust in roof spaces.

Canada

A similar debate has occurred as regards the long-term storage of sulphur in Canada, and whether it should be classified as a 'waste' product or a 'resource'. Regulation in Canada is conducted on a province by province basis, and in Alberta, where most of the sulphur is stored, this is mainly conducted via the Environmental Protection and Enhancement Act (EPEA). EPEA allows for landfill disposal of sulphur contaminated waste, although only as a "last option", and management and disposal plans must ensure protection of the environment and human health, as well as make the best practicable use of sulphur, with recovery the best option. The EPEA also mandates that a security bond for reclamation is required to cover the costs of closing, de-commissioning and reclamation of a site. While this is clearly intended to cover landscaping of mined areas etc, it would also cover disposal of sulphur stockpiles if a site was closed.

At the moment there is no regulatory pressure to move or dispose of the sulphur mountains in Canada. Alberta Environment and Water (AEW) has updated its Directive for Monitoring the Impact of Sulphur Dust on Soils this year, and this takes effect as of January 1st 2016, superseding an earlier (2011) version as well as soil monitoring guidelines from 1989, and requires mitigation strategies wherever pH-sensitive soils are found to be suffering any adverse effects from sulphur acidification.

However, that is not to say that there might not be more stringent regulations in future, and there is some agreement that blocking sulphur is not the best solution for very long term (for which read – beyond a few tens of years) sulphur storage.

Options

The option taken by TCO was simply to sell the sulphur, and Canadian Oil Sands Ltd (formerly the Canadian Oil Sands Trust), which owns just over one third of Syncrude, has considered selling its share of the sulphur stockpile, but this was subject to improvement in rail and port infrastructure to get the sulphur to Vancouver which did not, in the end, come to fruition, and of prices being sufficient to cover the cost of disposal, something unlikely to be the case in a sulphur surplus market. Shell has looked at other products into which sulphur could be incorporated as a way of dealing with excess sulphur,

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including concrete and asphalt, as well as sulphur enhanced fertilizers – the latter has so far proved the most promising use. However, none of these methods are likely to require the kinds of volume of sulphur that might end up having to be stored.

Reinjection

For sour gas production, the option of reinjection of the acid gas separated from the sales gas is a possible one, with numerous schemes in Canada and the USA, as well as Kazakhstan. However, there are complicated interactions between the acidified gas and underground rocks and water which could affect gas production from a well, as well as the highly corrosive nature of the gas and its effect on the piping systems needed to carry it to worry about.

Another option which ASRL has investigated is combustion of recovered sulphur to sulphur dioxide and then injection of this back into an underground storage reservoir, leading to underground reaction of H_2S and SO_2 to sulphur and water – the hydrogen sulphide effectively neutralises the sulphur dioxide, while the sulphur burning can be used to generate electricity. Of course, this removes the sulphur from future re-use, should that be desired, and there have been worries about sulphur ‘plugging’ of wells, although studies indicate that this may not in fact be an issue.

Underground storage

If the sulphur must be stored, and if it is required to be available for some future use, one option that is being actively explored is to store the sulphur underground. Alberta Sulphur Research Ltd (ASRL) was commissioned by the Canadian sulphur industry in 1999 to look into this. Two 100-tonne blocks were poured at Syncrude’s site, one below the water table and one above, with monitoring of surrounding water and land. The attraction of underground storage is that thiobacilli require air and temperatures of about 10°C to grow, preventing acid run-off. Results from the above water table block were encouraging, with no contamination detected in surrounding soils, but the below water table block showed biological degradation which would worsen if stored over decades.

In 2004, Syncrude applied to Alberta Environment (AENV) to begin a second sulphur storage research program designed to refine, gather data and investigate the feasibility of storing sulphur long-term below ground. Four 3,000 tonne pilot blocks were poured in 2005 and then covered with varying thicknesses of soil material. The research program is being conducted with support from the University of Saskatchewan and monitoring is in progress.

Meanwhile a second ASRL test series involved experimenting with different coverings for above ground sulphur blocks, including limestone (to neutralise any acid produced), a spray-on stucco material with similar properties, and an impermeable membrane encasement method to prevent water ingress. This study began in 2009 and ran to 2014.

Long-term storage of sulphur remains a potentially problematic area, subject to regulatory and environmental pressures. At the moment, underground storage in dry conditions looks to be the best bet, provided that it can be successfully reclaimed afterwards. But it might mean an end to the iconic, bright yellow blocks. ■

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Acid leaching for metal extraction

The slowdown in the Chinese economy has had a negative impact on metals markets, a major source of sulphuric acid demand for metal leaching.

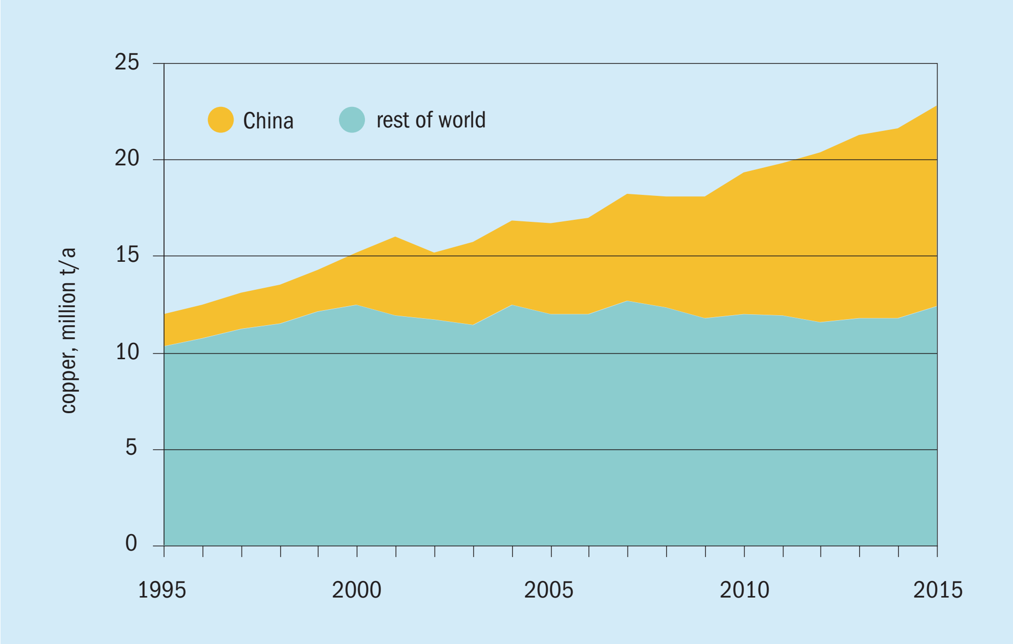
Around 10% of all sulphuric acid demand is for the extraction of metals – mainly base metals – from their ores. This makes it the second largest demand segment after phosphate processing, and one which has expanded more rapidly than most other segments of acid demand over the past decade. Copper has generally been the mainstay of metallurgical acid demand, but greatly increased use of acid for leaching of nickel and uranium has helped expand this sector to its current prominence.

Metals markets themselves have had something of a 'golden age' for two decades, as China's rapid industrialisation has led to greatly increased demand for industrial metals like lead, copper, zinc and nickel. Figure 1 shows that the incremental increase in demand in the copper market has come mainly from China, but a similar graph could be drawn for other base metals. However, this year the Chinese industrial economy has begun to slow, a combination of over-building and overcapacity, demographic change leading to a rapidly ageing workforce, and an attempt by the government to push the economy towards consumer-driven rather than industrial-driven growth. The result has been catastrophic for metal markets, which have slumped to their lowest levels for years, and hence promises to have a similar effect on growth in acid demand for metal production.

Copper

Copper is the major consumer of acid for leaching, due to the larger volumes of copper that are used around the world. Copper consumption in 2014 was 21.6 million tonnes, almost all in industrial and construction uses, electrical items, power supply etc. Incremental copper demand over the past 20 years has almost all been in China, where demand increased by 15% year on year during the country's crash industrialisation, with China's share of copper demand rising from 9% in 1997 to 45% in 2015. China's insatiable appetite for Copper led to major investment in copper mining and downstream production, and the slowdown in the Chinese economy, from 13% growth in 2006 to 7% this year, has led to a corresponding decline in the growth of copper demand at the same time that a lot of new mining and processing capacity has come on-stream, leading to the crash in global copper prices seen over the past couple of years, from $4.50/lb in 2011 to less than $2.50/lb in 2015.

Fig 1: **Global refined copper demand,** 1995-2015



Source: ICSG

Mined production of copper is expected to increase slightly (1.2%) to reach 18.8 million t/a in 2015, with an increase of 4% next year from expansions already under way, ramping up of production from new mines, and a small number of new projects. This takes into account a number of production cutbacks which have been announced by major producers, as well as production upsets and outages this year which have reduced planned output by up to 500,000 t/a. The International Copper Study Group (ICSG) also predicts that refined copper production in 2015 will increase by 1% to 22.7 million t/a. China's production of refined copper is expected to have risen by 7% this year, but there will be a net decrease in refined production in Chile, Japan and the USA. Demand, conversely, is expected to decline by 1.2% this year by OCSG, as apparent demand is relatively flat in China (underlying demand is expected to increase by 3-4% but most of the extra will be taken from stocks).

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Demand in the rest of the world will decline by 1.5%. Next year there is a rebound expected, however, with Chinese industrial demand predicted to grow by 4% and overall global demand by 3%. This indicates that the market should be essentially balanced for 2015, with a small deficit from 2016 as production cuts make themselves felt, and prices should increase.

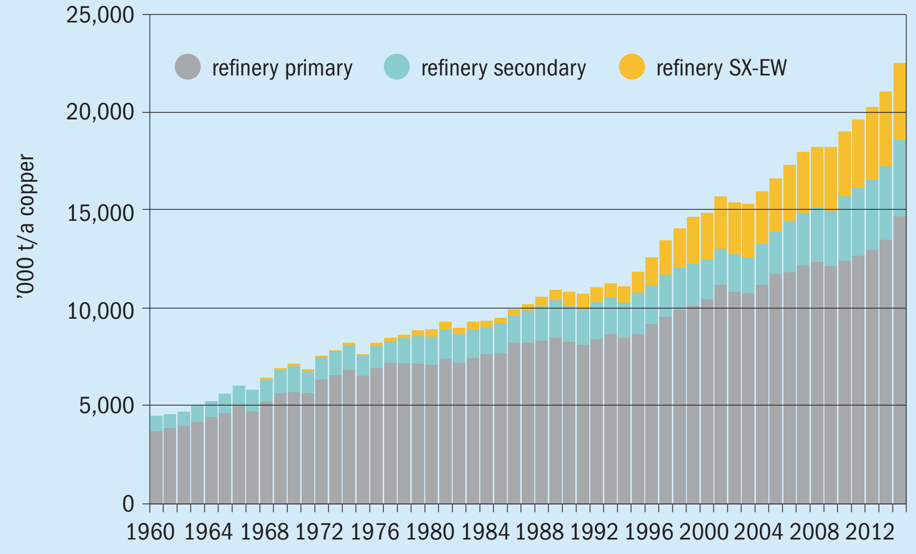
Copper leaching

As Figure 1 shows, the proportion of copper produced by acid-based hydrometallurgical techniques – principally solvent extraction and electrowinning (SX/EW) – has been increasing, accounting for about 20% of all copper production at present. Although the number of copper deposits amenable to acid leaching is restricted, it has been seen as a relatively lower cost technique, avoiding the large capital expenditure of a smelter. This has in turn led to a significant slice of sulphuric acid demand, as every tonne of copper extracted by SX/EW requires on average 3 tonnes of sulphuric acid. Thus the 3.9 million t/a of SX/EW copper which is expected to be produced in 2015 represents approximately 11.7 million t/a of acid demand – the largest slice of acid required for metal leaching operations, double that for nickel and three times that for uranium.

This capacity has become concentrated in three countries; Chile, Peru and the USA, which collectively represent almost 90% of leaching operations, although there have also been developments in the 'copper belt' of sub-Saharan Africa, in Zambia and the Democratic Republic of Congo (DRC). However, there are clouds ahead for the copper leaching industry. Chilean acid use for leaching – about two thirds of the acid used in the copper industry – is falling as ore grades decline in its main oxide mines, and although lower grade rock does also use more acid per tonne of copper extracted, this does not balance the fall in production. Furthermore, many of the production cutbacks announced in the copper industry this year are at SX/EW operations. Glencore is cutting back on SX/EW capacity in the DRC, Freeport has announced 136,000 t/a of cuts in copper production in the US and Chile, all of it from leaching capacity, and Asarco has done likewise with 30,000 t/a of cuts in the US and Anglo-American at the Collahuasi mine in Chile. The ICSG expects SX/EW production to fall by 4% this year and another 4% next year, although Morgan Stanley has indicated flat production this year and 5% growth next year. Some of this variability represents uncertainty about the large-scale leaching operation planned by the Southern Copper Corporation (SCC) at its Tia Maria site in Peru, which would consume about 500,000 t/a of acid, and which has faced considerable local opposition. Adding further capacity would be Rio Tinto's La Granja project, also in Peru, which could account for 700,000 t/a in 2017.

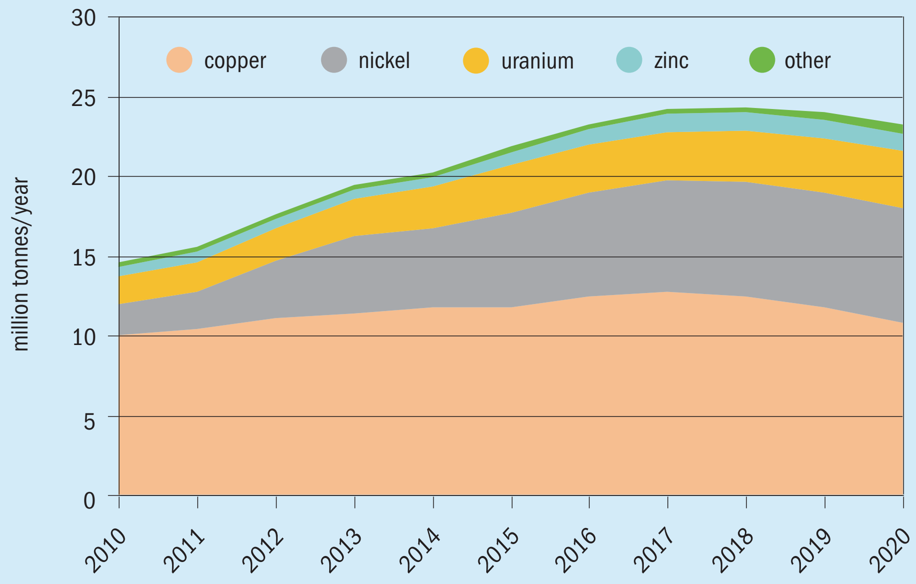
However, looking to the longer term all forecasts agree that in spite of new SX/EW capacity, declining production from existing Chilean operations means that overall SX/EW copper production will decline by 2020. Peak SX/EW production will be in around 2017, at 4.2 million t/a, falling back to 3.6 million t/a by 2020, or about 10.8 million t/a of acid equivalent.

Fig 2: **Copper production by source**



Source: ICSG

Fig 3: **Acid demand for metal leaching**



Nickel

Nickel is the second largest slice of acid demand for nickel leaching, and one which has grown considerably over the past few years. Use of nickel is mainly (70%) for stainless steel production, with overall demand at 2.0 million t/a in 2014, half of which was represented by China. As with copper, China's rapid industrial growth Chinese steel production has stagnated this year, dropping by about 1.5 % compared to 2014, when total steel production was 688 million tonnes. Global nickel demand went through a period of strong growth during China's rapid industrialisation, averaging around 9% growth year on year, but demand has slackened with the slowdown in the Chinese economy. There is nevertheless projected to be an increase in demand over the next few years, albeit at a slower pace than previously, perhaps of the order of 4% year on year.

Nickel production has historically been mostly based on smelting of higher grade sulphide ores, but available deposits of these are limited, and continually increasing demand has led to a renewed focus on laterite ores, which make up 70-75% of all nickel deposits. Extraction of nickel from laterite ores – which often contain as little as 1% nickel – can be problematical, however. Laterite ores can be furnace treated to make an iron-nickel alloy (ferronickel), useful for stainless steel production, but the encapsulated iron means that it is not suitable for other uses. Various leaching processes are also available, but the metal's low reactivity means that conventional heap leaching can be extremely slow, and this initially pushed large-scale leaching towards high temperature and pressures via the high pressure acid leach (HPAL) process.

In the 2000s this requirement for extra nickel from laterite sources drove large scale investment in a series of HPAL projects, with the main ones at Coral Bay and Taganito in the Philippines, Ambatovy in Madagascar, Ravensthorpe in Australia, Goro in New Caledonia and Ramu in Papua New Guinea. These projects required large investment for the huge titanium autoclaves needed to withstand sulphuric acid at high pressures and temperatures. They also required large quantities of sulphuric acid, which made them of considerable interest to the sulphur and sulphuric acid industries. But the technology is expensive, capital intensive and, in some cases has been plagued with difficulties, both technical and environmental. Coral Bay began operations in 2005, but the other projects were delayed for a variety of reasons into 2011-12, and by that time the nickel market had become oversupplied.

Part of this was due to several large HPAL projects all entering the market at the same time. But there is also a lower grade ferronickel process known as 'nickel pig iron', and this grew rapidly in popularity in China in the early 2010s because of its relatively low cost, especially when a new electric arc NPI process was able to use higher grade Indonesian laterites. NPI production grew rapidly to exceed 1 million t/a in 2013, and supplied 30% of China's nickel demand, but Chinese production depended heavily upon ore imported from Indonesia (Indonesia and the Philippines have about 40% of all nickel laterite deposits between them), and in 2014 Indonesia restricted the export of nickel ores.

Indonesia's strategy was to try and force producers to develop downstream domestic ore processing capacity and add value to the country's mined production, but the initial effect was to choke off supply to an oversupplied nickel market and push prices back upwards. Nickel prices had been languishing at $6/lb, but climbed rapidly to $9/lb. Since then, China has switched to importing Philippine laterites and running down global nickel stocks. The slowdown in Chinese steel consumption meanwhile led nickel prices to fall to $4.50/lb. There are signs that global nickel reserves are now depleted and prices are coming back up again, but prices have only climbed to $4.70/lb.

> **"The initial effect was to choke off supply to an oversupplied nickel market.**

The new HPAL production is now largely up and running, consuming about 6 million t/a of sulphuric acid, but the sector continues to be dogged by problems and low nickel prices. Ravensthorpe has generally run well aside from a shutdown in December 2014 over an acid spill, but has been forced to lay off workers to cut costs. SNC Lavalin is selling its stake in Ambatovy, where job cuts have led to strikes. Ramu has reached 80% capacity but faces continuing opposition from locals. Goro is not expected to reach capacity now until 2017 and is losing money at present nickel prices. Taganito started up in 2013 and reached 80% capacity in 2014. It is expected to reach full capacity in 2016 according to operator Nickel Asia.

Away from the high cost, high complexity world of HPAL, there have also been some nickel heap leach projects, in the Philippines, Finland, and at Caldag in Turkey, and there is a Vale demonstrator operation at Piaui in Brazil, but development has been slow, while Talvivaara in Finland, with a bio-heap leach operation, went bankrupt in 2014.

Uranium

The global requirement for uranium is primarily for nuclear power, and the actual tonnages are hence much smaller than for copper or nickel. Total tonnage of mined uranium was 56,200 t/a in 2014, according to the World Nuclear Association (WNA), with mined uranium meeting 90% of the world's nuclear fuel requirements (the rest comes from stockpiles and reprocessing plants). As uranium is a consumed resource in nuclear plants, uranium demand closely tracks power production from nuclear energy. For this reason, demand has plateaued over the past few years, after peaking in around 2003. A groundswell against nuclear power in Europe, especially Germany, has affected production there, and as ageing plants close they have not always been replaced, although France, Finland and the UK are building replacement capacity. The Fukushima accident in Japan which followed the devastation of the tsunami there has kept most of Japan's nuclear plants – a significant slice of world demand – offline since 2011, and in spite of some re-starts, demand has not materialised as quickly as expected.

Thhere has been new nuclear plant construction. China has connected five new plants to the grid in 2015, and another 20 reactors are under construction there. India has six reactors under development and Russia, Pakistan and South Korea also all have sizeable new construction programmes. However, reactor efficiency continues to increase in terms of tonnes U required per MW-day of capacity, and so proportional demand decreases with time. Uranium demand in 2014 was 66,000 tonnes U, and the WNA foresees this rising to about 100,000 tonnes U by 2025 in its reference case, the bulk of that due to plants which are already under construction, but with considerable variation in potential demand after that.

Uranium mine production is relatively concentrated, with 80% coming from just three countries – Kazakhstan, Canada and Australia. The largest ten mines (see Table 1) produced 54% of all uranium in 2014,

Table 1: **The world's 10 largest uranium mines**

Location	Country	Operator	Production 2014, tU
McArthur River	Canada	Cameco	7,356
Tortkuduk	Kazakhstan	KATCO	4,322
Olympic Dam	Australia	BHP Billiton	3,351
Arlit	Niger	SOMAIR	2,331
Budenovskoye 2	Kazakhstan	Kazatomprom/Uranium One	2,084
South Inkai	Kazakhstan	Kazatomprom/Uranium One	2,002
Priagunsky	Russia	ARMZ	1,970
Langer Heinrich	Namibia	Paladin Energy	1,947
Inkai	Kazakhstan	Cameco/ Kazatomprom	1,922
Mynkuduk	Kazakhstan	Kazatomprom	1,790
Total			**29,075**

and as can be seen, five of these were in Kazakhstan. Indeed, while production has been falling in Australia and to a lesser extent in Canada, it has continued to grow in Kazakhstan, as well as a few other countries like China and the USA.

All uranium extraction projects are leaching-based, as all uranium ores are oxides. Most use an acid leach, but where there are extensive carbonate deposits use of acid would often be too costly, and so some projects, especially in the US, use an alkaline leach, although Kazakhstan uses acid leaching in carbonate rocks which leads to larger consumption of acid. Conventional acid (heap) leaching is in relative decline, while conversely, in situ leaching (ISL) now represents 50% of production (up from 16% in 2000). Acid consumption in uranium leaching depends very much upon local geology and leaching technique. In Australia it can be as low as 3 tonnes/tonne U at Beverley, which closed in 2014, while in Kazakhstan it can be as high as 70-80 tonnes/tonne U. Consequently, the expansion in Kazakh uranium mining has led to significantly higher levels of acid demand for uranium leaching.

Uranium prices, meanwhile, have languished since Fukushima, dropping from a peak above $70/lg in early 2011 to lows below $30/lb in mid-2014, and stabilising in the region of $37.50/lb for most of 2015. Low prices have discouraged investment in new mining capacity, and Japan is known to have an overhang of almost 55,000 tonnes of stockpile which even at pre-Fukushima rates would take it six years to exhaust. Inventories in China, the US and Europe are reportedly even higher. The upshot is that increasing demand may take a while to filter through into higher prices, meaning that requirements for mined uranium need not increase as fast as demand does. Nevertheless, the expansion of mining in central Asia (Uzbekistan is now also a growing uranium producer) is using progressively higher volumes of acid. Kazakhstan now operates 2.2 million t/a of acid capacity and uses about 1.7 million t/a in uranium leaching. This has pushed acid demand for uranium leaching to over 3 million t/a, but further expansion depends to an extent on whether the re-start of Japanese plants and start-up of new Chinese, Indian and FSU reactors leads to an uptick in uranium prices.

Other metals, other solutions

Other metals are amenable to acid leaching, although the volumes used are relatively much smaller compared to the 'big three' of copper, nickel and uranium. Skorpion Zinc has long operated a zinc SX/EW leaching plant in Namibia, although the zinc mine is coming towards the end of its life. The mine was scheduled to close in 2015, but new owner Vedanta Resources initially extended this to 2017, and is now reported to be planning to extend mines life to 2019, with processing of mine output to continue until 2020. And now there is a second zinc SX/EW facility, this time in Moorseboro, North Carolina, USA, operated by Horsehead Corp. Mining began in 2014 and zinc processing earlier this year, and 40,000 t/a of zinc is now being extracted. At capacity, expected in the next year or so, 150,000 t/a of zinc will be being produced, making it equivalent in size to Skorpion. There is considerable interest in non-sulphide sources of zinc at present – although there are only a few deposits worldwide, the lower extraction cost is attractive in the current zinc market.

Likewise, gold, silver and rare earths can also be extracted by leaching, depending on the ore body. These can be part of existing mines, and sometimes require the treatment of mine tailings from base metal production. There are a number of rare earths extraction projects around the world looking at sulphuric acid leaching, but at the moment no large-scale developments.

Another issue for acid demand in leaching of metal ores is that sulphuric acid is not the only option. In the world of nickel, there are now two heap leach projects which are looking towards nitric acid as a leaching agent instead, including NiWest at Murrin Murrin in Australia, and Direct Nickel, another Australian-based company looking towards a project in Indonesia. Ammonia is used in precious metal extraction and has been trialled in the copper industry, at Escondida in Chile, but was discontinued due to issues with the process. In the uranium industry, alkaline leaches are used in the US where carbonate rocks would consume large quantities of sulphuric acid, although as noted above, this has not been a barrier to sulphuric acid's use in similar carbonate rocks in Kazakhstan.

While nitrogenous leaching has been touted as more efficient and with lower toxicity by-products, at the moment there seems little prospect of any large-scale take-up of nitric acid leaching in nickel due to its higher cost. It also depends upon the availability of ammonia production, a compound much more expensive and difficult to transport than sulphur.

Conclusions

Since we last looked at sulphuric acid demand for metal leaching, the situation has, if anything, deteriorated. Copper SX/EW production has been cut back, and faces lower demand over the medium-term future. Nickel leaching is plateauing, with not a lot of prospect for extra demand on the horizon, as the phenomenon of low cost nickel pig iron has changed the nickel market. Uranium markets have been hit by the fallout from the Fukushima accident, and while there has been a rapid expansion in demand from Kazakhstan, new production could take some years to arrive. There is some prospect for new demand from zinc leaching, and longer term possibly rare earth processing, but for the moment it looks like the rapid expansion of this demand sector is at an end. ■

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Managing the risk of H_2S

Sulphur industry worker using supplied air during unloading operations

Craig Jorgenson, Director of Transportation and Regulatory Affairs for The Sulphur Institute (TSI), describes the effects of hydrogen sulphide and TSI's work with attempting to help mitigate its risks.

Hydrogen sulphide, H_2S, is known as an environmental contaminant. Occurring naturally in the decay of organic matter and in crude oil and natural gas, it is one of the most commonly removed by-products in the energy industry, not only found at petroleum refineries and natural gas plants, but also livestock farms, landfills, paper mills, sewage lines and treatment plants, underground utility systems, and even food processing plants.

For sulphur industry professionals, working in an environment with the potential presence of H_2S is unavoidable, and it is imperative to manage risks of this potential hazard throughout the supply chain, protecting workers from exposure to damaging levels of this gas.

Table 1: **H_2S health effects**

H_2S Concentration (ppm)	Health effect
<1.0	Odour threshold
5-10	Obvious odour (rotten eggs)
50	Noticeable eye irritation
100	Loss of smell
200	Rapid loss of smell, stings eyes and throat
250	Pulmonary edema (fluid in lungs) with prolonged exposure
500	Dizziness, breathing ceases in a few minutes
700	Rapidly produces unconsciousness, stops breathing
1000+	Single breath can cause collapse, coma, and stop breathing

Source: Dr Glenn Millner at the Centre for Toxicology and Environmental Health

Properties

Hydrogen sulphide is a colourless, flammable gas that is heavier than air and has a tendency to collect in low-lying and enclosed areas such as sealed vehicles carrying molten sulphur by road, rail and water. It can also accumulate in stationary areas such as sulphur pits and storage tanks. The odour of H_2S is often compared to that of 'rotten eggs,' but the smell is normally detected only at low concentrations of H_2S in air. Through continuous low level exposure, workers lose the ability to smell the gas; H_2S affects the olfactory system and it is imperative not to rely on one's sense of smell to indicate either its presence or their safety. Additionally, it is important to understand permissible exposure limits (PEL) for employees working in an environment where they may be exposed to H_2S or other toxic substances. Exposure limits are usually established and enforced by governments; however, there can be confusion when local laws, company policy or independent standard setting entities publish alternative PEL information. It is important that employers and employees understand laws and rules that affect exposure levels specific to their location and workplace circumstances. Table 1 summarises exposure levels and associated health effects.

Mitigating risk

Through proper training and by establishing comprehensive work place procedures, there are many ways to mitigate exposure to H_2S. It is important that those who work in an environment where it may be present understand the sources of the gas and follow established procedures, including the correct use of personal protective equipment (PPE). As an example, during storage of molten sulphur in any container, H_2S can accumulate in the vapour space. Operators that are loading or unloading any container should always presume the presence of H_2S, especially when opening hatches and be cautious about presence of H_2S around fittings and other openings. Procedures such as wearing an H_2S monitor, properly affixed, within the breathing zone, and donning a source of supplied fresh air should be included as part of any safety program. Additionally, installing area air monitors, warning signs and wind socks in areas where H_2S may persist are additional practices that draw awareness and are measures that can be used to reduce potential exposure to an unprotected employee. The Institute has assembled many of these leading practices through loading site visits and recurring collaboration with operations and safety experts from member companies. Many of these reports are available on TSI's website.

TSI

The Sulphur Institute and its member companies are committed to educating workers and protecting them from H_2S exposures; TSI does this in a number of different ways. As a member of the US-based Hydrogen Sulphide Coalition, a group of trade associations with similar concerns about workplace exposures to H_2S, TSI maintains international regulatory oversight on government proposals to adjust H_2S exposure limits. In the past, TSI has contributed to coalition responses to regulatory initiatives that would have had significant impact to the sulphur industry. Additionally, TSI staff members are participants on the American National Standards Institute (ANSI) committee for Accepted Practices for Hydrogen Sulphide (H_2S) Training Programs. This committee is chartered to develop and maintain standards that set forth practices for hydrogen sulphide safety training. And finally, through its Environment, Health and Safety Working Group, TSI convenes forums and encourages member companies to share leading industry practices that minimise risk of exposure to H_2S.

Eliminating exposure to H_2S within the sulphur industry is a challenging goal. The risk of exposure can be mitigated by ensuring employees who work in an environment where H_2S may be present have the right training, the right equipment, and consistently follow established procedures. One accident is one too many. The Sulphur Institute's staff and member companies are committed to developing tools and maintaining continuous dialogue on this topic to keep sulphur industry workers well informed and protected from exposure to H_2S in the workplace. ■

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MESPON 2015

The 2nd Annual Middle East Sulphur Plant Operations Network Forum, MESPON 2015, organised by UniverSUL Consulting, took place in Abu Dhabi at the Sofitel Abu Dhabi Corniche from October 18-20, 2015.

This year's event attracted more than 180 attendees, with representatives from all major operating companies in the region.

Panel discussions were a key feature of the programme. Panel left to right: Hassan Al Hosani (GASCO), Kuppuswamy Thiyagarajan (ADNOC), Peter Clark (ASRL), Mike Smeltink (Jacobs Comprimo® Sulfur Solutions), Pavan Chilukuri and Stijn Pontfoort (Shell Global Solutions), Joëlle Castel (Technip France), Rashid Iqbal (GASCO) and Rajat Pal (Ali & Sons Oilfield Supplies & Services Co.).

MESPON aims to maximise utilisation of current local experience and expertise via networking.

Angie Slavens, managing director of UniverSUL Consulting and host of MESPON 2015, giving the welcome address.

With the Middle East home to some of the world's largest sour gas development projects, and on track to soon become the world's largest sulphur producer, there is an impetus to develop and enhance local capabilities for dealing with the challenges of gas sweetening and sulphur recovery. Following the success and regional support of the first Middle East Sulphur Plant Operation Network Forum (MESPON), organised and hosted by UniverSUL Consulting in 2014, this interactive conference has now become an annual event for on-going technical knowledge sharing, lessons learned capture and communication and the establishment of best practices and plant benchmarking.

Interest in this year's forum was substantial with over 180 participants, predominantly senior level sour gas and sulphur plant process, operations and maintenance personnel from the region.

The three day agenda was packed with presentations and panel discussions on gas treating, sulphur recovery, project execution and sulphur handling.

This year's MESPON forum contributors comprised some of the world's leading experts in sour gas treating and sulphur product handling, as well as senior level sour gas and sulphur plant operations personnel, experienced industry professionals from plant testing and monitoring companies and select major equipment providers and technology licensors. ■

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Soot formation on Claus catalyst

It is common for SRU operators to soot up the first catalytic bed during start-up, shutdown or low turndown operation. In this article we discuss the causes and effects of soot fouling in SRUs, how it can be prevented and how it can be treated if it does happen.

Soot formation is a problem which affects sulphur recovery units (SRUs) inside refineries and natural gas processing plants around the world. It is a direct result of operations. Soot accumulation may happen slowly over time or in a single flash of chemical imbalance. Gas plant sulphur recovery units can be particularly at risk for soot formation; co-firing or direct-fired reheaters may be necessary in order to reach sufficient process temperatures in the Claus converters due to the lean acid gas feed. These modes of operation introduce additional hydrocarbon into the SRU, which often results in soot formation. Anywhere that hydrocarbon combustion occurs, the possibility of soot formation exists.

Although the phenomenon of soot formation inside sulphur recovery units is not completely understood, the ramifications are well-known: increased pressure drop across catalyst beds with the potential to cause poor flow distribution, decreased conversion activity, and even reduced unit throughput. The issue of capacity reduction of sulphur recovery units is economically problematic when the SRU becomes the bottleneck of the refinery or natural gas processing plant.

Shutting down a Claus SRU takes 3-5 days depending on its size. Start-up adds a further 2-3 days, even without a catalyst changeout or maintenance work. As refinery throughput, and therefore revenue, falls while an SRU is off-line, operators are often under pressure to cut SRU turnaround times and extend the interval between them. Deferring catalyst replacement costs by extending catalyst life is also desirable. However, hastening shutdown and start-up processes or managing them poorly can lead to soot formation, reduced unit efficiency and more frequent catalyst changeouts.

Some operators take a precautionary approach and change the catalyst at every shutdown. This avoids the risk of catalyst deactivation during shutdown operations, but the fresh catalyst, or a catalyst retained because it is still performing well, may be damaged during start-up. When the catalyst performance has fallen below acceptable levels, another turnaround and more catalyst may be necessary as well as maintenance operations to deal with equipment fouling. This approach may also mean changing the catalyst more often than necessary.

So is the answer to prolong shutdown and start-up operations? Not necessarily. Shutdown and start-up operations cannot continue indefinitely and keeping the unit on fuel gas in a substoichiometric state for too long can cause soot formation. However, with the careful application of the right procedures, turnaround times can be reduced without damaging soot formation and catalysts need not be changed at every turnaround.

Careful consideration of the fuel selection, burner control and other parameters can help to reduce soot formation during SRU shutdown and start-up operations. This, in turn, can mean greater unit efficiency and longer catalyst life and, ultimately, better refinery economics.

Soot formation theory

Soot formation theory can be as complex as one wishes to make it. Suffice it to say that early intermediate radicals formed in a hydrocarbon flame include free atomic carbon, which quickly agglomerates into carbon spheres, cenospheres (porous or hollow sphere-like particles) and chains that behave as suspended solids when starved of oxygen. Soot formation cannot be explained by simple thermodynamic equilbria, and is generally concluded to be kinetically governed[1].

While methane is not generally considered a soot promoter (at >60-90% of stoichiometric air, depending on conditions), it has the ability to generate methyl radicals which, evidence suggests, can interact with heavier hydrocarbons to form polyaromatics and, ultimately, soot[2].

When burning hydrocarbon fuels sub-stoichiometrically, diluents such as steam, N_2 or CO_2 reduce the flame temperature to suppress the pyrolysis reactions long enough to reduce the free carbon available to make smoke/soot. Steam, however, has the additional advantage of thermally dissociating to H^+ and OH^- which react with free carbon to form more complex radicals which maintain the carbon in the gaseous phase pending oxidation, and thus inhibit solid carbon production. There is also reason to believe that H_2 (in addition to its combustion product, H_2O) similarly inhibits soot formation[2,3,4].

On the other hand, destruction of hydrocarbons in acid gas is arguably analogous to NH_3 destruction in that a minimum (or higher) temperature is required for efficient oxidation by SO_2. The actual threshold is site-specific, likely being affected by burner mixing efficiency, residence time, nature and concentration of hydrocarbons, concentration of SO_2, and accuracy of temperature measurement.

Unfortunately, very minor quantities of soot will discolour sulphur from the first condenser (or waste heat boiler), typically progressing from dull yellow to grey to green to brown to black with increasing contamination. Fortunately, colour comparison of solidified samples is thus a

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sensitive indicator of incomplete hydrocarbon destruction. Based on a review of collective field data, Clint[1] recommends the following nominal minimum temperatures for acid-gas hydrocarbon destruction in the Claus furnace:

C_1-C_6 alkanes	950°C
BTEX	1,050°C

Hydrocarbons

In normal operating conditions, the hydrocarbon level in the acid gas typically ranges from 0.05 to 3.00%. This amount of hydrocarbon is normally accounted for in the design basis and can be handled by extra air in the reaction furnace through the combustion air feedforward and feedback control system. Hydrocarbons in the range C_1 to C_4 do not normally cause soot production (but at higher concentrations the production of CS_2 becomes notable). Higher hydrocarbons, and especially aromatics such as benzene, toluene and xylene (BTX) are prone to produce soot when the temperature in the combustion chamber is not high enough (<1,050°C).

During upsets in the upstream gas treating units high hydrocarbon levels can accidentally be carried over with the acid gas from the amine regenerator and, if applicable, from the sour water stripper. Should this happen, the combustion air provided to the reaction furnace may not be adequate to combust these hydrocarbons; therefore, soot may form and contaminate the first catalytic bed.

A burner control system with a tail gas analyser (feed-back) can adjust the air demand for unexpected extra hydrocarbons in the feed gas, but in most cases the response of this system is too slow.

When the hydrocarbon content of the acid gas varies, such as when varying natural gas sources are being treated, some manner of forward burner control can help to prevent soot formation.

In the ABC+ technology, developed by Jacobs, the hydrocarbon content in the acid gas is measured before it arrives at the burner and the air demand adjusted accordingly. So application of ABC+ may help to prevent soot formation.

Causes of soot formation

Soot can be created in the SRU during both normal operation (during upsets) and/or during transient conditions such as start-up, shutdown or hot standby operation.

It is common for SRU operators to soot up the first catalytic bed during start-up, shutdown or low turndown operation. During start-ups and shutdowns (i.e. no acid gas) soot formation is a result of combusting fuel (preferably natural gas) with too little oxygen. On a molar basis, hydrocarbons consume much more oxygen than ammonia or H_2S. Available oxygen will be depleted and sooting may occur as a result.

Soot formation as a result of incomplete combustion of hydrocarbons in one or more of the burners in an SRU can happen in the main burner and also in direct fired heaters (reheaters and reducing gas generators). Since the thermal oxidiser is operated at excess oxygen, soot formation is not expected there. However, there are known cases where soot has formed when firing a low NOx burner with too deep substoichiometry, or when flash gas was introduced suddenly in the incinerator chamber.

Although incomplete combustion is often attributed to a lack of combustion air (oxygen), it can also arise when a burner has been worn or damaged, causing poor mixing of fuel gas and air.

While it is typical to fire fuel gas under substoichiometric conditions (in order to prevent free oxygen from lighting-off combustible materials that will exist in the SRU post-operation such as elemental sulphur or pyrophoric iron sulphide), soot can form if combustion is done with about 80-85% of stoichiometric oxygen or less when using a modern burner.

For older burners (essentially nothing more than a pipe and no vanes in the air box), soot can form when combusting with 85-90% of required oxygen or less due to poor mixing. Likewise, a modern burner that has been damaged from liquid carry-over, over-heating or some other cause can have poor mixing along with soot formation.

In normal operation, when processing H_2S (with minor quantities of COS and CS_2), no soot will be formed since there is no substantial source of carbon. The problem arises when there are high concentrations of hydrocarbons in the acid gas feed, when there is hydrocarbon carry-over or when the combustion is incomplete during co-firing.

Hydrocarbon carry-over

In designing an SRU, hydrocarbon carry-over is prevented by a number of measures: flashing and skimming of hydrocarbons upstream of the SRU and the use of knock-out drums and demisters.

So when hydrocarbon carry-over does happen, it is because of a maloperation, upset condition or equipment failure upstream of the burners.

Methanol carry-over has also been suspected to cause soot production, but there is no evidence for this in the literature. Methanol is normally completely converted in the burner, but any non-combusted methanol (e.g. form a split-flow operation) may react with sulphur in the catalytic reactors and the condensers.

Soot formation during transient conditions

Outside of normal operating conditions, most sulphur recovery units use natural gas on an intermittent basis for SRU start-up, shutdown and hot standby. For the case of start-ups where new catalyst has been installed, the main burner may be fired with excess air, preventing soot formation. For all other cases and for the majority of natural gas firing, the burner must be fired at slightly substoichiometric (air deficient) air conditions. This is necessary because any excess air will cause deactivation of standard alumina Claus catalysts and may result in sulphur fires that can be very damaging to catalyst and equipment. During this substoichiometric firing of natural gas, soot formation may be a problem.

When firing at near-stoichiometric conditions the composition of the fuel gas or natural gas must be known and remain constant. This is where a clear distinction between fuel gas and natural gas exists: natural gas is normally of fixed and known composition, while fuel gas can be made up of almost any mix of constituents (hydrocarbon and non-hydrocarbon) that can be found in a refinery. Furthermore, the only certainty with fuel gas composition is that it will change. The effect of varying fuel gas composition is illustrated in the following three oxidation reactions involving methane, propane and hydrogen, respectively.

Methane stoichiometric combustion:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Propane stoichiometric combustion:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

Hydrogen stoichiometric combustion:

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$

Thus, as illustrated, the stoichiometric combustion of propane requires two and

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one-half times more air than methane. Obviously, heavier hydrocarbons will require even more air. Not knowing the exact composition of the fuel gas runs the risk of either firing with excess oxygen, resulting in potential sulphur fires, or firing with significantly deficient oxygen, resulting in soot formation.

The effects of a sulphur fire in a catalyst bed are self-evident. The formation of a significant amount of soot will result in heat exchanger fouling, catalyst damage and the soot will reduce SRU capacity. If the additional pressure drop created by the soot cannot be tolerated, and if the soot cannot be removed on-line, a shutdown will be required to mechanically remove the soot and to clean heat exchanger tubes. The SRU must be designed and operated with known composition natural gas for start-up, shutdown and hot standby operation. During fuel gas operation the flame colour should be checked in the field. An orange flame colour is indicative of air-deficient operation, a blue flame is oxygen rich and a salmon-pink flame colour is indicative of stoichiometric burn.

The combustion stoichiometry in every burner should be maximum 95% under-stoichiometric, when there is sulphur in the train. This in itself should not be a big problem, but during start-up and shutdown the flows are much smaller, so the flow measurement becomes less accurate and serious air deficiency and soot production may result. Also, especially during a first start up, DCS operators tend to keep the burner flows in manual control until the controls have been tuned properly. When the fuel gas is a refinery gas, the composition may change, resulting in air deficiency. For example, in one case the quantity of butane in the fuel gas was higher than expected, thus causing a shortage of air and soot formation.

For this reason, Jacobs advises using natural gas for co-firing and for fuelling the direct fired heaters, whenever it is not possible to adjust the air demand by means of measuring the density in the fuel gas.

Fuel quality and process control

Fuel quality is important, so the fuel should be carefully specified. Once shutdown or start-up is underway, it is not easy to change the fuel, so the fuel needs consideration at the planning stage. In Shell-operated SRUs, natural gas is preferred over fuel gas, as it has a more stable

Fig 1: **Flame temperature as a function of stoichiometric air and steam injection**

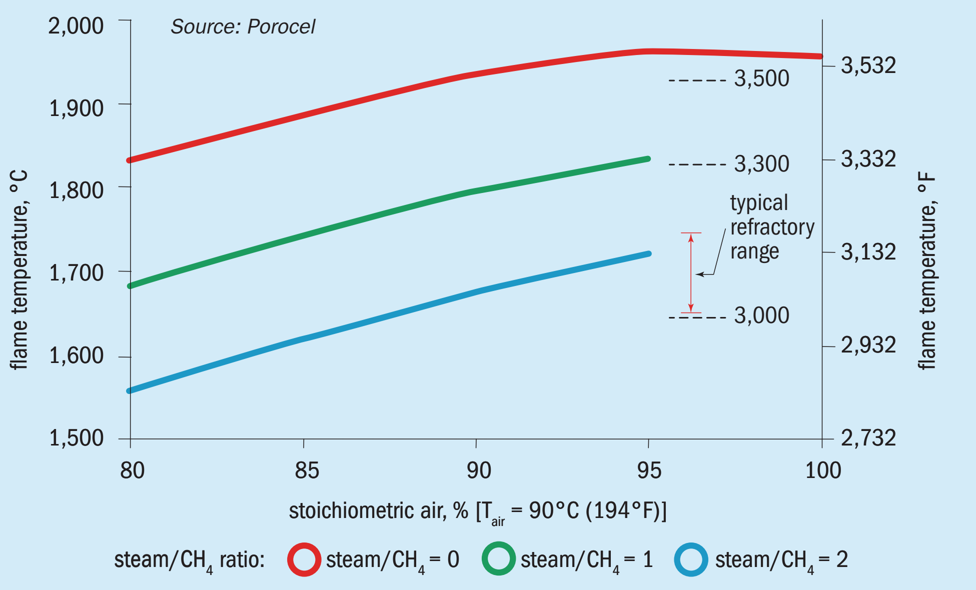


Fig 2: **Low pressure steam requirement for flame moderation when firing natural gas at 95% stoichiometry**

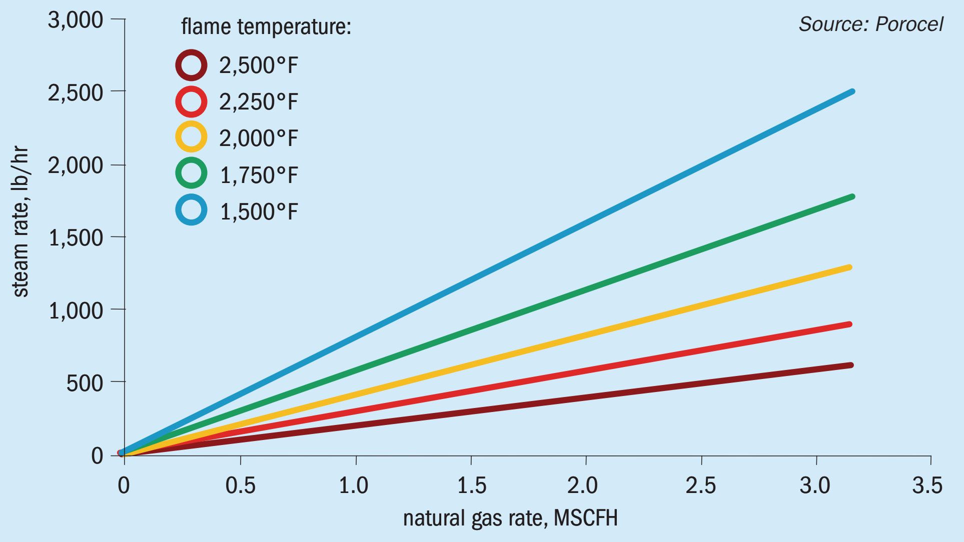
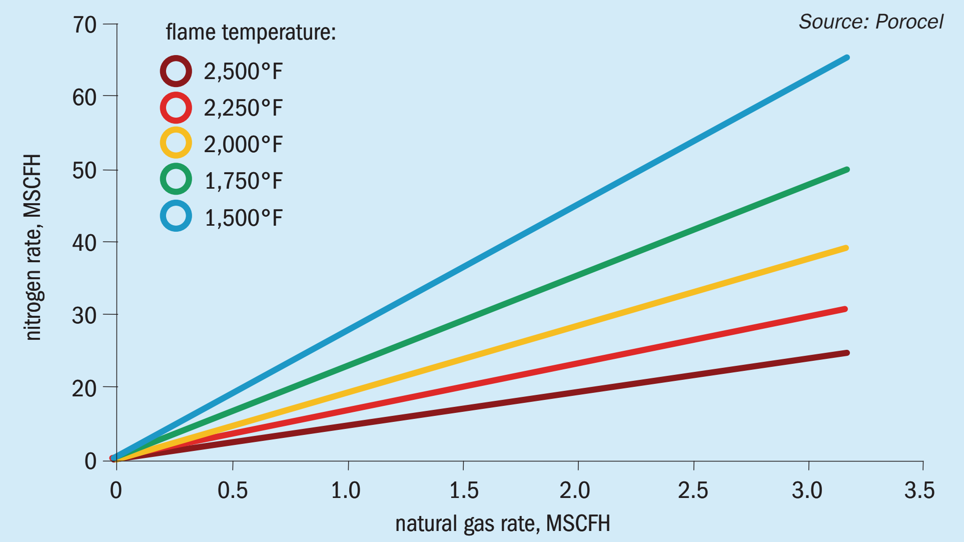


Fig 3: **Nitrogen requirement for flame moderation when firing natural gas at 95% stoichiometry**



composition. Shell uses typically 95% stoichiometry with natural gas application and 85% stoichiometry with other fuel gas because the effect of oxygen slip towards the catalyst can be more damaging for the catalyst than the potential soot formation from incomplete combustion.

Process control is important to ensure that proper combustion occurs. During shutdown and start-up, the main burner is in the lower end of its operating range, so control adjustments must be made carefully. The burner control scheme should have pressure and temperature compensation for air, acid gas and fuel gas. For fuel gas, a density measurement is advisable for calculating the air demand.

Sulphur recovery is maximised where there is only enough air introduced to “burn” approximately one-third of the H_2S in the gas feed to the SRU. Typically control of the air flow to the reaction furnace is a combination of feedforward and feedback control. The main air flow loop is ratio control, which represents 90% of the total air flow, and is controlled by feedforward control using the acid gas flow rate and assumed acid gas composition including H_2S and hydrocarbon constituents. The remaining 10% of the air is through the trim air loop, controlled via feedback from an air demand analyser located downstream of the final condenser. The accuracy of feedback control using tail gas air demand is limited due to the approximately two to three minutes process lag time; if the flow rate or composition of the acid gas changes rapidly, the feedback control system may not adjust quickly enough to prevent soot formation.

A recent improvement in the SRU control scheme is the use of feed analysers which measure both the H_2S content as well as the hydrocarbon content. This measured information provides feedforward information to improve the overall control scheme by addressing the limitations associated with the process lag in the traditional feedback loop.

Flame temperature moderation

During start-up, a stoichiometric natural gas flame can easily exceed refractory limits (see Fig. 1) and flame moderation is required. Depending on the situation, flame moderation can be provided in the following ways:

- **Excess air:** This option is only viable when there is new catalyst throughout the entire SRU and thus no risk of sulphur fires due to the presence of oxygen.
- **Steam moderation:** This option can be utilised when all SRU temperature measurements in the SRU are above 140°F (60°C) in order to prevent water condensation. Condensed water vapour from the natural gas fired flue gas will lead to SRU corrosion. It is recommended to add the steam to the centre gun to avoid coating the air swirl vanes and/or to avoid condensing steam in the low and cold spots of the burner housing. Figure 2 provides the steam rate versus natural gas rate to achieve the indicated flame temperatures of 1500, 1750, 2000, 2250 and 2500°F, respectively.
- **Nitrogen moderation:** This is the most expensive option but can be safely utilised at any time regardless of the SRU temperatures or catalyst condition. The nitrogen can be added to either the air stream or natural gas stream. Figure 3 provides the nitrogen rate versus natural gas rate to achieve the indicated flame temperatures of 1500, 1750, 2000, 2250 and 2500°F, respectively.

Of these three options, only steam moderation has been shown to mitigate the formation of soot.

Operation guidelines to avoid soot formation

RATE regards the use of natural gas to heat the SRU for start-up or sweep with hot inert gas on shutdown of sulphur plants as the most critical element to avoid soot formation. If natural gas is not available hydrogen can be used (refinery fuel gas is not permitted).

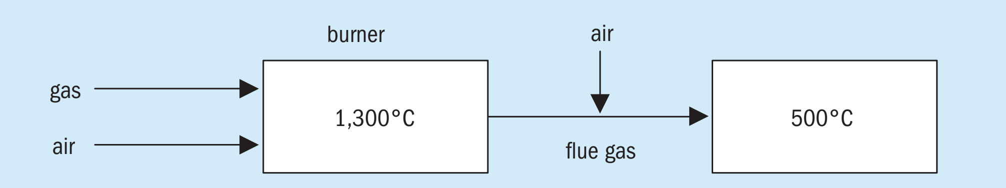
The second critical element is to use tempering steam to moderate the temperature and prevent soot formation. As excess air is increased, steam addition should typically be discontinued at <1,300°C, as overcooling will tend to put the flame out.

Stoichiometric air is the amount of air required for complete combustion of natural gas (predominantly CH_4) to CO_2, with no excess. As additional, or excess, air is added, the heat release is the same, but the flame temperature will decrease because of the cooling effect of the additional air. Expressed another way, the air absorbs heat.

One Nm^3 of natural gas nominally requires 10 Nm^3 of air for stoichiometric combustion. An air:gas ratio of 20:1 (100% excess air) is a good target for clean combustion for process warm-up when excess O_2 can be tolerated.

As excess air is progressively increased above 20:1, flameout will eventually occur when the temperature is below that required for stable combustion. To achieve temperatures below 750-800°C, secondary air must be injected downstream of the burner (Fig.4).

Fig 4: **To achieve temperatures below 750-800°C, secondary air must be injected downstream of the burner**



Source: RATE

Substoichiometric air will result in incomplete combustion of methane to carbon monoxide and hydrogen:

$$2\ CH_4 + O_2 + 4\ N_2 \rightarrow 2\ CO + 4\ H_2 + 4\ N_2$$

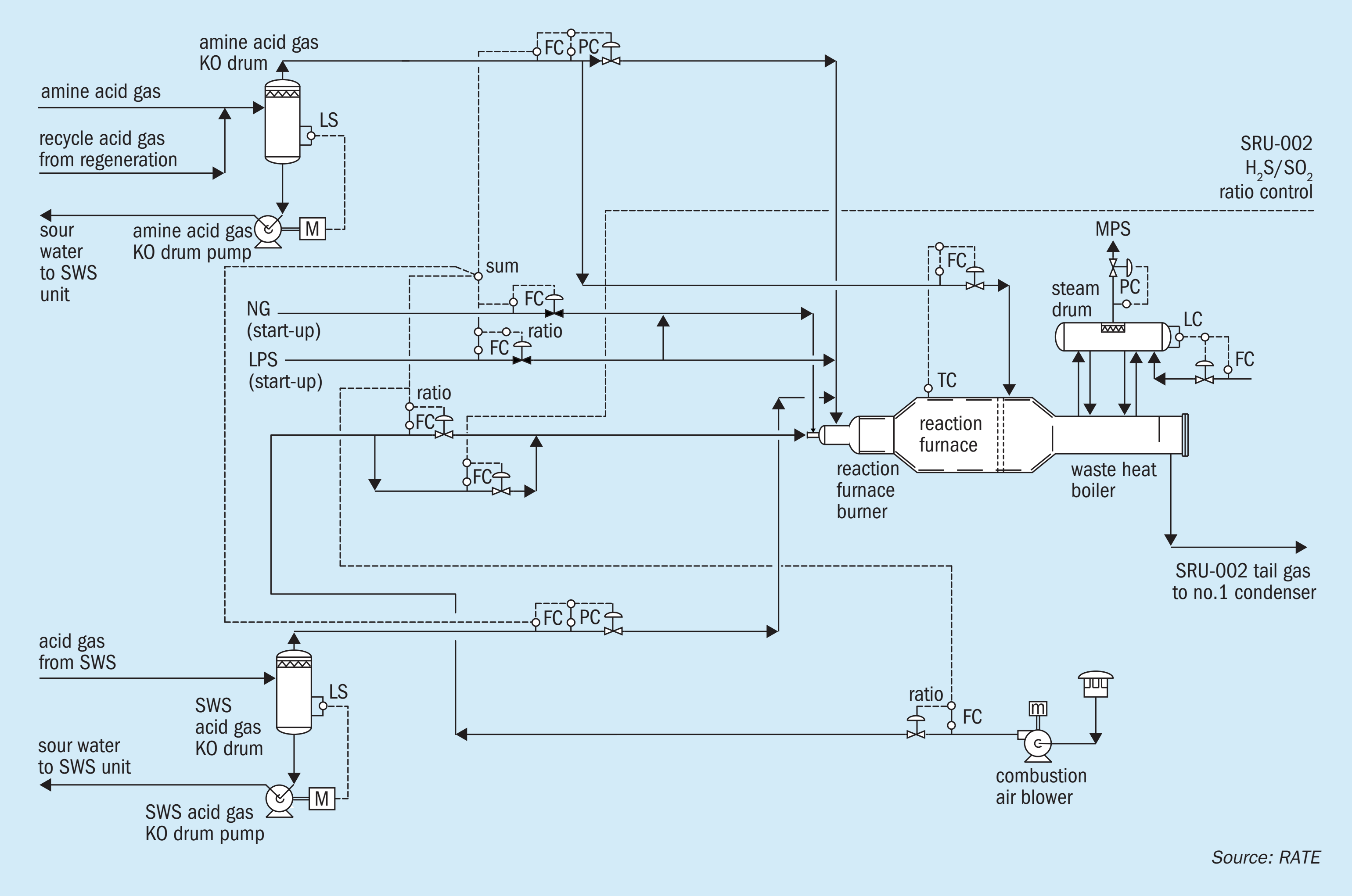
As sub-stoichiometric air rates are progressively reduced, a point will be reached when soot (small carbon particles) is formed.

With a high-intensity burner in good condition, operation at 80-90% of stoichiometric air should still be “clean” (soot-free). If air/gas mixing is poor, however, soot can also result from localised low air/gas ratios despite stoichiometric conditions on average.

Clean combustion at as low as 65-70% of stoichiometric air is possible by injecting LP steam into the burner. Due to the potential for flowmeter error or poor mixing due to burner damage or fouling, operation at less than 80% of stoichiometric air is generally avoided, and 90% is the preferred target for SRU shutdown. A ratio of 1:1 steam:fuel (≈ 1 kg steam/Nm^3 gas) is required to avoid making soot. In the case of the reaction furnace, additional steam (up to 3:1 steam:fuel) may be required to limit furnace temperatures to 1,500°C.

When firing substoichiometrically, the “rag test” can be used to verify no soot by passing a downstream process gas

Fig 5: **Control system and the burner management system using natural gas, steam and air during start-up and shutdown**



Source: RATE

sample through a white cloth and checking for a grey or black stain.

RATE recommends the following steps should be taken as minimum during shutdown with natural gas:

- ensure that the main air flow controller is in cascade so as to automatically adjust the air flow in proportion to total calculated air demand (acid gas + NG);
- establish natural gas flow and ramp up to 50% of scale, while ramping down acid gas to zero;
- initially establish tempering steam flow of 0.6 kg/Nm³ steam/gas to the natural gas gun and/or combustion air and increase up to 1.5 kg/Nm³ if necessary to limit the furnace temperature to 1,540°C;
- initially, maintain stoichiometric air, and adjust as necessary to maintain tail gas H_2S:SO_2 between 2:1 and 4:1.
- gradually increase combustion air to the extent possible without substantial increase in bed temperatures or stack SO_2;
- when most SO_2 generation has ceased, progressively increase combustion air to 100% excess air;
- shut down burner steam at 50% excess air (to avoid flameout);
- ramp down firing rate 10%/hour to 10-20% of design to cool the furnace at a controlled rate.

Figure 5 shows a control system and burner management system using natural gas, steam and air during start-up and shutdown.

Fluor recommends the best means for avoiding soot formation involves doing stoichiometry checks during initial burner firing. The very first light-offs (no sulphur/pyrites downstream of the reaction furnace) are typically done using excess air and depending on the burner design and flame scanner positioning, it may be possible to fire with 100% excess oxygen. However, not all burners can achieve this for first time firing.

After the burners are lit and firing with excess air, fuel gas can be held constant and combustion air flows reduced while measuring oxygen level in the flue gas (downstream of the first sulphur condenser is a good sampling point since it is cooler there than at the outlet of the WHB) to establish measured air:fuel ratio and corresponding excess oxygen levels. By calculation, it is possible to determine the air:fuel ratio for 95% and 90% of stoichiometry and the corresponding control valve positions. These control valve positions can then be programmed into the burner management system (BMS) as presets for light-off at all start-ups, and the 95% stoichiometric air:fuel ratio can be used during hot standby/shutdown.

This should minimise or eliminate any soot collecting on the catalyst during fuel gas only operations. At the same time as the air:fuel ratios are being established, the required steam addition for flame tempering and reaction furnace temperature control, can be determined.

Start-up

Cold start-up is preferably accomplished with a minimum natural gas (or H_2) flame and maximum excess air. This undoubtedly extends refractory life, but requires that the catalyst be rendered non-pyrophoric via "passivation" during the preceding shutdown. There are two reasons for skipping the passivation step: to minimise the out-

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age or to avoid repeating unpleasant "runaway" exotherms and soot formation. The former may or may not be justified when weighed against the cost of shorter refractory life, which is difficult to quantify (in advance). The latter is just poor operation.

When the catalyst beds are non-pyrophoric, RATE recommends maintaining sufficient excess air to limit the reaction furnace temperature to 1,540°C. When necessary to operate near stoichiometric conditions, moderating steam must be added, typically 4 kg steam to 1 kg natural gas. The operator sets the natural gas flow and the steam is automatically ratio-controlled in proportion to the hydrogen. Excess natural gas should be minimised to avoid leaching silica out of the refractory, which not only damages the refractory but can permanently foul the waste heat boiler tubes.

Start-up procedure

Operating many Claus and Shell Claus off-gas treating (SCOT®) units across the world helps Shell to understand what drives operating companies. This vast experience feeds back into Shell licensed technologies and its troubleshooting and technical support services. The experience is also fundamental to the development of SRU shutdown and start-up procedures that are successfully limiting soot formation in units worldwide. Lessons learned from the operation of these SRUs are used for continuous improvement of shutdown and start-up operations.

Shell's recommended start-up procedure is outlined below. The start-up sequence has three main steps:

- heating through fuel gas combustion with excess air;
- substoichiometric firing of fuel gas to remove oxygen from the system;
- taking in acid gas intake and stopping gas fuel firing.

During the first step, the burner initially uses only fuel gas with excess air to control the temperature. The system is gradually heated at a certain maximum rate to avoid damaging the refractory of the burner and combustion chamber. During this time, the burner's operation is very important. The aim is to achieve a stable flame and good mixing. A yellow flame, as seen through the burner and combustion chamber's sight glasses, may be a sign that soot is forming. The flame should be blue with as little orange flicker as possible during excess air firing.

Operators may be tempted to use the burner very close to its turndown capabilities. However, this may limit mixing and promote soot formation. Sometimes, a start–stop sequence is required to limit the temperature rise to 50°C/h. This sequence during heating is preferable to operating the burner below its turndown capabilities.

In addition to soot formation when the burner operates below its turndown capabilities, backfiring damage may occur. Achieving the target burner and combustion chamber temperature may take 20-24 hours of continuous heating. The burner's operation changes many times during this heating period, which makes feedback from the field operators to the control room essential. Frequent verification of correct operation of the burner is advisable, including during nightshifts or environmentally unpleasant conditions.

During the second step, the burner operation changes from excess-air to air-deficient (substoichiometric) firing of fuel gas. Substoichiometric firing of fuel gas can lead to flame temperatures above 1,700°C, which can damage the refractory. To avoid this damage, steam is injected with fuel gas to serve as a quench medium to limit the flame temperature in order not to damage the refractory.

Steam quality is an important factor in soot prevention. Normally, low-pressure steam (about 5 bara) is used. The steam should be dry and the steam trap close to the injection point should be operating correctly. Injecting wet steam may disturb the flame pattern and enable local cold spots to occur, which may lead to soot formation. During this period, field operator feedback on the flame pattern and colour is important. Substoichiometric firing of fuel creates an orange to pink (salmon pink) rather than a blue flame.

This phase is also referred to as hot standby of the SRU. For units that do not apply co-firing of fuel during normal operation, this period is generally the most vulnerable to soot formation. It is therefore advisable to make frequent field checks on the flame pattern and colour. The amount of time that SRUs can be kept in this mode largely depends on the propensity of the burner to form soot.

The third step consists of taking in acid gas by the burner. Careful timing and planning are required to achieve a smooth start-up of the SRU and the amine system that generates the acid gas for the SRU. Stable operation of the amine system is key in avoiding hydrocarbon carryover or even amine carryover from the amine system to the SRU. Both upsets can cause soot formation in the SRU burner. The amount of acid gas at the moment of intake should ideally be above the minimum turndown of the SRU. This will ensure correct measurement of the flow and calculation of the air demand of the acid gas.

Thus far, avoiding soot formation has been about planning and operation. Operating sites can also help to control soot formation through fuel selection and quality and SRU burner control.

Shutdown

According to WorleyParsons, shutdown is ideally accomplished by initially burning natural gas at 90-95% of stoichiometric air, which is where most plants get into trouble. Excess air will auto-ignite residual sulphur on the catalyst, nominally generating 95°C ΔT per mol-% O_2, while insufficient air will generate soot, thus fouling the catalyst beds (at least). An alert console operator will promptly recognise excess air by increased catalyst temperature (assuming intermediate bed TIs), but soot formation is less evident without field monitoring of flame and tail gas.

Monitoring of tail gas (in addition to flame appearance) following switch to "fuel" is critical. Indicated air:gas ratio is often inaccurate, typically due to flowmeter error or poor or non-existent P/T compensation (or lack of fuel gas measurement in some cases). In addition, some plants must use plant-produced fuel having variable air demand.

Two common misconceptions in WorleyParsons' experience are that O_2 = zero at stoichiometric air, and that a few hundred ppm, for example, of CO (or H_2) confirms substoichiometric air:gas. Theoretical flue gas compositions in Fig. 6 show the extent to which both are fallacies. Without tempering steam, for example, O_2 exceeds 0.5 mol-% at stoichiometric air, and CO still exceeds 0.2 mol-% at 10% excess air.

One takeaway from Fig. 6 is that, if free oxygen is evidenced by an exotherm, the air:gas ratio can safely be decreased by, for example, at least a 10% step change without risk of soot.

Tempering steam is generally advised in the absence of excess air, in large part to reduce risk of soot if air:gas ratio

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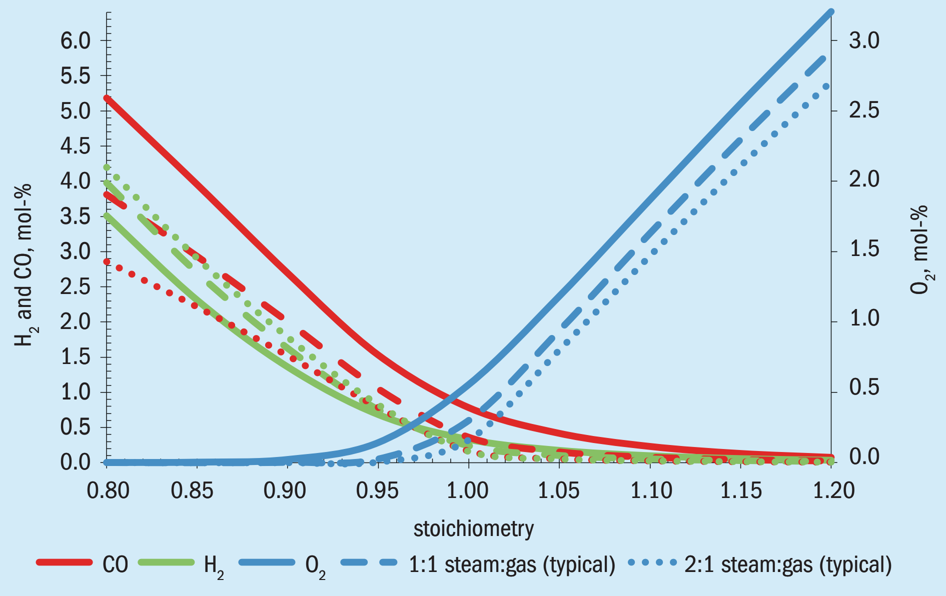
Fig 6: **Equilibrium flue gas concentrations for typical natural gas**



Source: WorleyParsons

is inadvertently lower than intended. A high intensity burner, barring damage or extreme turndown, can typically operate soot-free at as low as 80% of stoichiometric air without steam, and as low as 65% of stoichiometric air with steam.

As previously metioned, a ratio of 1:1 steam:gas is recommended for soot suppression, while up to at least five kg/kg is normally possible without flame instability if necessary for temperature moderation. Steam and natural gas often have nominally the same molecular weight, in which case steam:gas weight ratio = mole ratio. What really counts, however, is the mole ratio of H_2O:C, which the weight ratio of steam:gas maintains essentially constant for carbon numbers >1.

Figure 6 also reveals the curious fact that, at stoichiometric air for example, 1:1 steam:gas results in a nominal 50% reduction in equilibrium O_2 compared with no steam, and 2:1 steam:gas results in a further 50% reduction in O_2 compared with 1:1 steam/gas. This is attributed to reduced thermal dissociation of CO_2 and H_2O at the lower flame temperatures[5].

Tempering steam should be injected into the acid gas line to cool the acid gas gun, and optionally also into the combustion air if desired. Contrary to not uncommon practice, steam arguably should not normally be injected into the fuel gas gun for a couple of reasons:

- heat release is derated by at least 50% when steam is required, compared with when not by virtue of excess air;
- small fuel gas ports are more likely to become plugged with minor corrosion scale from normally-idle steam piping.

A common industry practice is to adjust the air:gas ratio to achieve, for example, 0.5% O_2 measured periodically with a portable analyser at the first condenser outlet. This would appear pointless when the plant has an online air demand analyser to measure the SO_2 resulting from subsequent O_2 consumption by sulphur on the catalyst. Perhaps unexpectedly, tail gas H_2S also tends to respond accordingly to the air:gas ratio. It is easy to understand that tail gas SO_2 is proportional to excess air, but perhaps less obvious that H_2S is inversely proportional. To WorleyParsons' knowledge, the explanation is still open to debate. One possibility is that adsorbed H_2S is being stripped from the catalyst, another that sulphur is being hydrogenated to H_2S to a minor extent. In any event, it is logical that equilibrium H_2S is influenced by SO_2 concentration.

Another useful indication of air:gas ratio is residual % H_2 if Claus tail gas initially continues to flow through a hydrogenation-amine tail gas treating unit (TGU) with an online H_2 analyser, i.e.; adjust air:gas ratio to maintain 2-3 mol-% H_2 (Fig. 6). After a few hours, the Claus tail gas H_2S/SO_2 may be depleted to the point that the air demand readings are no longer useful, but % H_2 remains key, particularly if fuel gas air demand varies.

After, say, 12-24 hours, the plant would like to start slowly adding excess air, usually after bypassing the TGU, and ultimately cool down with air. Excessive exotherms upon addition of excess air is a common reason why many have become "gun-shy" about attempting passivation. (This is often referred to a temperature "runaway", arguably a misnomer because oxidation heat promptly subsides with reduced excess O_2.) To reduce this risk, it is important to shut down reheat and allow the converter to cool to <200°C, well below the auto-ignition temperature of sulphur, before increasing air.

Sometimes, despite no appreciable exotherm while ramping up to, say, 100% excess air, temperature excursions subsequently occur upon attempted cool down with air. Most likely this is due to residual pockets of pyrophoric material resulting from channelling due to low sweep rates. Initial fuel gas firing should be maximised, as typically limited by burner capacity or reaction furnace temperature. Channelling aside, shutdown duration is inversely proportional to sweep rate, since rate of sulphur removal from the catalyst is limited by equilibrium concentrations of H_2S/SO_2 in the tail gas.

Anecdotal evidence suggests that start-up burner damage or restriction due to sulphidation and/or solid sulphur is far more prevalent than generally appreciated. Probably the most common cause of sulphidation is insufficient purging of the fuel gas gun with N_2 (or steam if necessary) during acid gas operation. Often the reduction in fuel port ID is so uniform as to go unrecognised unless the inspector is aware of the original dimension. In extreme cases, poor flame pattern can simultaneously generate soot and excessive residual oxygen, despite bulk stoichiometric air:gas.

Often, after repeated incidents of sooting, clients will switch from a hydrocarbon gas to hydrogen. Because hydrogen has a much higher flame speed than other gases, it is particularly important to avoid undue turndown conducive to burner overheating. When utilising a burner not originally designed for hydrogen, the manufacturer should be consulted for a revised operating range.

A common mistake is failure to appreciate the fact that excessive residual hydrogen can leach silica out of the refractory. In one case, the waste heat boiler inlet tubesheet refractory failed after several days of standby firing with H_2, apparently because operators considered it prudent, in the absence of

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concern over soot formation, to operate under excessively substoichiometric conditions to ensure no excess air.

In addition to compromising refractory insulating properties, silica will tend to re-deposit on the boiler tubes to form a thin, hard, and often unnoticeable, layer resulting in serious reduction in heat transfer efficiency and virtually impossible to remove.

In one project, a new unit was designed for hydrogen firing, but only late in construction was it realised that the supply could be either essentially-pure PSA hydrogen, or reformer hydrogen containing ~10% hydrocarbons, and the SRU operator was often unsure of the source. Molar air demand of the reformer hydrogen was around twice that of the PSA hydrogen,and variable.

Shutdown procedure

Shell's recommended shutdown procedure is outlined below.

During normal operation, the Claus main burner operates with acid process gas and burns under deeply substoichiometric conditions, i.e., with very little air. Only a third of the available hydrogen sulphide burns to sulphur dioxide to achieve the Claus equilibrium.

The shutdown sequence has the following steps:

- heat soak operation of the catalyst beds to remove elemental sulphur from the catalyst;
- sulphur stripping of the SRU with fuel gas firing with controlled excess air.

Heat soak operation

Sulphur is removed from the catalyst beds before a shutdown during a heat soak operation in which the burner uses acid gas. For units that use a fuel-gas-fired inline heater upstream of the catalyst beds, there is the additional risk of soot forming during this procedure. To raise the catalyst bed temperature, the inline burner must fire at an increased rate when the throughput is kept constant. Careful consideration should be given to the operation of the inline burners during this procedure. When firing at maximum rate, the burner may produce more soot. In addition, there is less controllability of the fuel gas air to the burner. Decreasing the acid gas load to the SRU should be considered as a way to achieve a heat soak operation using the inline burners at the normal operating range.

The use of steam reheaters in the SRU is beneficial is this respect. They eliminate the risk of soot formation and oxygen slip from the inline burner. For new designs, steam heating of the catalyst bed is the standard approach.

Sulphur stripping operation

After the heat soak, sulphur stripping is performed to remove as much sulphur from the system as possible. This operation uses fuel gas only. The starting point for sulphur stripping is the addition of fuel gas to the SRU burner and the reduction of acid gas firing to zero. The temperature of the catalytic bed temperature is reduced to normal operating temperature. The fuel gas firing is substoichiometric. Therefore, quench steam is required to moderate the flame temperature. This situation is equivalent to the hot standby mode described for start-up operation.

Sulphur stripping starts by gradually adding air to the same amount of fuel gas. The excess oxygen oxidises the iron sulphide to sulphur dioxide and iron oxide. These reactions are both exothermic and can cause any sulphur accumulated in piping and equipment to ignite. Careful temperature monitoring of the catalysts beds is required to avoid sulphur fires.

During sulphur stripping, the same guidelines for soot prevention are applicable as for start-up of the unit when transferring to substoichiometric firing of fuel gas. However, avoiding sulphur fires is paramount. In the event of a sudden temperature rise anywhere, the recommended action would be to ensure substoichiometric firing of the fuel gas. This removes oxygen from the system and stops the exothermic reactions.

When full excess air is reached, the temperature can be dropped, the flame can stopped and the unit purged with air to cool it down. This shutdown operation may take 3–5 days, depending on the size of the unit.

Extreme turndown

As rates are increasingly reduced below 20% of design, ambient heat losses account for a greater share of the process heat, eventually leading to one or more of the following limitations:

- reaction furnace temperature too low for hydrocarbon and/or NH_3 destruction;
- sub-dew-point converter temperatures;
- sulphur fogging in the condensers;
- sub-freezing condenser temperatures.

Co-firing natural or plant-produced fuel gas is common and many, but not all, plants do so without making soot. As discussed elsewhere, soot formation is presumed due to insufficient furnace temperature. In all cases, Claus recovery suffers due to increased COS/CS_2 and tail gas dilution with CO_2, H_2O and N_2.

In a 2-zone reaction furnace (for NH_3 destruction in zone 1), WorleyParsons prefers to co-fire natural (or plant-produced fuel) gas with excess air in zone 1 while routing all amine acid gas to zone 2, avoiding all risk of soot and increased COS/CS_2. However, this rules out NH_3 processing, which would have to be done in zone 1 with deficient air to avoid NOx conducive to downstream sulphuric acid.

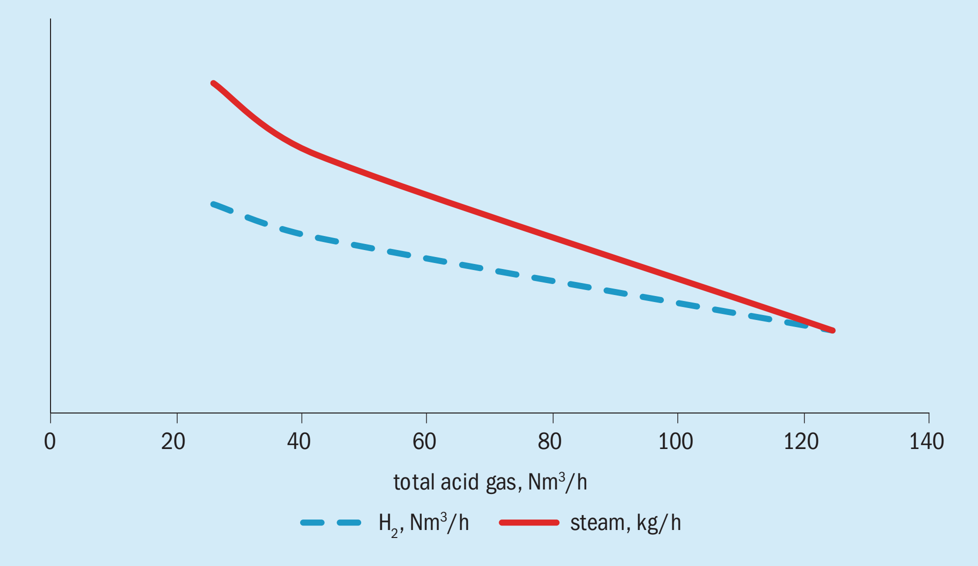
A 10-t/d SRU was successfully operated at 10/1 turndown for four years by co-firing natural gas in zone 1 with all amine acid gas (50% H_2S) routed to zone 2. However, WorleyParsons was reluctant to endorse NH_3 processing for fear that failure to optimise conditions would result in soot or NOx, and frequently excessive hydrocarbons in the amine acid gas often generated soot which, in addition to producing dark sulphur, fouled the catalyst beds.

A subsequent study by WorleyParsons recommended enrichment of the acid gas (including NH_3) with reformer H_2, with all feed to zone 1. In order to sufficiently increase mass flow to maintain converter temperatures above the dew point, LP steam was also injected into the burner to limit reaction furnace temperature to 1,400°C (Fig. 7)

Some optical pyrometers will not accurately register the H_2-rich flame temperature, although some more recent pyrometers are able to do this. An alternative is to install triple-redundant thermocouples in the 4" sight port on the side of reaction furnace zone 1, essentially measuring the temperature at the refractory face. Upon switching to H_2 mode, pyrometer temperature indication dropped more than 200°C as anticipated, but thermocouple indications also dropped unexpectedly by almost as much (Fig. 8)

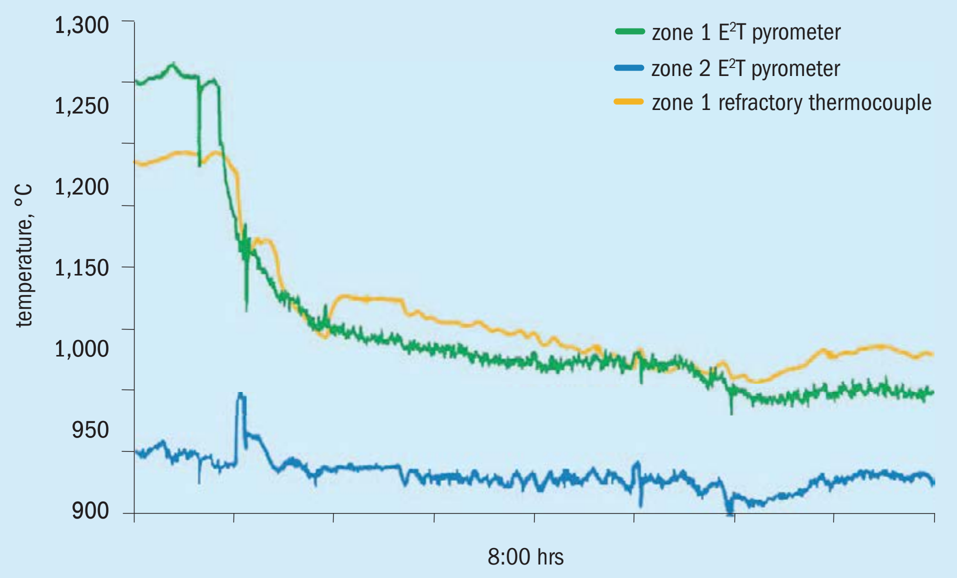
Eventually it was recognised that radiation, and hence refractory temperature, is relatively high for a hydrocarbon flame, whereas H_2 has virtually no luminosity. In addition, heat loss relative to release is higher in a small unit because shell surface area is proportional to diameter squared, whereas heat release is proportional to diameter cubed, i.e. larger furnaces tend to operate hotter[5].

Fig 7: **Steam and H_2 rates as a function of load** sanitized



Source: WorleyParsons

Fig 8: **Effect of H_2 co-firing on reaction furnace temperatures** ad hoc trend



Source: WorleyParsons

Success of H_2 enrichment exceeded expectations in the sense that soot generated by frequent hydrocarbon excursions was virtually eliminated. This is attributed to the combined effects of higher temperatures, soot-suppression by H_2/H_2O, and increased mixing and residence time achieved by routing all acid gas to zone 1.

Removing soot

Soot initially collects on top of the catalyst downstream of the burner and can be distributed throughout the train, with some of it ending up in the sulphur pit.

The impact on operations depends on the amount of soot deposited. The catalyst bed acts like a filter, impeding particulate flow. As soot builds up, pressure drop increases and flow through the unit diminishes. Blockage of this type is typically dealt with by shutting down the SRU and skimming the top layer of catalyst. Fluor typically recommends skimming and replacing at least the top 100 mm of catalyst in the converter(s). Determining how much catalyst to replace is relatively easy because the catalyst contaminated with soot will be black or dark gray and the catalyst without soot is white.

Many facilities, however, do not have excess SRU capacity, so an SRU shutdown for catalyst replacement can be very costly due to reduced plant production for three or more days. An alternative method that does not require an SRU shutdown is to perform a "sulphur wash".

According to BASF, the sulphur wash procedure will restore pressure drop, but not catalyst activity. Only removing and replacing the effected catalyst will regain the activity lost by soot deactivation. However, this deactivation rarely extends very far into the catalyst bed. Since only a small portion of the entire bed is affected, conversion through a "washed" bed will be the same as before the sooting episode.

Another method, whereby excess air is introduced to burn off the soot, is not recommended because of the uncontrolled nature of this burn off and the inherent danger of a sulphur fire.

Sulphur wash

The concept of the sulphur wash was first brought to the attention of the worldwide sulphur recovery industry by Saudi Aramco in 2001[6]. In this paper, the authors reveal a procedure which involves operating the Claus converter bed below its sulphur dew point, causing elemental sulphur to condense and build up inside the catalyst bed. After a certain time, the Claus converter is heated back to above the sulphur dew point and the liquid elemental sulphur is released from the catalyst bed, bringing with it the soot deposits which have collected on the bed. After this procedure, the pressure drop across the Claus converter was restored to its original condition.

Since this first milestone paper, others have presented their experiences with sulphur washing at other industrial conferences. Toor and Balken reported similar experience to those described by Saudi Aramco, with a few minor differences[7]. Their experience indicates that the pressure restriction is removed during the heat soak step (i.e. as sulphur begins to leave the catalyst), rather than during sub-dew point operation. In a paper presented by Akram, the evidence presented seemed to indicate that catalyst activity – in addition to pressure drop – could be decreased due to the soot collection on the catalyst bed[8]. However, due to other circumstances mentioned in the paper, the relationship between soot formation and decreased catalyst activity was not conclusive.

The effect of a sulphur wash on the catalyst has also been studied by Jacobs. It was found that catalysts (including SUPERCLAUS catalyst) are not damaged by such a sulphur wash.

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Not all process licensors recommend this method in their licensed units but each of these authors and many other operators agree that the sulphur wash is a useful method for removing flow-restricting soot deposits from the Claus converter bed.

In cases where catalyst activity appears to be affected, the form of carbon contaminating the catalyst may not be soot. The formation of carbon-sulphur polymers by interaction of aromatic hydrocarbons in the process gas with elemental sulphur on the catalyst to produce "carsul" is now a fairly well-understood phenomenon (see photos in Figs 9 and 10 and article p.46). Several papers by ASRL provide a thorough review of the formation of carsul, and why catalyst activity is so difficult to regain after carsul has formed and deposited on the catalyst bed. In their most recent paper on the subject of carsul, ASRL demonstrates that online treatments, including the liquid sulphur wash, are unsuccessful at removing these contaminants[9].

Fig 9: **BTX contamination**

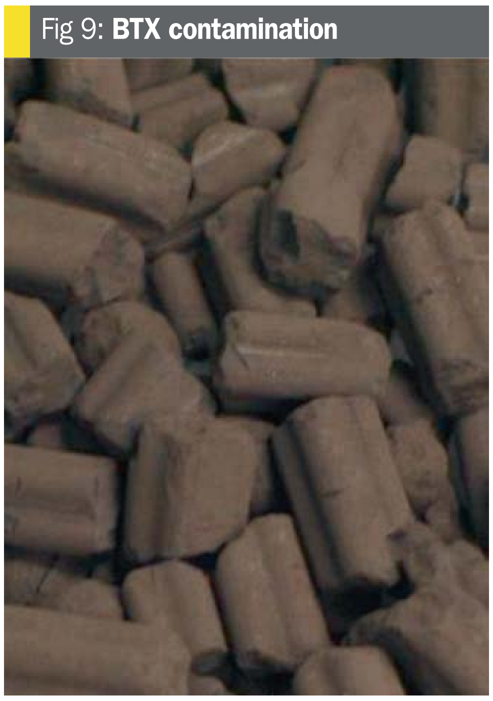

Fig 10: **Sooting**

PHOTOS: BASF

Sulphur wash procedure

The recommended method for sulphur wash may be broken down into four steps. First, preparation for the sulphur wash must be made both in modified unit operation and in completing some key analysis. Second, the Claus converter that has been affected by soot is cooled to the sulphur dew point. Third, liquid elemental sulphur collects inside the catalyst bed. Finally, the Claus converter is brought back up to and above normal operating temperatures and the sulphur is released from the catalyst bed, removing soot deposits.

Unit monitoring during normal operation

Normal unit operation should include tracking of front-end (reaction furnace) pressure, typically measured at the air plenum on the main burner. There are three ways in which reaction furnace pressure may be measured. The simplest method is simply using the pressure indication at the main burner. This pressure is typically tied to the emergency shutdown system (e.g. "high reaction furnace pressure") to prevent deflagration of the reaction furnace.

A more accurate indication of the pressure drop is the "normalised" pressure drop; this method corrects the measured pressure at the main burner for variation in the volumetric flow rate through the SRU. Tracking the normalized pressure (P_{norm} in the equation below) can help to identify when increases in front-end pressure (ΔP, below) are due to increases in flow (F_i, below) or due to other process abnormalities.

$$P_{norm} = \frac{\Delta P}{\sum(F_i)^n}$$

Applying this equation to the ideal case of flow through a straight length of pipe, the exponent $n = 2$. The exact value of n will vary with sulphur recovery unit design; however, the overall principle of pressure drop increasing with flow remains true[10]. Because of this, using the exponent $n = 2$ will provide a fair representation of normalized pressure drop.

With careful monitoring, an operator can use relevant historical operating data and unit design information to monitor normalized pressure drop over time. This is completed using a quantity called the capacity ratio (CR), or "plugging index" (adapted from[10]). The CR for a given SRU is calculated as follows.

$$CR = \frac{X}{X_O}$$

$$X = \frac{\Delta P}{\sum(F_i)^{n_i}}$$

$$X_O = \frac{\Delta P_O}{\sum(F_{Oi})^{n_i}}$$

Where: X = Current Ratio

ΔP = Current front-end pressure, or unit pressure drop

F_i = Volumetric flows through unit

X_O = Ratio at Design or "Clean" conditions

ΔP_O = Front-end pressure, or unit pressure drop, at Design or "Clean" conditions

F_{Oi} = Volumetric flows through unit, at Design or "Clean" conditions

n_i = Exponent for each flow component F_i

The capacity ratio method more accurately accounts for variation in flow rates, and also relates the magnitude of the change to the design value. Some operating engineers report that they are able to identify a flow restriction in the SRU most rapidly by monitoring capacity ratio. Others determine the value of the ratio at "clean" start of run conditions, and determine the exact value of each exponent n_i for their SRU. Certainly, the more accurately the front-end pressure is corrected to differences in flow rate, the more exactly the operating engineer could determine when plugging may be an issue.

When plugging occurs, no matter where in the unit the flow restriction is located, the capacity ratio and normalised pressure drop will show a marked increase from normal operation. This is the process engineer's first sign that a sulphur wash may be necessary.

Step 1: Preparation for sulphur wash

When it has been confirmed that the front-end SRU pressure is higher than expected at the given operating conditions, the location of the restriction should be identified. The process engineer's tools for identifying a flow restriction are rundown line monitoring and pressure surveys.

Sulphur rundown lines which include a look box or other view of the flowing sulphur may be monitored in order to identify the general location of a flow restriction

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(e.g. "between the second condenser outlet and the third condenser outlet"). The relative or absolute flow of liquid sulphur from each condenser would in this case be compared to the predicted or typical sulphur flow, as determined using computer simulation or prior plant testing data.

However, monitoring look box sulphur flow is not the safest method for identifying a flow restriction. Especially in abnormal operating cases, the "look box" is the most dangerous location within the SRU: look boxes can and have been the source of release of hot liquid sulphur and process gases outside the seal leg, putting nearby personnel at risk.

The best available alternative to monitoring sulphur flow in the rundown line is to conduct a pressure survey. While the pressure survey is not the most glamorous (and certainly not the least labor-intensive) method of determining locations of exceptional pressure drop, it is the most definitive. Typically, a pressure survey will identify a single location which accounts for the majority of the pressure drop through the unit. If the identified location of high pressure differential is across one of the converter beds, soot may have formed and caused a flow restriction within the bed.

Step 2: Determine duration of sulphur wash

Once the affected catalyst bed has been identified, the duration of the sulphur wash must be determined.

It is instructive to recall at this point that the goal of the sulphur wash is to collect some elemental sulphur inside the catalyst pores, then to evaporate that sulphur to "wash" away soot particles which have collected on the outer portions of the catalyst particle or between catalyst beads. In other words, filling the catalyst pores completely with sulphur is not a requirement for a successful sulphur wash. Since the soot particles do not penetrate far within the catalyst pores, the entire *pore volume* of the catalyst need not be filled with sulphur to push the soot out. To the contrary, since soot particles tend to collect at the outer surface of the catalyst – and, by becoming situated between catalyst particles, cause restriction to flow through the catalyst bed evidenced by increased pressure drop – only a small amount of sulphur is needed to "wash" away the soot.

In addition, since the entire pore volume of the catalyst will not be filled with sulphur, the catalyst will retain some catalytic activity. Certainly, if the entire pore volume of the catalyst were filled with sulphur, mass transfer of reactants to and products from the surface active sites would be restricted and conversion would decrease to below acceptable levels. However, as demonstrated in earlier work, modern high-macroporosity Claus catalysts can achieve close approach to Claus equilibrium even when operated below the sulphur dew point as sulphur collects on and deactivates the catalyst[11], although this has been demonstrated to vary with time on stream[12]. By determining the required duration of the sulphur wash, the procedure may be completed with minimal impact on plant recovery efficiency.

The duration of the sulphur wash is determined by two factors: the desired sulphur loading and the rate at which sulphur is produced in the reactor. Past work by others specifies a sulphur loading of 35% of the catalyst bed by weight[6,7]. For example, during a sulphur wash completed in a reactor containing 10,000 pounds of alumina Claus catalyst, 3,500 pounds (mass) of sulphur would be accumulated. For modern high-macroporosity Claus catalysts, 35% of the catalyst bed by weight represents less than half of the maximum sulphur loading capacity of the catalyst bead and is considered a conservative target value. Some sub-dew point Claus converters are designed to achieve a maximum sulphur loading of 50% by weight of the catalyst bed.

The maximum sulphur loading capacity may be limited by the crush strength of the spherical bed support below the catalyst bed, or by the mechanical strength of the steel supporting the catalyst bed. The exact crush strength of the spherical bed support will vary with the type (active or inert spherical bed support) and manufacture of this material. Although typical active or inert bed supports are sufficiently strong to withstand the added load during a sulphur wash, the strength of the material should be compared to the predicted loading of sulphur onto the Claus catalyst. In addition, the design of the steel support structure located below the catalyst bed must have sufficient strength to withstand the additional weight load of sulphur, in addition to the weight of the catalyst bed, at operating temperature.

The rate at which sulphur is produced in the reactor is a function of reactor feed composition, flow rate, and temperature. In addition, Claus conversion (and thus rate of sulphur production) will be increased at the lower temperature condition during the sulphur wash. Predicting the rate of sulphur production at the sulphur wash conditions is most easily completed using a Claus plant simulation software, since the operating temperature of the affected Converter will be lower than normal operating conditions. Alternatively, the rate of sulphur production within the converter may be determined by measuring or estimating the rate of liquid sulphur flow from the condenser immediately downstream of the affected converter.

The final point of preparation for the sulphur wash is to identify the sulphur dew point of the affected catalyst bed based on the current feed composition and conditions. As with the rate of sulphur production, this is most easily completed using a simulation software. If a computer simulation is not available, the sulphur dew point may be determined empirically by lowering the converter temperature step-wise until the bed temperature profile begins to indicate deactivation.

As a final preparatory step for sulphur washing, it is recommended to minimise the liquid sulphur level in the sulphur pit (or rundown tank) to the minimum level. The sulphur wash procedure may produce liquid sulphur that is contaminated with carbon, and may appear grey or black. Therefore, it is desirable to minimise the amount of sulphur product that is contaminated with this grey or black appearance; minimising the level in the sulphur pit restricts the amount of contaminated sulphur to the minimum.

Step 3: Sub-dew point operation

This portion of the procedure has been documented well by several sources, and essentially involves the following procedure:

- cool reactor to sulphur dew point;
- allow sulphur to condense for a predetermined amount of time;
- monitor bed deactivation;
- raise reactor temperature;
- heat soak.

As the reactor is cooled to and then below the sulphur dew point, elemental sulphur will condense in the catalyst pores. Sulphur will condense first in the catalyst micropores by capillary condensation, and will gradually fill the successively larger pores. The catalyst will begin to lose activity over this period, although laboratory studies have indicated that the extent of activity loss is rather small[11], especially for the portion of the converter which remains above the sulphur dew point[12]. Bed deactivation may be monitored using the bed thermocouple profile. Extensive discussion on the topic of using bed thermocouples to monitor catalyst activity has been provided previously[13].

Once the pre-determined time of sulphur condensation has been reached (reference Step 2 above), the affected converter is gradually heated to 30-60°C above normal operating temperature. With this "heat soak" step, the operator will ensure that the maximum amount of sulphur is driven out of the catalyst bead. The greater the amount of sulphur driven out of the catalyst, the greater is the propensity for soot removal from the bed.

During this heat soak step, the sulphur produced from the condenser downstream of the affected converter will contain the soot driven off of the catalyst bed. Typically, this sulphur is not suitable for sale on its own, although sulphur quality requirements may differ by region and application.

Step 4: Return to normal operating conditions

After completing the sulphur wash and heat soak, it is important to re-evaluate unit operation to determine whether the sulphur wash successfully removed the flow restriction in the affected converter. At this time, the capacity ratio and/or normalized pressure drop should be determined and compared to design values. In addition, a replicate pressure survey through the SRU can help to identify whether the restriction was removed entirely or partially.

Future work

Future work on this topic can shed some additional light on both the sulphur wash procedure and the design of equipment, controls, and catalyst. The formation of soot in hydrocarbon-only combustion is known to occur below a certain critical carbon-to-oxygen ratio (C/O_{crit}), which varies with the hydrocarbon species being combusted[14] – there is a specific sub-stoichiometric limit below which soot is known to form, in the vicinity of C/O = 0.5. However, in sulphur recovery units, no value such as a critical C/O has been identified. Such a determination would be central to the instrumentation and design of co-firing systems to produce minimal soot.

Studies on the mechanisms of hydrocarbon destruction in the Claus reaction furnace have indicated that any oxygen present would be more rapidly consumed by oxidation of H_2S, rather than the hydrocarbon compounds[15]. It may be concluded that the conversion of hydrocarbons is completed via oxidation with S, SO_2, and other potentially oxidizing species. Then, perhaps identification of a critical C/(O+S) ratio would facilitate more accurate prediction of soot formation limits in SRUs.

The behaviour of the catalyst during the sulphur wash also remains somewhat unknown. The value in examining the catalyst particles themselves during the process of removing soot via sulphur wash, as could be simulated in a laboratory environment, would be not only in optimising the sulphur washing procedure, but also in potentially designing a catalyst that is more resistant to plugging with soot or more amenable to soot removal. This may be particularly useful for tail gas hydrogenation catalysts, as these materials cannot be washed with sulphur online in the way the Claus catalyst can be.

A successful sulphur wash can alleviate rate restrictions on sulphur recovery units that have suffered from soot deposition on a Claus catalyst bed, but consideration of natural gas firing situations must be taken in the design phase to prevent the formation of soot altogether. While the exact conditions and mechanism of soot formation in Claus gas environments has not yet been identified, burner assemblies and control systems may be designed to minimise soot formation even in natural gas co-firing applications. ■

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How to avoid problems with BTX

Incomplete destruction of BTX in the Claus reaction furnace can lead to degradation of the Claus catalyst and reduced sulphur recovery. In this article we describe how BTX reaches the sulphur plant, how to minimise the amount of BTX in the acid gas feed to the SRU, and how best to deal with benzene toluene and xylene when present in the sulphur plant.

Hydrocarbons contained in the feed stream to a sulphur recovery unit (SRU) are not uncommon. Typically, they are destroyed in the Claus reaction furnace and pose no contamination issue to the Claus catalyst. By contrast, the recovery of sulphur from very lean acid gases (<50% H_2S) containing significant amounts of aromatic contaminants, such as benzene, toluene and xylene (BTX) is very challenging.

Gas treating

BTX enters the SRU via the acid gas feed from the upstream amine unit. The amine unit operates by contacting an amine solution with the sour gas or liquid feed countercurrently in an absorber column. H_2S and CO_2 in the feed are absorbed by the amine in the solution, and the sweetened gas exits the top of the column. Rich amine exits the bottom of the column and is sent through the regeneration system to remove the acid gases and dissolved hydrocarbons, including BTX. The lean solution is then circulated to the top of the absorber to continue the cycle. The sweetened gas exiting the absorber is saturated by water from its contact with the amine. If the raw gas contains appreciable amounts of H_2S, the overheads from the rich amine stripper, including BTX, are sent to a sulphur plant. This treatment normally destroys any BTX or other hydrocarbons.

Several operating parameters directly affect the amount of BTX absorbed in an amine unit, such as inlet BTX composition, contactor operating pressure, amine circulation rate, solvent type, and lean solvent temperature. MDEA absorbs the lowest amount of BTX compared to DEA and MEA; therefore, it is recommended to use MDEA where BTX is observed in the sour gas (if it is applicable).

The following strategies can be used to limit the BTX emissions from gas plants:

- minimise the lean amine temperature;
- use the best solvent for treating requirements;
- minimise the lean circulation rate
- the higher the stripper pressure, the lower the overall BTX emissions.

BTX destruction in the SRU

After BTX has been routed to the sulphur plant the challenge is to successfully destroy these aromatic hydrocarbons by the most optimal method.

BTX destruction in the SRU depends on an adequate combustion temperature in the reaction furnace which is a function of the H_2S concentration in the acid gas feed. If the H_2S concentration is low or medium, the combustion temperature should be calculated using a commercial simulation.

Often a minimum temperature of 1,050°C is quoted for BTX destruction; however, the required minimum temperature also depends on the residence time and mixing characteristics in the reaction furnace. Proper control systems and information from instrumentation is necessary to ensure good mixing and burning while maintaining a reducing atmosphere in the furnace.

The decomposition temperatures for BTX are:

Benzene:	1,050°C
Toluene:	~950°C
Xylene:	925°C

BTX is often found in lean acid gases (<50% H_2S). One of the solutions often applied for processing lean acid gases is a split-flow arrangement. By bypassing part of the acid gas, a higher front end temperature can be achieved in the reaction furnace. The disadvantage of this in the case of BTX is that unconverted BTX bypasses the hot zone and can lead to degradation of the Claus catalyst and reduced sulphur recovery.

The deactivation rates caused individually by benzene toluene and xylene are not equal. Xylene is the most unstable, deactivating most catalysts over very short periods. By contrast, the deactivation potential of benzene is over 80 times less than xylene, making it a minor contaminant at low levels.

Various engineering solutions exist in order to avoid BTX problems. Saudi Aramco published the results of its evaluation of available solutions to find the most appropriate solution to the operating problems faced in Shedgum and Uthmaniyah gas plants due to the presence of hundreds of part per million of BTX in the lean acid gases (<26% H_2S) processed there. After the consideration of several technologies it was concluded that most were not applicable.

Oxygen enrichment was concluded to be inappropriate, since calculations showed that acid gases of H_2S content lower than 38% could not be processed using a straight through furnace configuration with 100% oxygen, as the furnace temperature would be too low to achieve good flame stability. Fuel gas co-firing would have resulted in larger furnace off gas volumes to be processed (resulting in larger amounts of sulphur losses by vapour entrainment) and would have required revamping the reaction furnaces to keep the residence time that would allow BTX destruction. Co-firing fuel gas would also have resulted in a much larger proportion of the sulphur being present as CS_2

downstream of the furnace. Although acid gas enrichment could have been applicable, this option was rejected by Saudi Aramco for cost reasons. Finally, an original process was developed based on the adsorption of BTX on activated carbon.

This BTX adsorption process is of high interest since it solves the aromatic problems by preventing BTX from entering the sulphur recovery unit. Its principle is rather straight forward: the BTX containing acid gas is passed through a bed of activated carbon in which aromatics are adsorbed. The acid gas, once free of aromatic contaminants, can be safely processed using the existing bypass configuration units. Since the activated carbon bed has a limited BTX adsorption capacity, periodic regeneration of the beds is performed using high pressure steam. Three vessels per unit are required in order for the adsorption process to be continuous.

Despite its effectiveness in removing BTX, this process has a few major drawbacks that may limit its applicability for the treatment of acid gases that contain relatively high contents of BTX. For example, the installation costs tend to be high and a significant plot space is required. The steam required for the regeneration of the carbon beds and disposal of the contaminated water result in high operating costs. In addition, carbon beds have been found to form fines because of the adsorption/regeneration cycle and the presence of other heavy hydrocarbons in the feed reduces the adsorption capacity for BTX.

As mentioned, several options are available to increase the reaction furnace temperature but the best option for one case may not be feasible for another. A case by case approach to study the best solution is therefore required.

FEED preheat

Sometimes preheating the feed will provide an adequate combustion temperature in the reaction furnace. Both the combustion air and the acid gas can be preheated in order to raise the flame temperature. Usually, the combustion air is the first choice since it is more benign than the acid gas. There are also important pressure drop considerations. The upstream amine unit often limits the available acid gas pressure.

The extent of combustion air preheat is basically an economic decision, i.e. available heating medium and metallurgy. Steam at a suitable pressure level is preferred over a fired heater due to ease of operation and lower investment cost. It is also desirable to use carbon steel rather than more exotic and expensive piping and equipment material.

The extent of acid gas preheat is further complicated by the possibility of thermal cracking of its constituents.

When applying preheat, it is important to ensure that the burner is properly designed in terms of both process performance and mechanical integrity.

Oxygen enrichment

Oxygen enrichment raises the reaction furnace temperature, which ensures complete destruction of heavy hydrocarbons and ammonia, reduces formation of COS and CS_2, and shortens gas residence time requirements for contaminants destruction. Two major effects in using oxygen or oxygen-enriched air in place of air for combustion are higher temperatures and higher flame speeds. The degree of change depends on the degree of oxygen enrichment, but in the case of pure oxygen, temperatures may increase by 1,000°C and flame velocities by 10 times in round numbers. The combination of these two effects is to produce a hotter, shorter, more intense flame that is much better suited to the rapid destruction of combustible materials.

The potential of oxygen enrichment is limited however and cannot be applied with very lean acid gas. In addition, due to the large quantities of acid gas and thus of oxygen, oxygen enrichment requires an air separation unit on site.

Co-firing

Natural gas can be added to raise the flame temperature. Of course, this goes against conventional wisdom. Natural gas, if not completely combusted, causes catalyst deactivation even plugging and off-colour sulphur products. Even when it is completely combusted, the size of equipment will be larger due to the increased process gas flow, investment and operating costs will be higher and the overall sulphur recovery efficiency will be lower, because of higher sulphur vapour losses.

Natural gas supplement has been applied successfully for operating the Claus unit at greater than ten to one turndown. In any case, when contemplating natural gas supplement, investing in a high performance, high intensity and high cost burner is a must.

Scheme for very lean gas application

RATE has developed a scheme for cases with very lean H_2S in which fuel gas (not natural gas) is burned with excess air first in a proprietary high intensity burner. Most, or all, of the acid gas goes to the first zone of the reaction furnace, not to the burner.

The concept in this configuration is that the fuel gas and excess air burn stoichiometrically (conventional SRU is sub-stoichiometric) so there is no soot formation and the composition of the fuel gas is not important because additional excess air is provided while processing the lean gas. In this configuration, the residence time in the reaction furnace for destruction of BTX will be at least double that of conventional designs.

Acid gas enrichment

Lean acid gas with low H_2S concentration can be enriched with an acid gas enrichment unit to easily achieve a high enough reaction furnace temperature for BTX destruction. Paradoxically, the BTX concentration in the enriched acid gas has increased, but because of the higher reaction furnace temperature this is not a problem. An added advantage (as with oxygen enrichment) is that the SRU becomes smaller, because of the lower hydraulic throughput. Acid gas enrichment is very effective where the H_2S/CO_2 ratio is low and will achieve high CO_2 slip.

Rich “S-MAX”

RATE has developed a unique acid gas enrichment process called Rich “S-MAX” with a proprietary 2-zone reaction furnace and high intensity burner.

In the conventional scheme for a two-zone reaction furnace, hydrocarbons and mercaptans are bypassed to the second zone where the combustion temperature is inadequate for the destruction of heavy impurities, which cause soot formation and catalyst deactivation.

The combustion temperature is always higher in the first zone of the reaction furnace.

In the RATE scheme up to 75% of the amine gas is sent to the first zone of the reaction furnace and the remaining 25% is routed to the tail gas absorber in addition to the quench overhead that flows to the tail gas absorber. The tail gas amine unit is designed with a much higher amine loading (0.2 to 0.3 mol/mol) similar to the amine unit. The acid gas loading in

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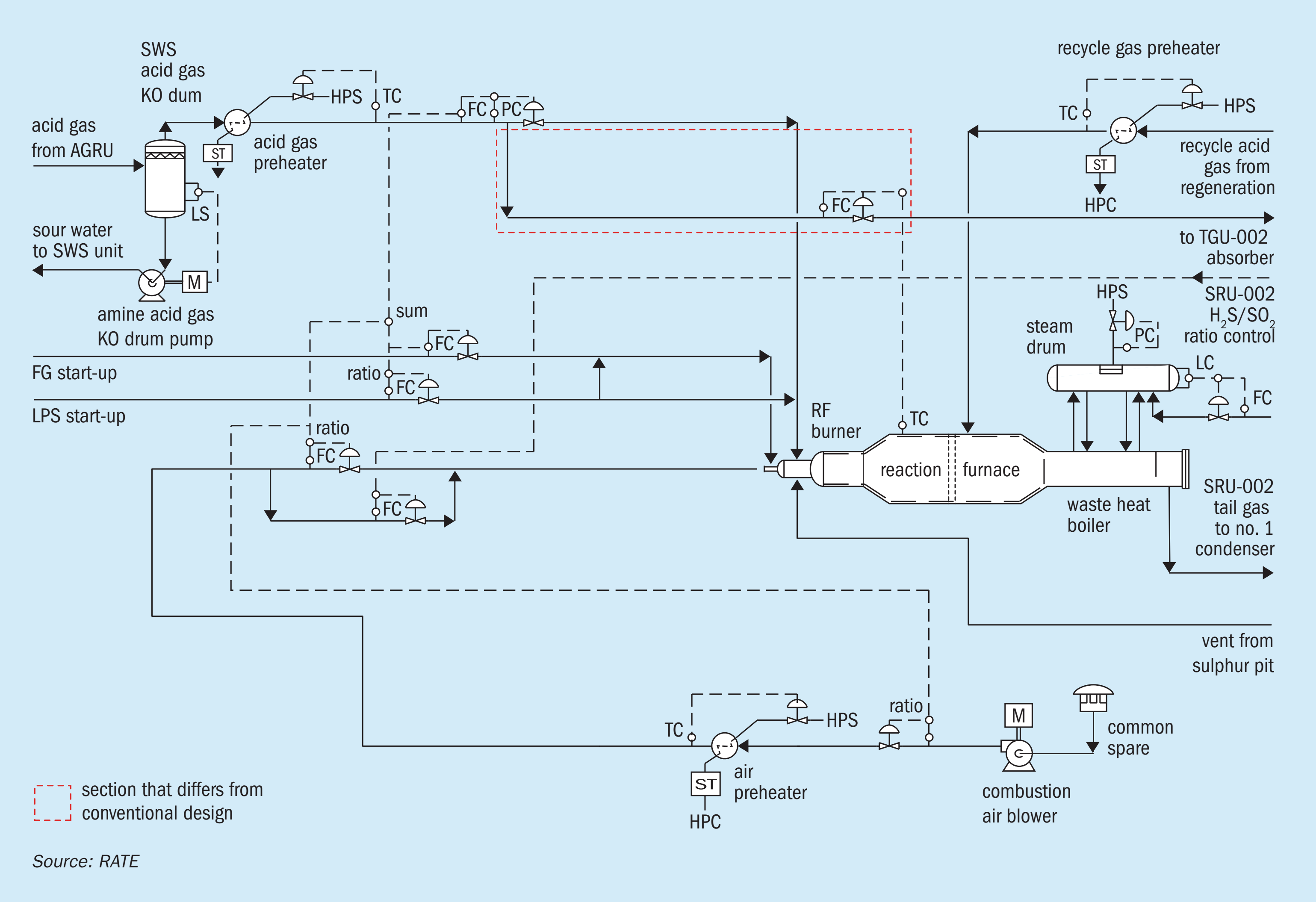
Fig 1: **RATE proprietary scheme of partial oxidation Rich-SMAX with the unique SRU scheme.**



Source: RATE

the tail gas absorber is normally 0.1 mol/mol maximum, and the acid gas loading for the amine absorber is normally 0.3 mol/mol, which means that there is significant free amine in the tail gas absorber to process the portion of the acid gas. The tail gas absorber acts not only as a tail gas absorber but also as an enriched absorber without adding significant cost to the project. This scheme also removes the hydrocarbons and mercaptans, which cause problems in the second zone of the reaction furnace. As the H_2S concentration increases, the 25% slipstream from the SRU feed to the tail gas absorber may be reduced as long the combustion temperature of 1,100-1,150°C is achieved in the first zone of the reaction furnace.

Figures 1 and 2 represent the RATE proprietary scheme of partial oxidation Rich-SMAX and the unique SRU scheme.

Jacobs engineered solution

As discussed in the previous sections, there are several options to cope with BTX in an SRU. To assess the deactivation by BTX in every option, Jacobs has developed a BTX estimating tool: BTX-Protect (part of the Comprimo® SRU Tools). BTX-Protect can be used both for new designs and for verification of existing equipment or operation.

With this tool the destruction of BTX in a reaction furnace can be estimated, based on parameters such as furnace temperature, residence time and split factor (if split-flow is used).

The tool further estimates the decrease of the CS_2 conversion rate as a function of Claus reactor temperature. BTX-Protect is used routinely by Jacobs in designing SRUs for acid gas containing BTX.

Preventing carsul formation

It is well known that higher hydrocarbons, especially BTX, can form carsul in a Claus plant. Carsul is a polymeric material containing carbon and sulphur, that is deposited in the pores of Claus catalyst whether it is alumina or titania. Carsul cannot be removed by conventional heat soak procedures or catalyst rejuvenation. The large carsul molecules plug the catalyst pores, prevent the reactants from reaching the active sites and the produced sulphur from exiting the catalyst.

The effect of this deposition is firstly experienced as a reduction of the hydrolysis activity of notably CS_2 on the catalyst. After prolonged deposition the Claus activity also deteriorates.

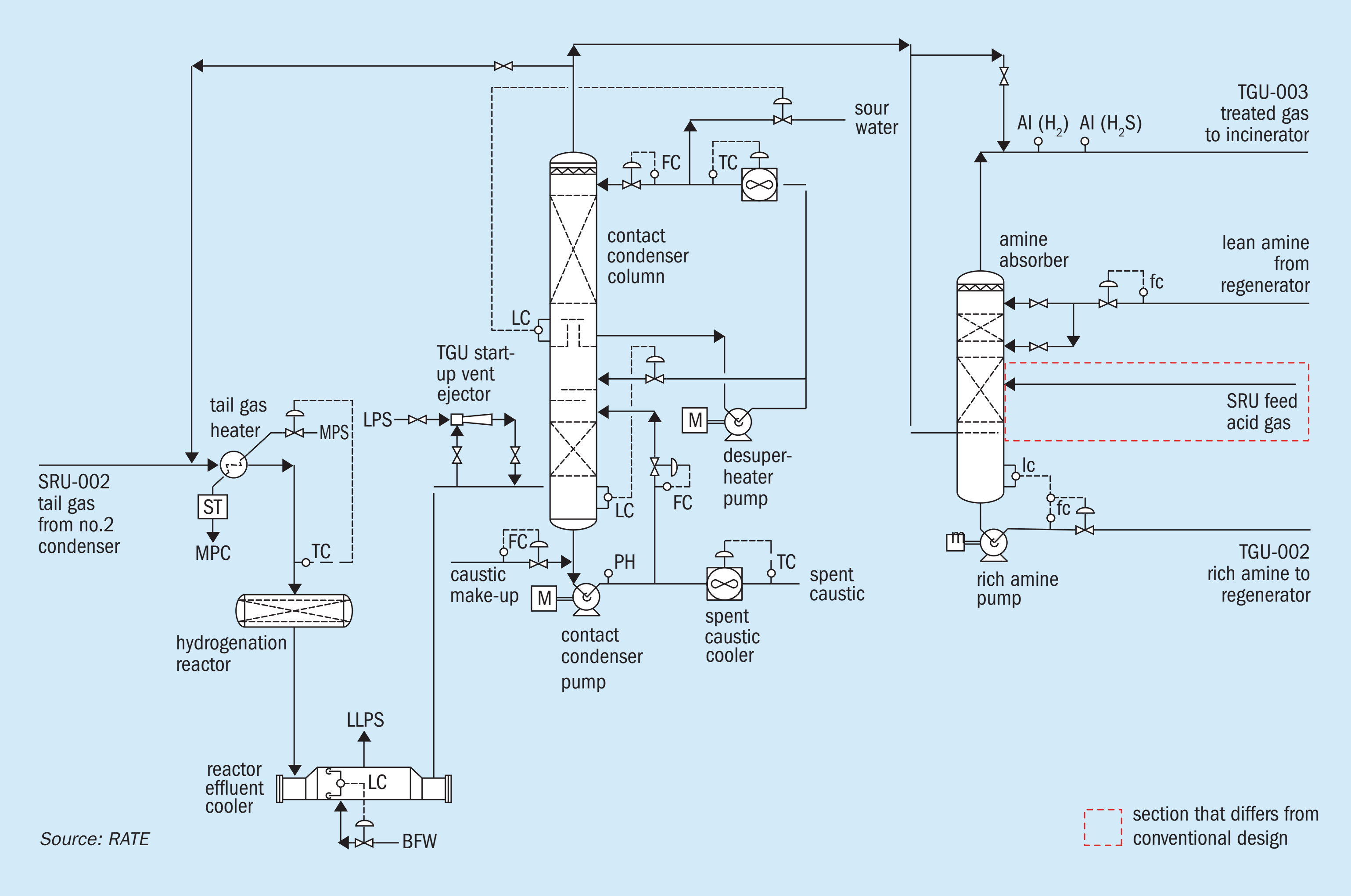
The mechanism by which BTX causes these deposits to form has been studied by ASRL. During these studies it was confirmed that the temperature in the catalyst bed is a major factor in BTX formation.

Besides carsul formation, BTX can also lead to soot formation and poor sulphur quality.

There are two strategies to limit the effect of BTX on the performance of a sulphur recovery unit (SRU): keeping BTX away from the Claus catalyst and, if that fails, minimising carsul formation on the catalyst.

Since carsul is only formed at high temperatures, an obvious approach is to limit the temperature in the bottom of the first Claus reactor to below 280°C. Because of this lower catalyst temperature the

Fig 2: **RATE proprietary scheme of partial oxidation Rich-SMAX with the unique SRU scheme.**



Source: RATE

hydrolysis of CS_2 is reduced. In such cases titania catalyst is preferred over an alumina catalyst because of its higher CS_2 conversion activity.

Axens BTX management catalyst

Axens has developed a BTX management catalyst (CSM 31) that can give some resistance to deactivation by BTX. It is applied in the top half of the first Claus reactor in combination with titania and protects the titania layer from deactivation. A possible explanation of this effect is that the BTX management catalyst converts part of the toluene and xylene into benzene and methane via hydro-dealkylation. Although deactivation by BTX still occurs, a longer catalyst lifetime is found with the combination of CSM 31 and titania catalysts.

Industrial experiences

The following cases illustrate some of the challenges and problems when treating lean gas containing BTX and the serious impact that carsul formation can have in Claus plants.

Case 1: Successful treatment of lean gas containing BTX

Qatar Liquefied Gas Company Limited (Qatargas) has executed a major debottlenecking of its existing facilities at Qatargas 1 in order to maintain the LNG production, while coping with increased levels of H_2S and CO_2 in the inlet feed gas streams. As part of this plateau maintenance project (PMP), a new pretreatment acid gas removal unit (AGRU), upstream of the existing gas sweetening facilities, an additional sulphur recovery unit (SRU) and a tail gas treatment unit (TGTU) have been added to existing facilities.

One of the challenges to be addressed for the design of the AGRU, the SRU and the TGTU of the PMP project was to treat 1,100 million std ft³/d of a lean gas containing BTX and to recover 880 t/d sulphur within the SRU + TGTU and incinerator within a limited surface area allocated to the project. This challenge was successively met thanks to the integration of the enrichment section and the TGTU absorber with the AGRU. The proposed scheme is based on a patented process of the AdvAmine™ technology licensed by Prosernat.

The main design features of the 1,100 million std ft³/d single train AGRU which treats lean gas with BTX within an integrated AGRU + low BTX enrichment section + TGTU absorber are highlighted below.

Feed gas and outlet specifications

The new gas treatment unit is designed to cover the complete range of feed gas flow rates and compositions given in Table 1, with a H_2S:CO_2 ratio down to 1: 2.51.

The main outlet guaranteed specifications are reported in Table 2 along with the performance test results.

AGRU + enrichment + TGTU absorber + common regenerator

The use of selective acid gas removal technology with MDEA was an obvious choice. However, the acid gas sent to the SRU in some cases contains less than 50% H_2S contaminated by up to 1200 ppmv of aromatics and mercaptans, which can adversely affect the good operation of the SRU unit. Therefore, the question of whether to use acid gas enrichment was raised. An independent acid gas enrichment unit (AGEU) could not be considered

Table 1: **Operating cases of new gas treatment plant**

	Design case P90 Summer/ winter	Normal case P50 Winter 2011	Turndown case 1% mol H_2S
Feed gas flow rate, million std ft^3/d	1 100	975	620
Feed gas temperature, °C	40.0	22.4	40.0
CO_2 content, % mole dry basis	3.2874	3.117	2.5136
H_2S content, % mole dry basis	2.0741	1.8273	1
H_2S in acid gas to SRU, mol-%	54 / 60	60	54
H_2S:CO_2	1:1.58	1:1.71	1:2.51
CycloC$_5$+ (ppmv)	395	286	496
Aromatics (ppmv)	401	400	400
COS (ppmv)	30	30	30
Mercaptans (ppmv)	270	270	270

Source: Prosernat

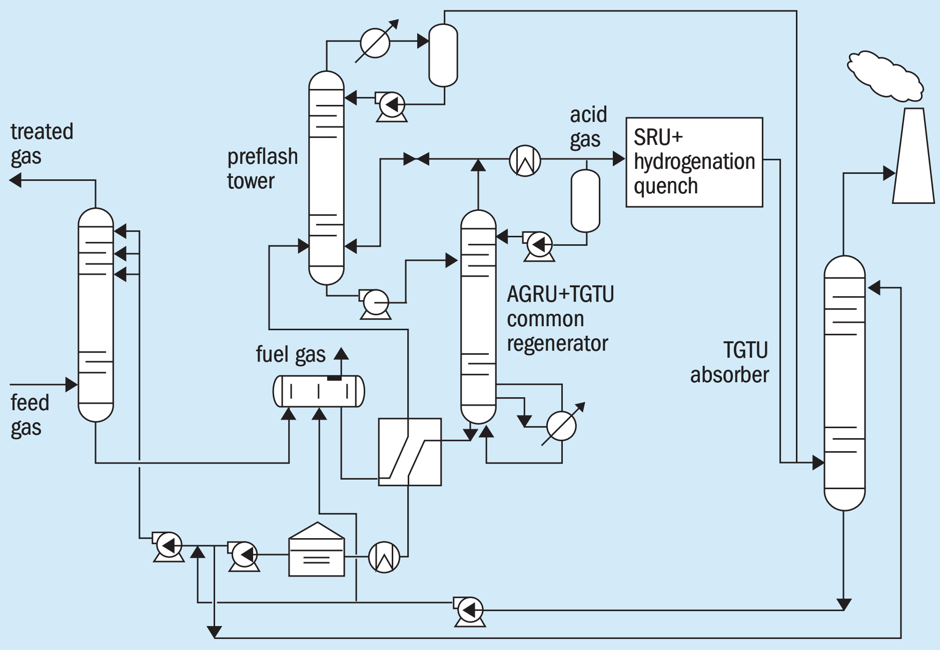
because of the limited plot area allocated to the new plant as well as the increase in capex and opex associated with the addition of an AGEU.

Different solutions were studied by Prosernat. After an international bidding phase Qatargas selected the AdvAmine™ MDEAmax technology, based on open market MDEA solvent, and integration of the AGRU + preflash low BTX acid gas enrichment section + TGTU absorber + common regenerator (see Fig. 3).

HP absorber

In the high pressure section, all treated gas specifications are achieved by contacting the raw feed gas with an amine solvent that is a mix of a very lean solvent and of "semi-lean amine solvent" already used in TGTU absorber. The fraction of each amine solvent can be adjusted to be as close as possible to the required H_2S specification, and the number of trays in the absorber is adjustable to control the CO_2 slippage.

Fig 3: **General AdvAmine™ process scheme of integrated AGRU + preflash low BTX acid gas enrichment section with acid gas recycle to TGTU + TGTU amine section + common regenerator**



Source: Prosernat

The recycling of semi-lean MDEA from the TGTU in the HP absorber allows the overall solvent flow rate to be reduced by re-using the semi-lean solvent, which is not fully loaded, in order to be above 0.67 mole of acid gas per mole of amine in solvent. In addition, it contributes to acid gas enrichment by increasing the quantity of H_2S in the solvent sent to the thermal regeneration.

Preflash for low BTX and acid gas enrichment

After the rich amine recovered at the bottom of the MDEA absorber is released to 7 barg through a level control valve in the MP flash drum, the rich solvent is preheated with the lean solvent from the bottom of the regenerator through the rich/lean MDEA exchangers. The hot rich solvent then feeds the preflash column at reduced pressure. The advantages of this new system are:

- the low pressure flash of a rich amine solvent preferentially vaporises CO , which is a simple way to enrich the rich solvent in H S, then the acid gas from the regenerator;
- the flash of the rich amine solvent also releases a large fraction of aromatics, which are sent to the absorber of the TGTU and then on to the incinerator.

The operating pressure can be adjusted by the operators. It controls the differential ratio of CO_2 and BTX released versus H_2S in respect of the composition and flow of sour feed gas to the HP AGRU. The lower the operating pressure of the preflash column, the higher the content of H_2S in the acid gas to the SRU will be. The configuration allows the concentration of the acid gas to be adjusted between 54 mol-% (when the operating pressure of the preflash column is 4 barg) to 60 mol-% or more, at lower operating pressures.

The new AGRU is equipped with an acid gas line that allows the acid gas to be recycled from the top of the regenerator to the preflash column. This facility is used to maximise H_2S content of the acid gas even when the feed gas contains only 1% of H_2S. The line can also be used during turndown conditions.

TGTU absorber

The LP flash gas from the preflash column is mixed with the tail gas from the SRU hydrogenation section and feeds the TGT absorber, where it is contacted with fresh

1 47 2 48 3 49 4 50 5 51 6 52 7 53 8 54 9 55 10 56 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46

Table 2: **Guaranteed and measured performances test results**

	Licensor guaranteed values	Measured performances during tests
AGRU design capacity, million std ft^3/d	1,100	1,100
Treated HP gas H_2S content, ppmv (dry basis)	< 600	463
Treated HP gas CO_2 content, mol-% (dry basis)	< 1.8	< 1.5
Treated tail gas H_2S content, ppmv (wet basis)	< 250	219
Flash gas H_2S content, ppmv (wet basis)	< 50	< 25
Flash gas pressure (upstream of PCV), barg	7	7.24
Acid gas pressure (upstream of PCV), barg	1.2	1.22
H_2S content in acid gas, mol-% (wet basis)	> 54	57.2
BTX in acid gas, ppmv	< 300 expected	< 80
Maximum reboiler duty, MW	≤ 115	< 10

Source: Prosernat

solvent from the regenerator to achieve the 250 ppmv H_2S specification and further sulphur emissions at stack.

Thermal regenerator

The rich amine from the preflash column is sent to one common regenerator where H_2S and CO_2 are stripped by the vapour generated in the reboiler. Finally, this single regenerator treats all the solvent flow used to remove acid gases in the HP absorber, in the MP flash absorber and in the TGTU.

Cooled lean amine solvent feeds the HP absorber, the MP absorber on the MP flash (in order to achieve 50 ppmv H_2S in the flash gas) and the TGTU absorber.

The plant is also equipped with a direct condensing section and vertical direct cooler with recycled water wash, on acid gas and treated gas in order to limit the pressure drop and also minimise the solvent losses. Filtration of the inlet gas and part of the solvent is also performed based on operational feedback from the licensor in order to achieve smooth operation of the unit.

Improved flexibility and operability

Depending on the feed gas composition (H_2S/CO_2 ratio and feed gas flow), the operating conditions of the AGRU are adjusted to achieve the required specifications, especially the concentration of H_2S in the acid gas. Two parameters are essential and specific to the good operation of the unit: the recycle rate of semi-lean amine in the solvent feed to the HP absorber and the operating pressure of the preflash column.

Performance tests

Performance tests took place at the beginning of 2015. Results measured during the performance tests are reported in Table 2.

The AdvAmine™ design meets the multiple process requirements with high operational flexibility: it meets the H_2S and CO_2 removal specifications in the treated gas, the high capacity plant cleans up the H_2S from the tail gas from the 880 t/d SRU to meet environmental emissions regulations and it secures the H_2S, RSH and BTX content in the acid gas (by a dedicated preflash column) in order to satisfy the design of the SRU furnace section. An additional acknowledged benefit of this giant unit is the decrease of the solvent circulation and of the solvent regeneration duty achieved by the recycle of semi lean solvent from the TGT column to the HP absorber.

All guarantees associated with the AdvAmine™ license of the integrated AGRU and TGT amine section at design and turndown capacities have been demonstrated without operational issues. In addition, operators have reported the simple and efficient management of the H_2S and BTX content of acid gas by the preflash column.

Case 2: Carsul formation in first converter

In November 2014, during a scheduled shutdown of Hellenic Petroleum's Thessaloniki Refinery due to a problem in the CCR unit, an unexpected phenomenon occurred in the sulphur recovery unit, which resulted in the shutdown of the SRU, making it impossible to operate the refinery.

The incident took place about an hour after starting the fuel gas stoichiometric combustion to provide heat-soak of the SRU to purge liquid sulphur from the catalyst. During the heat-soak procedure, there was a sudden and sharp increase of the firebox pressure in the SRU furnace. The pressure rose to above 0.4 kg/cm²g, activating the first priority alarm, and shortly afterwards increased to 0.5 kg/cm²g, activating the emergency shutdown system (ESD) set at 0.45 kg/cm²g and shutting down the SRU. The indication was that there was plugging at some point in the SRU and an investigation to identify the location of plugging was initiated.

Firstly, the five seals were checked. By purging nitrogen to the seals it was observed that there was nitrogen at the outlet of the second and third seal but not at the outlet of the other three seals.

The pressure at the first catalytic converter was then measured and was found to be 0.25 kg/cm²g, at the reactor inlet and zero at the reactor outlet. This was a strong indication that partial or full plugging of the reactor had taken place. It should be noted that the pressure measurements were made after the sulphur condenser (reactor inlet) and before the heat exchanger (reactor outlet), at existing sampling points.

The stoichiometric combustion effort was continued and for a period of about 12 hours several attempts were made to ignite the fuel gas burner, but all attempts resulted in a pressure increase of the firebox and consequent activation of the ESD.

A circuit purge with a hot nitrogen stream was carried out for about 24 hours at a rate of 300-400 m³/h. This was followed by a circuit purge with a cold nitrogen stream for another 24 hours at a similar rate. It is assumed that even a shorter period of purging, e.g. eight hours for each case of hot and cold nitrogen streams would be sufficient.

As a result of these actions, the reactors were sufficiently cool to be opened for inspection.

It was decided to inspect the part of the line between the reactor outlet and the heat exchanger inlet. In the event that no plugging was found, the suggestion was to change the catalyst. It was decided that the catalyst in the second catalytic reactor did not need to be changed since there was no indication of malfunction.

No plugging was found between the reactor outlet and heat exchanger inlet so the next step was to open the first catalytic converter and change the catalyst.

All actions were taken after communication and agreement with the manufacturer of the unit, Siirtec Nigi.

Reactor opening

The temperature of the catalyst when the reactor was opened was well below 50°C. Since there was more than enough circuit nitrogen purging, no special protection measures were required.

Before opening the reactor a directive was issued for the opening of the specific reactor as the procedure that was about to be followed would differ from previous procedures, since no stoichiometric combustion took place. Any gases trapped in the catalyst, as well as the pyrophoric nature of FeS, that would likely be present in the reactor, constitute a serious cause of possible problems while performing the work.

After opening the reactor a compact layer of material about 5 cm thick with some pockets at the surface was observed in the upper part of the catalyst.

Fig 4: **Compact material found on the top of the catalyst of the first converter**

Below this layer, the catalyst was in good condition with only a quantity of black powder (soot) around the catalyst that is typical for the catalyst when it is changed.

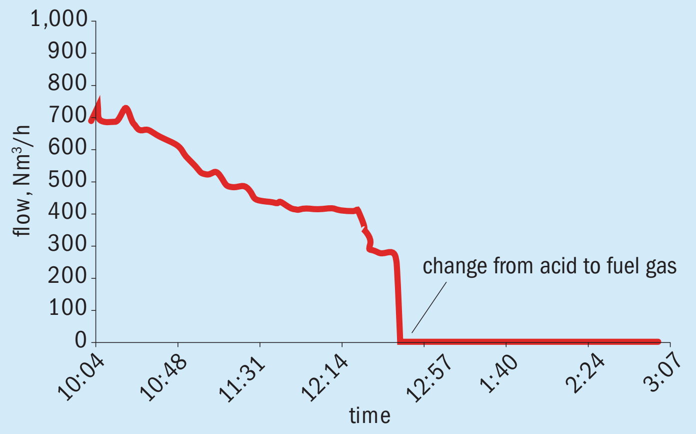
It should be noted that never before in the 30 years of operation of the SRU had such a thick, compact layer been found in the reactor. Previously only soot around the catalyst had been observed.

Fig 5: **Sample compact material sent to the laboratory for analysis**

PHOTOS: SIIRTEC NIGI

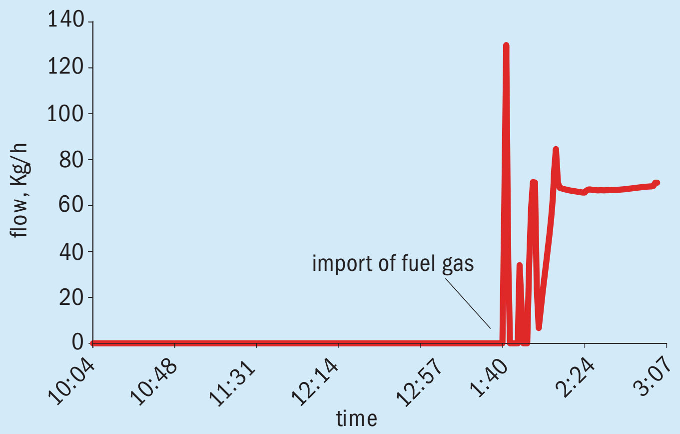
After the discovery of this phenomenon, it was decided to change the entire catalyst charge in the first catalytic reactor. Afterwards, the SRU returned to normal operation but remains under close monitoring as the efficiency is not yet satisfactory at about 93.5% on average, compared with a design efficiency of 96%.

Fig 6: **Change from acid to fuel gas in the furnace**



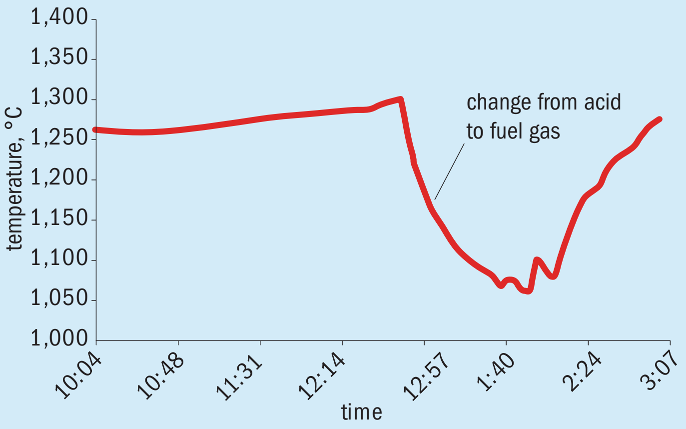
Source: Siirtec Nigi

Fig 7: **Import of fuel gas to the furnace**



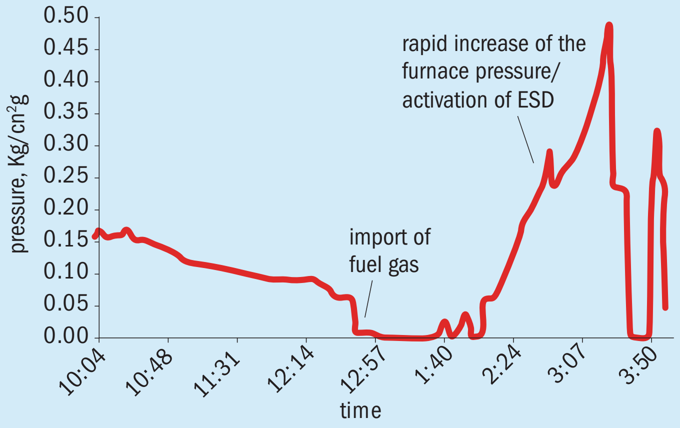
Source: Siirtec Nigi

Fig 8: **Fluctuation of the furnace temperature during the change from acid to fuel gas**



Source: Siirtec Nigi

Fig 9: **Fluctuation of the furnace pressure during the import of fuel gas/activation of the ESD**



Source: Siirtec Nigi

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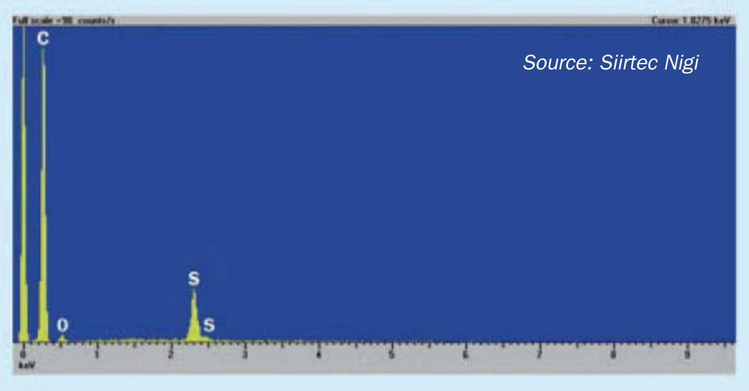
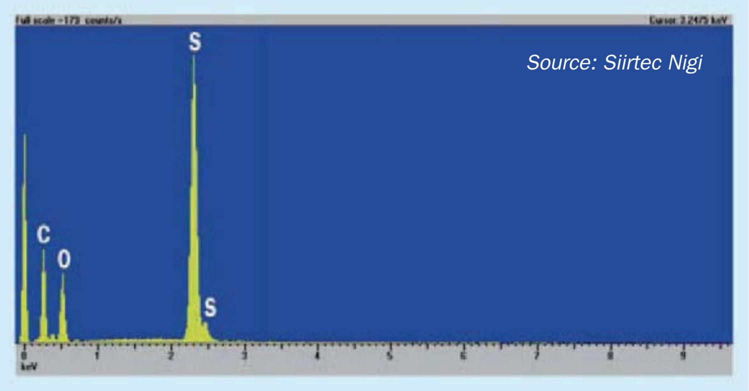
47 48 49 50 51 52 53 54 55 56

Fig 10: **Identification of metal compounds in the powder sample**



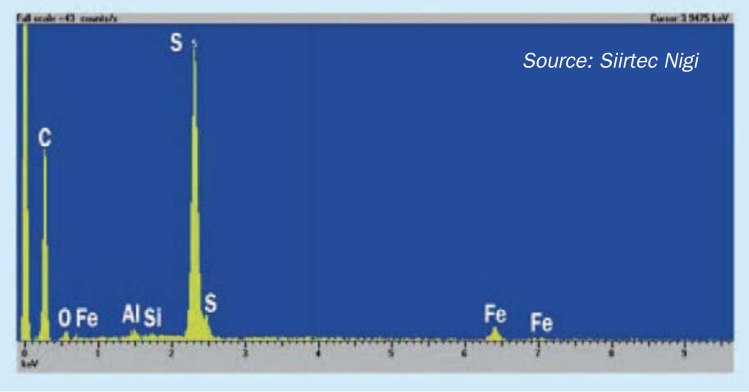
Source: Siirtec Nigi

Fig 11: **Individual grain in the powder sample with higher proportion of Sulphur**



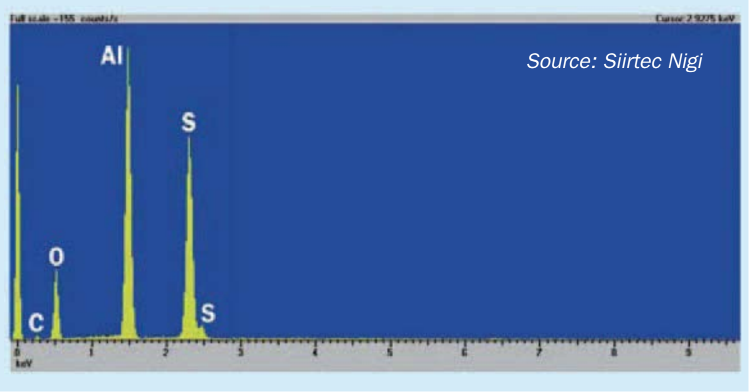
Source: Siirtec Nigi

Fig 12: **Indentification of metal compouds on surface of catalyst spheres**



Source: Siirtec Nigi

Fig 13: **Indentification of the composition inside the catalyst spheres**



Source: Siirtec Nigi

The photos in Figs 4 and 5 show the compact material that was found on the top of the catalyst of the first converter.

Main operating parameters

The main operating parameters of the SRU are shown in Figs 6-9.

Figure 6 shows the change in the furnace from acid gas to fuel gas. Figure 7 shows the import of fuel gas to the furnace. Figure 8 shows the fluctuation of the furnace temperature during the change from acid gas to fuel gas. Figure 9 shows the fluctuation of the furnace pressure during the import of fuel gas and activation of the ESD.

Laboratory sample analysis

A small quantity of the compact, black material was sent to an external laboratory for analysis.

An analysis was carried out to detect and identify the metal compounds in the mass using scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS).

In the test sample, the following components were analysed (see Figs 10-13):

- The black powder, which mainly consisted of carbon C and sulphur S.
- The surface of the spheres, where apart from carbon C and sulphur S, a quantity of ferrum Fe was found (Al: 2%, S: 89%, Fe: 9% – semi quantitative determination)
- The inside of the spheres, where it was found that it was alumina spheres (Al: 47%, S: 53% – semi quantitative determination)

The results of the laboratory analysis indicate that the compact material formed on the top of the catalyst in the first converter was the carbon-sulphur aromatic polymer, carsul.

According to ASRL, the rapid formation of carsul on the first converter is the result of the sudden incursion of a significant amount of hydrocarbons, perhaps in the form of amine.

It is also possible that the presence of large amounts of toluene or xylene could have been responsible. It has to be noted that benzene only minimally forms carsul. These aromatic compounds usually come from the hydrotreaters, which subsequently are treated in the amine (MDEA) unit and can pass to the sulphur recovery unit.

It all depends on how long the hydrocarbon ingress continued and if the catalyst is able to convert the CS_2, which is another product of the hydrocarbons. Laboratory studies have shown that carsul contaminated alumina Claus catalyst cannot be regenerated by any method that might be applicable in a field application. Once carsul has formed, the Claus unit has to be stopped and the catalyst replaced, i.e. it is not a reversible procedure. ■

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