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Number 367

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SULPHUR

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Sulphur markets

Sulphur and alternative energy

Waste heat boiler design

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Cover: *Magnified sulphur crystals. Paul Zahl / Getty Images*

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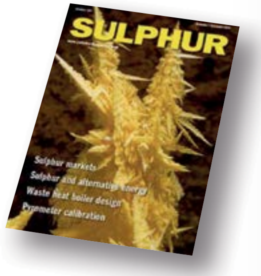
IMO pushing hard on sulphur phase-out



> **This is a seismic shift on an unprecedented scale in the history of refining and shipping.**

On October 28th, literally just around the corner from the offices where *Sulphur* magazine is put together, the International Maritime Organisation concluded the 70th meeting of its Marine Environment Protection Committee (MEPC70). The meeting decided on a number of issues, including a phase-out of the use of heavy fuel oil in Arctic waters. However, for readers of *Sulphur*, arguably its most important decision concerned the deadline for a global move from the present 3.5% limit on sulphur content of marine fuels (although this is already as low as 0.1% in designated emission control areas – ECAs) to a 0.5% cap on sulphur content outside of ECAs. Back in 2008, when the MEPC had first decided this, the date for the global sulphur cap could not be unanimously agreed and was left deliberately vague, with a target date of 2020, extendable to 2025 if this proved impractical. With 2020 fast approaching, the time had come to decide whether or not to extend that compliance deadline, and while the IMO had originally said it would decide this by 2017-18, it was agreed by all parties concerned that this was insufficient notice for refiners to gear up to producing sufficient low sulphur fuel, and so the decision was brought forward to this year instead.

In advance of the decision, there has been – inevitably – considerable lobbying by shipping companies and refiners that a deadline of January 1st 2020 would still not give the refining industry enough time to invest in the desulphurisation technology required to produce sufficient low sulphur marine fuel oil (LSFO) to go around, with the inevitable knock-on effect on fuel availability, and hence on fuel costs, and hence on the cost of shipping goods around the world. The international shipping association BIMCO criticised the study that the IMO had carried out into potential availability of LSFO, and had helped fund its own study, in cooperation with the International Transport Forum (ITF) of the Organization for Economic Cooperation and Development which said that the proposed 2020 cap would have a "significant effect" on shipping costs, increasing them by anywhere between 20-85%, and potentially adding total annual costs of $5-30 billion for the container shipping industry, while postponement to 2025 would result in a more modest increase of 4-13%. Conversely, environmental NGO Seas at Risk argued in its own health-related study that the five year delay would "contribute to 200,000 extra premature deaths due to the toxic fumes, mainly in coastal communities in the developing world that barely benefit from global trade" The EU had also previously said that it will impose its own 0.5% sulphur cap within 200 miles of European coasts from 2020 regardless of the IMO decision.

In the end, the IMO, taking the view perhaps that refiners are unlikely to invest in new sulphur removal capacity until they have a firm date to work to, took the decision to press ahead with the January 2020 deadline for the switch to a 0.5% sulphur cap. The news has, needless to say, been welcomed by proponents of other clean marine fuels such as liquefied natural gas (LNG) and methanol. However, the International Bunker Industry Association says that this is a "seismic shift on an unprecedented scale in the history of refining and shipping" equivalent to the switch in the early 20th century from coal to fuel oil to power ships. The 0.1% cap on sulphur in emission control areas affected around 100,000 bbl/d of fuel capacity, and still led to a spike in the price of marine gasoil, but the 0.5% worldwide cap will affect 2 million bbl/d of fuel production. It would also necessitate, assuming all fuel use switches to LSFO or marine gasoil (MGO) rather than using LNG or exhaust scrubbing technology, to an additional 5 million t/a of sulphur needing to be removed, over and above current installation of desulphurisation capacity to meet road transport fuel sulphur caps.

The implications for refiners are a potential scramble to install new coking capacity to process residual fuel oil, but the implications for the sulphur market are even more refinery sulphur finding its way onto an already oversupplied market over the next few years.

Richard Hands, Editor

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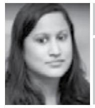
Price trends



MARKET INSIGHT

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

SULPHUR

Prices rise despite uncertain outlook

Global sulphur prices continued to rise through September and October as bullish sentiment prevailed from major producers. Continued downward pressure from the processed phosphates market has not stymied the push for higher prices in the Middle East. Producers have cited being sold out recently, concentrating on contract commitments and are holding expectations of revived interest from key markets China and India. Uncertainty is the key theme however, as buyers have been making purchases on a hand-to-mouth basis. On the supply side, we continue to see a relatively balanced market for 2016 overall, while the potential of two major projects starting up in 2017 would add more length to the market.

Monthly price postings from Middle East producers in October reflected further increases compared to September. Adnoc announced a $4/t increase to $81/t f.o.b. Ruwais for the Indian market. In Qatar, Tasweeq posted its price at $76/t f.o.b. Ras Laffan, up by $2/t. Meanwhile, in Saudi Arabia, Aramco Trading increase its October price by $3/t to $78/t f.o.b. Jubail. Despite the upward shift, sulphur prices in the Middle East still remain 50% below year ago levels and are down by around 30% since January 2016. Production in the Middle East for 2016 is expected to total almost 16 million tonnes, up by over 2 million tonnes on 2015, due to the ramp up of Al Hosn's Shah gas project in the UAE. Qatar's Barzan project was also expected to start up in 2016 but delays earlier in the year led to the project stalling. Another start-up was expected in October, however a gas leak in a pipe led to further delays. Both phases of the project are expected to add over 800,000 tonnes of sulphur recovery capacity once online, further strengthening the Middle East's position as the leading regional sulphur producer.

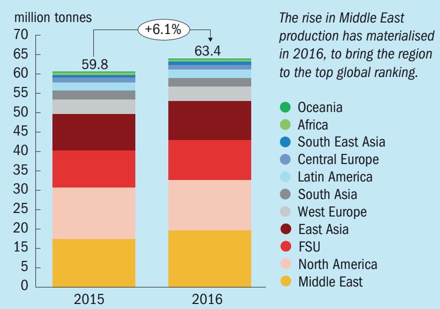
Spot prices in China also edged up on the back of the rise in the Middle East benchmark, also led by higher domestic sulphur prices. The ongoing issue for the market prevails however, as the downstream processed phosphates market remains a challenge. Sulphur and sulphuric acid imports for 2016 in China paint a different picture from a demand perspective however, as both have exceeded year ago levels. Sulphur imports to China totalled 9.4 million tonnes in January-September 2016, up almost 7% on the same period in 2015. Saudi Arabia continues to dominate trade to China, although we continue to see shifts across other trade routes. Molten sulphur from Japan and South Korea has increased by over 30% year on year. Meanwhile, shipments from the UAE now reflect an 84% increase. The drop seen in trade from Kazakhstan (60% down) reflects the depletion of TCO's block sulphur. Sulphur stocks at the nine major ports in China reached a peak of around 1.8 million tonnes this year, but has started to erode in October, heard down to around 1.6 million tonnes.

Over in India, spot prices increased in line with international prices, up to the low/mid $90s/t c,fr in early October. However, following tender activity, this eased slightly to the low $90s/t CFR. Sulphur consumers FACT, Coromandel, SPIC and MMTC all made purchases for October-November cargoes in the low-$90s/t c.fr range. IFFCO meanwhile was understood to remain comfortable, with price a factor in considering further purchases in November.

Fourth quarter contract discussions in North Africa led to settlements in October, with rollovers cited by one major buyer. In Morocco, OCP continues to ramp up its raw material requirements, with imports of sulphur and sulphuric acid increasing in line with the expansion of its Jorf Lasfar processed phosphates facilities. However, in Tunisia, sulphur consumption remains well below capacity, with disruption to the movement of phosphate rock impacting downstream production of phosphates. Looking ahead, GCT continues to target higher rates of production for 2017 of around 70% capacity, which would mean an increase in sulphur consumption compared to 2016.

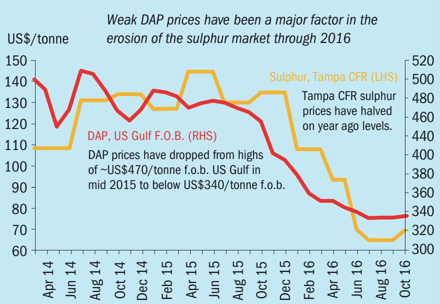
Elsewhere in Africa, Foskor was expected to purchase two cargoes of sulphur in the spot market for November and December arrival at Richard's Bay. Trade from the Middle East has continued to grow to South Africa in recent years, with the spot volumes expected to be sourced

Fig 1: **Sulphur supply by region, 2015 to 2016**



Source: Integer

Fig 2: **Sulphuric acid and sulphur prices, Mar 14 to Oct 16**



Source: Integer, ICIS

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there. Foskor's processed phosphates capacity is expected to be at 60-70% for the remainder of the year.

In the US market, sulphur production in the oil refining sector has continued to improve through the year. While refinery utilization rates have been slightly below year ago levels and gas based sulphur continues to show a drop, the switch back to heavier crudes has led to an uptick in oil based sulphur output. For 2016, Integer expects to see production at around 8.9 million tonnes. Exports from the US Gulf in the 1H of 2016 were on track to hit 900,000 tonnes for the year. However, refinery turnarounds in Q4 are expected to lead to a tighter balance, and current estimates for exports are lower, at around 825,000-850,000 tonnes.

Trade from Vancouver has seen an uptick in year to date of over 4% in January-August data. The main market has been China, a reversal on trends seen in the last couple of years. Australia had become the major market for Canadian sulphur, with a diminishing market share in China. With the start-up of the Cuba sulphuric acid plant, we would also expect to see increased trade to this market.

SULPHURIC ACID

Uncertain outlook

The slightly firmer footing in the global sulphuric acid market has dissipated, but stability remains. Northwest European export prices eased slightly, hovering at $5/t f.o.b. on the low end throughout October. Expectations going into November and December are to see continued stability, with potential for some softening. Smelter acid producer Nyrstar had operational issues at its Balen facility in Belgium during the third quarter, leading to a disruption in production. In Poland, KGHM conducted a three month maintenance turnaround, leading to significant loss of acid production. The smelter was due back online at the end of October.

Market focus is firmly on Latin America in the fourth quarter as discussions for 2017 contracts in Chile are getting underway. Price discussions may be protracted due to the gap between the buyers and sellers. Spot prices in Chile have dropped in recent months down into the $20/t c.fr Mejillones range on the low end. This compares to contract prices set for 2016 in the $50s/t c.fr. The downturn in the copper market continues to weigh on demand in Chile, leading to softer imports of sulphuric acid so far. Based on data through to June, expectations are for the deficit to drop below 2 million tonnes.

Spot demand in Brazil has led to prices easing in October, slightly lower at $35-45/t c.fr. There has been a weaker sentiment in both sulphur and sulphuric acid trade to Brazil through the year, bringing to light the challenges in the downstream markets in weak macroeconomic conditions. In January- September data, acid imports are down by 25% on a year earlier. The key trade drops have been from Belgium, down by 70%, Germany, down by 59% and Poland, down by 65%. At the same time, we continue to see increases from Spain.

Over in Asia, demand for spot volumes has kept the market relatively balanced in South Korea through September and October. Prices have remained in the $0-10/t f.o.b. Northeast Asia range and are expected to remain unchanged through the remainder of the year. Exports of acid from South Korea have been strong in the first 8 months of the year, up by 4%, totalling 2 million tonnes. Increased trade has been to Thailand and Indonesia. MMC and Toyo Zinc are also expecting to see reduced output on the back of turnarounds. The tighter balance supports expectations for a stable few months ahead.

Despite the slowdown seen in China in October due to seasonal holidays, sulphuric acid demand and imports remain strong. Imports in the January-August period were up by 34% year on year. Favourable acid prices earlier in the year from Northeast Asia encouraged trade to China.

Another trade hotspot through the year has been Morocco, with OCP increasing its sulphuric acid imports even further. Based on data so far, expectations are for imports to reach record highs this year, exceeding 1 million tonnes. In the last two years, acid imports totalled close to 900,000 tonnes, almost double on historical levels. The question for the outlook remains whether this will continue.

Price indications

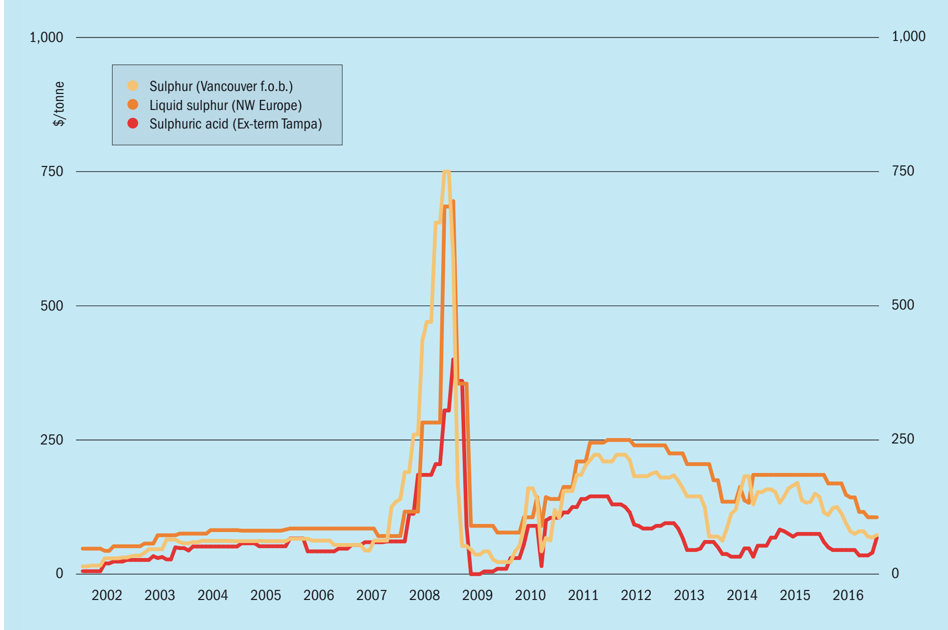
Table 1: **Recent sulphur prices, major markets**

Cash equivalent	May	June	July	August	September
Sulphur, bulk ($/t)					
Vancouver f.o.b. spot	80	80	70	68	73
Adnoc monthly contract	86	80	80	70	77
China c.fr spot	85	78	74	77	83
Liquid sulphur ($/t)					
Tampa f.o.b. contract	70	70	65	65	65
NW Europe c.fr	116	116	106	106	106
Sulphuric acid ($/t)					
US Gulf spot	35	35	35	40	40

Source: Various

Market outlook

Historical price trends $/tonne



Source: BCInsight

SULPHUR

- The global sulphur market remains in balance, providing producers with support to increase prices in the short term. However, further increases are likely to be followed by a downward correction later in the year, as downstream market fundamentals remain uncertain and the slowdown in DAP markets will limit any upside.
- Projects in Qatar and Kazakhstan are expected to add new supply in the short to medium term outlook. Once online, these will impact the global balance and represent a bearish factor for the market.
- Shifts in production of sulphur in China from oil and gas could impact the longer term outlook for trade due to the slower rate of growth in demand. As China is the leading importer of sulphur, any decreases in trade could impact pricing.
- Storage capacity of sulphur will become an increasing focus in the outlook, particularly during periods of oversupply. Those producers that have the capacity to pour to block or hold large volumes of sulphur may be able to utilize storage during periods of slow demand and low pricing. However, the cost of bringing sulphur back to the market from storage will also be a consideration.
- **Outlook:** Sulphur prices are likely to remain relatively stable through to the end of the year, although producers may seek further increments which is likely to be met with resistance due to the continued weakness in the processed phosphates markets.

SULPHURIC ACID

- The price point for annual sulphuric acid supply contracts for 2017 in Chile will be a key factor in the coming month, as this will set the tone for the Chile market.
- Spot demand in Brazil in upcoming tenders will test market prices as we move towards the end of the year. Acid imports to Brazil have slowed this year, with high hopes for a market recovery in 2017.
- Potential demand in Morocco remains crucial for the acid market balance, particularly in Europe. It remains to be seen whether acid imports will exceed 1 million tonnes in 2017. The ramp of phosphates facilities continues to support the market and displaced acid previously exported to Cuba.
- European smelter acid producers are relatively comfortable in the fourth quarter, but any slowdown in spot demand may lead to softer prices.
- In Japan, Pan Pacific Copper is expecting to see a production drop in the second half of its financial year due to planned maintenances.
- **Outlook:** Acid prices are expected to remain on a stable footing, following recent softening. The full impact of the Cuba sulphuric acid plant will likely be seen in 2017. Maintenance turnarounds at smelters in Northeast Asia will aid stable pricing in the region.

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Sulphur Industry News

KAZAKHSTAN

Kashagan restarts oil production

Kazakhstan's Energy Ministry says that oil is flowing again from the offshore Kashagan field. As of late October, four wells were up and running and around 185,000 barrels had been pumped, via two pipelines, one owned by the Caspian Pipeline Consortium, the other the state company KazTransOil. Production at the field is expected to reach 75,000 bbl/d by the end of October, rising to 150-180,000 bbl/d by the end of 2016, according to the Kazakh government. The statement added that start-up work and testing is continuing and getting the field into stable operation would still take some time.

Kashagan's troubled history has seen costs for the operating North Caspian Operating Company (NCOC) consortium rise to an estimated $55 billion to develop the giant offshore field, which operates from several artificial islands. NCOC is currently 16.8% owned by Kazakhstan, Eni, Total, Shell and ExxonMobil, with smaller stakes held by CNPC of China and Inpex of Japan. After 16 years of development, oil and gas production finally began in September 2013, but it was forced to shut down within weeks after sour gas being pumped to a treatment station onshore corroded the transit pipelines leading to a leak and necessitating the replacement of the entire double pipeline.

Production is now targeted to reach 370,000 bbl/d by the end of 2017, according to Kazakhstan, although analysts Wood Mackenzie put a more conservative estimate of 230,000 bbl/d on this. Unfortunately for NCOC, Kashagan's start-up comes at a time when global oil markets are already oversupplied, with OPEC discussing production cutbacks. The second phase of Kashagan could take that to 1 million bbl/d, but that expansion is unlikely to go ahead in the near future. Of most concern will be the sour gas production from the field. There are plans to reinject a significant proportion of the sour gas, beginning about six months into production, but for the moment it will be mainly treated onshore, generating 1.1 million tonnes per year of sulphur.

IRAQ

Mishraq ablaze after recapture from Islamic State

As Iraqi forces fighting against the self-declared Islamic State (IS) for control of the northern city of Mosul continue their advance on the city, the nearby area of the Mishraq sulphur mine 30km to the south of the city has reportedly been recaptured by Iraqi troops. IS forces have however been engaged in a 'scorched earth' policy of destroying infrastructure as they retreat, and sulphur stockpiles at Mishraq were reportedly set on fire during this in order to generate sulphur dioxide fumes to cover their retreat. At least two civilians are said to have died from inhaling sulphur dioxide, with over 100 more seeking medical attention.

Mishraq was once the largest sulphur mine in the world, producing up to 1 million t/a of sulphur in the 1990s. However, it was badly damaged by Iraqi forces during the 2003 US invasion in order to deny it to the enemy, and the large sulphur stockpile was set on fire, burning for 21 days and sending a massive plume of SO_2 across northern Iraq. Since then production had been piecemeal, but a major revamp of the site had been commissioned by the Iraqi government and pre-fabricated modules designed to treat the sulphur produced at Mishraq were on their way to the site when IS overran it in 2014. The sulphur plant modules, designed and built by Devco in the US, are currently still in Jordan.

The most recent reports said that the fire at Mishraq was still not under control, and could take days to extinguish. Tackling the blaze is complicated by its proximity to the front line and booby traps left behind by fleeing IS fighters.

QATAR

Delay for Barzan project

Qatar's Barzan gas processing project faces delays, Reuters reports, after a leak was discovered in an upstream gas pipeline. The $10 billion project, had been due to start operations in November this year. A revised date is not yet known, but a start-up in 2016 is now said to be "not likely". Barzan, a joint development between ExxonMobil and RasGas, will boost Qatar's gas production by 1.4 billion cubic feet/day to help meet rising domestic energy demand in time for the 2022 World Cup. It is intended to process gas from the massive offshore North Field reservoir, generating around 1.4 bcf/d of sales gas, as well as 22,000 bbl/d of field condensate, 6,000 bbl/d of plant condensate, 34,000 bbl/d of ethane, 10,500 bbl/d of propane and 7,500 bbl/d of butane. The sulphur recovery facility will also process around 800,000 t/a of additional sulphur from the development when at capacity. The Barzan sulphur recovery facility is using ExxonMobil's 'Flexsorb SE Plus' for tail gas treatment of the sulphur recovery plant to allow the facility to achieve 99.4% recovery efficiency.

KUWAIT

SRU contracts awarded

Schlumberger Reservoir Products FZE has contracted Siirtec Nigi to design and supply two modular sulphur recovery units (SRUs) for the Kuwait Oil Company's Sabriya and East Raudhatain gas treatment plants. The contracts are part of the KOC Jurassic Production Facility (JPF) project to develop gas fields in the north of Kuwait. The two SRUs will produce 200 t/d of liquid sulphur, each with a recovery rate of 99.9% and will each consist of two Claus units of 100 t/d, a gas treatment unit based on Siirtec Nigi *HCR*™ proprietary technology, two degassing units, an incinerator, two sulphur storage and loading sections and a steam condensate recovery and recycle system.

Maurizio Locarno, Siirtec Nigi Managing Director, stated: "We are proud to have been selected to support Schlumberger in this important project. These contracts further consolidate Siirtec Nigi's reputation both as a licensor and contractor in the sulphur recovery sector".

IRAN

Iran nears deals on smaller oil and gas fields

As the country attempts to expand its oil and gas industries in the wake of the lifting of sanctions, Iran is looking towards joint venture deals with foreign companies to progress the development of several smaller oil and gas firms. The deals will combine elements of the new Integrated Petroleum Contract (IPC) with existing engineering, procurement, construction and finance (EPCF) and buyback contract models. Fields being offered include the Danan and Cheshmeh Khosh oil fields in Ilam province, and the Dey and Sefid Zakhour gas fields. OMV is said to be in talks with the Iranian Central Oil Fields Co. (ICOFC) to develop the Cheshmeh Khosh field, which currently produces 18,000 bbl/d of oil and 3.3 million m^3/d of gas, while PetroVietnam is leading the field among foreign firms in line to sign an updated contract for the further development of the Danan oilfield (incorporating the Bangestan and Asmari reservoirs) using enhanced oil recovery. Danan is currently run by the ICOFC and produces around 26,000 bbl/d of oil. Iran also aims to generate production of 5.1 and 10 million m^3/d respectively from the Dey and Sefid Zakhour gas fields, to be processed at the Farashband refinery.

WORLD

Slow market impacts refining capacity expansion

Global crude distillation unit (CDU) capacity will grow by 16.7% by 2020 based on planned and announced refineries, according to research and consulting firm GlobalData. Current global CDU capacity is 98.9 million bbl/d, with planned projects bringing this to 115.2 million bbl/d. This estimate is down from the previous, February outlook of 118.2 million bbl/d. China and Nigeria have the most planned capacity for the next four years, with an estimated $84 billion spend and a combined CDU increase of 3.16 million bbld. Regionally, Asia is the largest investor in new capacity, with an additional 4.47 million bbl/d, in order to satisfy the region's incremental oil demand. For the first time ever, the Chinese government is allowing private investors to participate in a mega-refinery project near Shanghai. In the Middle East, eight countries have a total of 3.7 million bbl/d planned during the forecast period, with associated capital spend totalling $80.2 billion. A further $36.5 billion will be spent in the former Soviet Union to increase the region's CDU capacity by 918,000 bbl/d. In September 2016, Vladimir Putin and Xi Jinping signed an agreement to progress the FEPCO Nakhodka project in Eastern Russia. The refinery expands Russian's aim to strategically position itself to satisfy the next billion new middle class consumers in Asia.

MOROCCO

Shell licenses Thiogro technology to OCP

Shell has licensed its Thiogro sulphur encapsulation technology to Office Cherefien des Phosphates (OCP) of Morocco, the world's largest phosphate producer. Shell says that Thiogro will enable OCP to produce highly concentrated sulphur-enhanced fertilizers, helping end-users unlock greater crop yields and improved soil health. The technology will be installed at OCP's Jorf Lasfar site in Morocco, enabling the company to incorporate micron-sized particles of elemental sulphur into its existing ammonium phosphate, NPKs and current sulphur-enhanced products.

"This partnership with Shell will bring us one step closer to achieving our goal of offering farmers a wide selection of customized products tailored to the specific needs of their soils," said Mustapha El Ouafi, OCP's Managing Director. "We look forward to working with Shell as we implement the Thiogro technology which will provide OCP with a new solution to address our customers' needs for balanced, sulphur-enhanced fertilizers."

"We are pleased to license our technology to OCP," said Michael Lumley, Vice President of Shell Sulphur Solutions. "Our team of sulphur experts have worked hard to develop a safe and efficient technology for the incorporation of elemental sulphur into fertilizers, and we have no doubt that this agreement will have a positive impact for OCP and the farmers they serve."

The technology is expected to be installed and commissioned in 2017.

INDONESIA

Axens in refinery licenses for Pertamina

Axens has signed several technology licensing agreements with Pertamina for the latter's major expansion project to upgrade residue into gasoline in Balikpapan and for a new middle distillate hydrotreater in Cilacap, to comply with new regulations. The Balikpapan project consists in a grassroots residual fluid catalytic cracker with a design capacity of 90,000 bbl/d, an LPG sulphur removal unit (*Sulfrex*™), a propylene recovery unit (PRU), and a new 80,000 bbl/d middle distillate hydrotreater (*Prime-D*™). The gasoline produced by the FCC will be selectively hydrodesulphurised in a Prime-G+™ unit with a design capacity of 48,000 bbl/d to produce ultra-clean gasoline. The Cilacap project consists in a 36,000 bbl/d grassroots Prime-D ™ distillate hydrotreater unit allowing the production of ultra-low sulphur diesel. The production of ultra-clean fuels will enable Pertamina to significantly reduce Indonesia's dependence on foreign imports of transportation fuels.

UNITED STATES

TSI launches new sulphur fertilizer website

The Sulphur Institute (TSI) has launched a new web resource designed for sulphur fertilizer producers, marketers, and consumers. "Sulphur – The Fourth Major Plant Nutrient" is available on at www.SulphurInstitute.org/Fertilizer.

"Sulphur is now increasingly recognized for its role as an essential element for the efficient production of food, thereby enhancing farmers' ability to meet the nutritional needs of an expanding global population. TSI is committed to sharing this critically important information," said Robert McBride, TSI president and CEO. "This website is only part of a larger outreach program conducted by TSI and we invite all sulphur stakeholders to actively participate."

INDIA

IOC to expand two refineries

The Indian Oil Company (IOC) will invest $1.24 billion to expand its refinery at Barauni in Uttar Pradesh, and $230 million to expand its Panipat refinery in Haryana. Barauni will expand from a capacity of 6 million t/a to 9 million t/a, along with the addition of a downstream polypropylene unit and implementation of N olefin recovery project along. At Panipat, there will be an expansion of the existing naphtha cracker unit, a revamp of the MEG (monoethylene glycol) unit and an expansion of the benzene unit, according to IOC. Panipat has a capacity of 15 million t/a and also operates a world-scale naphtha cracker, with four downstream units for production of polymer (plastics) intermediates.

UNITED KINGDOM

IMO to impose sulphur cap from 2020

The International Maritime Organization's (IMO) Marine Environment Protection Committee, meeting in London from October 24-28, has decided to set the date for the move from a 3.5% cap on sulphur content of marine fuels to 0.5% from 2020 rather than

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2025. The decision is a controversial one for shipowners, who have expressed doubts as to whether refiners would be geared up to produce sufficient low sulphur fuel from the implementation date. Other options include the retrofitting of sulphur scrubbers and switching to alternative fuels such as LNG and methanol, but the latter are not likely to have a major impact within the envisaged time frame, and the former still remain a potentially expensive and untried technology. The International Transport Forum (ITF) of the Organization for Economic Cooperation and Development in May said the cap planned for 2020 will have a "significant effect" on shipping costs, increasing them by 20-85%, depending on the availability of low sulphur fuel, and potentially adding total annual costs of $5-30 billion for the container shipping industry." Postponement to 2025, however, would result in a more modest increase of 4-13%, according to the ITF. However, the EU had previously said that it will impose its own 0.5% sulphur cap in European water from 2020 regardless of the decision taken this October. Shipowners already have to use low sulphur fuels or other remediation technologies in designated emission control areas (ECAs) in the Baltic and North Sea around Europe and the west and east costs of North America. China now also has three ECAs: Pearl River Delta, Yangtze River Delta, and Bohai-rim.

Marine fuel oil accounts for around 22% of the global fuel oil market. Russia is the world's largest exporter of fuel oil – with an 18% per cent share of seaborne trade in 2015 – and is thus most exposed to a sharp decline in the use of fuel oil for bunkers. Fuel oil accounted for close to half of Russian refined product exports in 2015.

CANADA

New sour gas processing plant

Gas processor SemCAMS has announced that it will build a sour gas plant near Wapiti to produce up to 120 million cf/d. The value of the agreement with NuVista Energy to construct the plant southwest of Grande Prairie is estimated between C$300-350 million. Construction is expected to start in the second quarter of 2017, with the plant on-stream by the second quarter of 2019. SemCAMS first announced plans for the new plant, to be located at Gold Creek, in August after receiving approval from the Alberta Energy Regulator. The Wapiti Gas Plant will have the capacity to process up to 200 million cubic feet of raw sour gas and 20,000 barrels per day of condensate. It will link with SemCAMS's existing Wapiti and Simonette pipelines, which are connected to two SemCAMS sour gas plants in Fox Creek.

One of the modules being shipped to the Fort Hills oil sands project.

Last modules shipped for oil sands project

Fluor Corporation says that all 358 modules have been fabricated and shipped to site for its portion of the Fort Hills Energy L.P. oil sands mining project in the Athabasca region of Alberta. Fluor is performing engineering, procurement, fabrication and construction for the utilities scope of the project. The project used Fluor's 3rd Gen Modular Execution approach, which optimises process block layouts and provides the capability to fully modularise large-scale industrial facilities, which the company says leads to improved safety, lower costs, increased productivity and schedule predictability through the transfer of a significant amount of traditional site work to fabrication yards. Fluor's SFMI joint venture fabrication yard in Canada and three other Canadian yards built the modules.

The Fort Hills Project, an open-pit truck and shovel mine, is owned by Fort Hills Energy LP, a joint venture partnership between Suncor Energy, Total E&P Canada Ltd. and Teck Resources Ltd.

MALAYSIA

Refinery to install sulphur dioxide scrubbers

DuPont MECS *DynaWave*® technology has been selected by a major international oil and gas services provider for the installation of three custom-engineered scrubbing systems for sulphur dioxide removal at the Petronas PRPC Refinery & Cracker Sdn. Bhd. The units are to be delivered to the company's RAPID project refinery in Pengerang, Southern Johor, before the end of the year for subsequent fitting.

"Each of the specially engineered scrubbers will treat the off-gas of one sulphur recovery unit (SRU) and its dedicated tail gas treatment unit (TGTU)," said Angus Yip, MECS sales manager for South East Asia & Australia-New Zealand. "PRPC requires SO_2 emission levels to be lower than 150mg/DNm³, which *DynaWave* technology can guarantee under any given set of upstream conditions."

All three scrubbers consist of two reverse jet stages located in an inlet barrel which is connected to a disengagement vessel. They are capable of handling high inlet acid levels, which make it possible to bypass upstream TGTUs while still meeting and even exceeding regulatory emissions requirements. Thje scrubbers can be designed to cope with inlet temperatures of up to 1,200°C, but for PRPC the choice fell on optimising heat recuperation from the incinerator so that these scrubbing units will take incoming gas at around 300-350°C.

The RAPID (Refinery and Petrochemicals Integrated Development) project represents a significant investment of $16 billion for PRPC. Scheduled for completion in 2019, it is expected to be capable of processing 300,000 bbl/d and will operate three 470 t/d sulphur recovery units. ■

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Sulphuric Acid News

INDIA

OCP in Indian NPK joint venture

Moroccan phosphate leader OCP has announced the creation of a 50-50 joint venture company with Indian fertilizer cooperative Kribhco to develop a large-scale greenfield fertilizer plant in Krishnapatam, Andhra Pradesh state. The $230 million cost of the project will be borne equally by both companies. The plant's output will be 1.2 million t/a of NPK fertilizer. In a press statement, Mostafa Terrab, CEO of OCP, said that he was confident that the venture will be a "win-win" for all parties involved. "OCP has always been, and remains fully committed to contribute to India's agricultural development. We believe large-scale local investments designed to respond to farmers' specific needs is the key ingredient to successful agricultural ecosystem development. As one of the major cooperatives in India, Kribhco is an excellent partner to develop a farmer-oriented agricultural input joint-venture."

OCP and Kribhco also say that they hope to expand the project towards "development of logistical infrastructure in the region". As part of additional envisaged cooperation, Kribhco is also envisaging investing in construction of a phosphoric acid plant in Morocco.

FACT looking to more acid production

Fertilizers and Chemicals Travancore, recently the recipient of a $150 million government loan, says that it is pressing ahead with expansion plans which will increase its fertilizer output from 600,000 t/a to 1.0 million t/a in the 2016-17 financial year. The production expansion will see ammonium phosphate sulphate production at Kochi rise from 330,000 t/a to 390,000 t/a. It also includes a recent re-start of the company's caprolactam production at the site, totalling 50,000 t/a. The caprolactam plant had been closed for four years as part of the company's financial troubles. Sulphuric acid production is also expected to be boosted. Last year the company made 200,000 t/a of acid, against 300,000 t/a for the previous year.

Longer term, FACT is looking to build a new 330,000 t/a ammonium phosphate sulphate plant at Kochi, and build a 500,000 t/a urea plant which will use production from the 900 t/a ammonia plant completed at the site a few years ago, and operating on LNG imported via Petronet. A 660,000 t/a sulphuric acid plant is also on the drawing board.

UNITED STATES

Kemper County plant producing acid

Mississippi Power Co. says that its long-delayed coal gasification-based power plant in Kemper County has generated electricity using synthesis gas produced from coal for the first time. One of the two turbines was run on a 50-50 syngas/natural gas mix during initial testing of the gasification system – the plant has been generating electricity using natural gas since 2014. Mississippi Power says the plant will continue to generate electricity normally as tests continue, using a mix natural and synthetic gas. The $6.8 billion plant is expected to be fully running on both gasifiers by the end of November. However, the associated carbon capture and storage (CCS) facility, which will pump the CO_2 captured to enhanced oil recovery (EOR), is not yet on-stream, and CO_2 is being vented to atmosphere. Ammonia and sulphuric acid recovered from the syngas is however being collected and offered for sale, according to the company.

Non-acid aklylation route

Chevron is converting the alkylation catalyst used in one of its refineries from hydrofluoric acid to an ionic liquid. Alkylation produces high octane gasoline components, with sulphuric or hydrofluoric acid the main processes, but Chevron has been developing its own technology based on an ionic liquid since 1999 at a demonstration plant in Salt Lake City, and now plans to build a full commercial scale unit by 2020. Ionic liquids are salts which turn liquid at temperatures below 100°C, have strong acidic properties that allow them to behave like acid catalysts, but without the volatility.

Chevron has also licensed the technology to Honeywell, who will offer the technology under the brand ISOALKY, and supply the chloroaluminate catalyst, an ionic liquid with a proprietary composition. "Ionic liquids alkylation offers a compelling economic solution compared to conventional liquid acid technologies while delivering the same yields and high levels of octane," said Mike Millard, vice president and general manager of Honeywell UOP's Process Technology and Equipment business. "This is a revolutionary new technology for refiners to produce alkylate and improve the quality of their gasoline pool. It is the first successful liquid alkylation technology to be introduced in 75 years."

Phosphoric acid leak at New Wales

Mosaic has reported a 50,000-gallon leak of phosphoric acid at its New Wales site in mid-October. The leak follows a 97,000-gallon leak of phosphoric acid solution at the Bartow plant earlier in the month, and issues caused by the appearance of a massive sinkhole at the New Wales site beneath one of the phosphogypsum stacks which led to 215,000 gallons of contaminated water being released into the local aquifer. Mosaic said that the most recent leaks were both contained within the plant, and that there was no potential risk to public health or any impact on local water or air quality. Work at the sinkhole at the New Wales plant continues.

EGYPT

Ecophos announces further international expansion

EcoPhos has signed a joint venture agreement with Evergrow for the construction of a 110,000 t/a dicalcium phosphate (DCP) factory to produce animal feed. The new plant will be built in Sadat City and will require an estimated investment of $120 million. The new complex will comprise plants for the production of low-cadmium fertilizer (100,000 t/a SSP), as well as a 600 t/d sulphuric acid plant and a 60,000 t/a calcium chloride plant. In addition to these plants, further investment is planned with the construction of an NPK production plant. The DCP will be sold and distributed by Aliphos. Manufacture will be based on innovative technologies developed by EcoPhos that will maximise the value of the raw phosphate mineral obtained directly from the mine. EcoPhos will provide the technology, the outline and detailed engineering and the equipment for the project.

MACEDONIA

Outotec supplies SX/EW technology

Outotec has been awarded two orders, worth a total of €25 million, for its new *VSF®X* modular solvent extraction technology. The company says it will deliver detailed engineering and a complete technology package for a modular copper solvent extraction and electrowinning (SX/EW) plant for Sardich MC in Kazandol, Macedonia. After leaching oxide ores, copper will be extracted from the leach solution at the solvent extraction and electrowinning plant to produce high grade cathode copper. The production is expected to start-up already in the summer of 2017.

The other contract is with Italian engineering company Desmet Ballestra. Outotec will design and deliver a solvent extraction plant to purify fertilizer phosphoric acid before evaporation, in connection with the El Nasr Co. for Intermediate Chemicals (NCIC) fertilizer plant in Egypt. Outotec's scope of supply includes *VSF®X* technology, license, equipment for crude treatment and a cooling tower. Outotec's deliveries will take place in the end of 2017, and the entire plant is expected to be operational a year later. In June 2016, Outotec agreed on the delivery of two sulphuric acid plants for the same project.

"We are happy to be able to provide both Sardich and NCIC our new modular *VSF®X* technology and benefits that come with it – a fast-track delivery and installation as well as environmentally friendly and safe performance of the plant. These new orders also demonstrate that this concept can be used for various solvent extraction applications", said Jyrki Makkonen, head of Outotec's Metals, Energy & Water business unit.

GERMANY

Order for acid pumps

CP Pumpen AG says that it has won an order to supply five of its magnetic drive MKP pumps to a customer in Benelux. The pumps deliver a performance from 250-500m³/h for a total head of 17-31 metres. Made of high-quality Hastelloy they will handle 98.5% sulphuric acid with a maximum temperature of 100°C. The sulphuric acid pumps have to operate reliably and safely in order to prevent any downtime of the plant, so the pump design is based on a unique drive configuration which the company says is particularly robust and reliable. The MKP pumps are also monitored by a responsive thermocouple mounted on the containment shell which measures the shell's temperature. In case of an overheating of the pump it sends a signal to the operator to prevent non-permissible operating conditions. The sealless magnetic drive pumps also feature a single impeller-bearing assembly that is optimally lubricated and cooled by the pumped fluid.

MADAGASCAR

Sherritt revises Ambatovy production estimates downwards

Tornoto-based mining company Sherritt has revised downwards its estimates for output at the Ambatovy nickel and cobalt processing plant in Madagascar, in which the company holds a 40% stake. Ambatovy has suffered a tailings pipe blockage and total shutdown during June and July, followed by a slower than expected ramp-up of production and consequent weak output in August. Sherritt's current estimates for 2016 output are 40-42,000 t/a of nickel, down from its initial estimate for the year of 50,000 t/a, and a nameplate capacity of 60,000 t/a. Sherritt says it is expected to achieve full capacity at the high pressure acid leach (HPAL) plant during 2017

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People

The Sulphur Institute (TSI) has announced the selection of **Ms. Kerry Kurowski**, CMP as Senior Manager, Meetings, Member Relations, and Office Services. Robert McBride, TSI president and CEO, remarked, "We look forward to Kerry's meeting planning experience and her additional skills which will enhance programs and operations."

Ms. Kurowski has worked in the events industry since 2002 having previously been employed in a similar capacity at The Biscuit & Cracker Manufacturers' Association. She is a Certified Meeting Professional and earned a bachelor's degree from the University of Maryland. Ms. Kurowski also serves as the Director of Communications for the Professional Convention Management Association Chesapeake Chapter.

Outotec has announced changes to its management; **Kalle Härkki** has been appointed executive vice president, as well as president of Outotec's Metals, Energy & Water business unit as of October 24th, 2016. Kalle Härkki has been a member of the Outotec executive board since 2008, first as head of the Services business area and since 2013 as head of the Minerals Processing business unit. **Jyrki Makkonen**, who has been acting head of the Metals, Energy & Water business since April 2016 will return to his position as head of Non-Ferrous business line of Metals, Energy & Water. **Taneli Salervo**, vice president Strategy & Business Development of Minerals Processing, will lead the Minerals Processing business unit until Kalle Härkki's permanent successor has been appointed.

"I am very glad that Kalle Härkki, who has a long and versatile experience in leading Outotec businesses, accepted the position as head of Metals, Energy & Water. I would also like to thank Jyrki Makkonen for leading the Metals, Energy & Water business in the interim. The recruitment process for the new head of Minerals Processing will start immediately", said Markku Teräsvasara, CEO of Outotec.

Oilfield Helping Hands (OHH), a non-profit charitable organisation comprised of volunteers devoted to providing financial assistance to oilfield workers in financial crisis, has appointed **Gregory Rachal** as president. As president of OHH, Rachal will ensure that OHH remains a premier support resource for oilfield families in crisis within six regional chapters in active oilfield communities across the US. Since it was founded in 2003, OHH has raised more than $3.3 million for more than 300 families affected by financial hardships.

Rachal said, "My goal is to ensure OHH continues to work in the most economical fashion to maximize the amount of monies available for distribution to our recipients each year, raised through corporate memberships, donations and annual fund-raising events. I firmly believe that we must help each other in times of crisis."

Rachal has extensive experience in drilling fluids, previously holding positions with M-I SWACO and Halliburton in sales, product line and account management, operations and project management across the US and working with major and independent operators in the Houston and New Orleans markets. He holds a bachelor of science degree in industrial art from Northwestern State University, Natchitoches, LA., and post-graduate qualifications in management and computer science from Tulane University, New Orleans.

Gregory Rachal

Calendar 2016-17

NOVEMBER

7-10
CRU Sulphur 2016 Conference and Exhibition, LONDON, UK
Contact: CRU Events
Tel: +44 20 7903 2167
Email: conferences@crugroup.com

14-16
European Refining Technology Conference, (ERTC) LISBON, Portugal
Contact: Eliot Morton, GT Forum
Tel: +44 20 7316 9832
Email: eliot.morton@gtforum.com

2017

FEBRUARY

26 – MARCH 1
Laurance Reid Gas Conditioning Conference, NORMAN, Oklahoma, USA
Contact: Tamara Powell, Program Director
Tel: +1 405-325-2891
Email: tsutteer@ou.edu

MARCH

8-9
European Fuel Markets and Refining Strategy Conference, LONDON, UK
Contact: ACI, 5/13 Great Suffolk Street
London, SE1 0NS, UK
Tel: +44 616 46 7047
Email: adam@acieu.co.uk

12-15
Phosphates 2017,
TAMPA, Florida, USA
Contact: CRU Events
Tel: +44 20 7903 2167
Email: conferences@crugroup.com

19-21
AFPM Annual Meeting,
SAN ANTONIO, Texas, USA
Contact: American Fuel and Petrochemical Manufacturers (AFPM)
1667 K Street, NW, Suite 700,
Washington, DC 20006, USA
Tel: +1 202 457 0480
Email: meetings@afpm.org
Web: www.afpm.org

26-30
SOGAT 2017, ABU DHABI, UAE
Contact: Dr Nick Coles, Dome Exhibitions
Tel: +971 2 674 4040
Email: nick@domeexhibitions.com

APRIL

24-26
TSI World Sulphur Symposium,
DUBLIN, Ireland
Tel: +1 202 331 9660
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Web: www.tsi.org

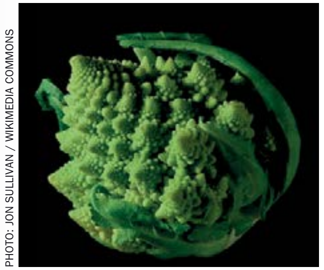

PHOTO: JON SULLIVAN / WIKIMEDIA COMMONS

Sulphur and human health

Don Messick of The Sulphur Institute considers sulphur's important role in human health.

We all know that we need protein in our diet and that proteins are made up of amino acids, but do you know sulphur has a role? Biology text books typically present the amino acids as a selection of 20 acids found in proteins. Amino acids build proteins, and from proteins the body constructs enzymes, hormones, haemoglobin and DNA, to name a few more commonly recognised compounds. Two of the amino acids contain sulphur – cysteine and methionine.

Despite being the seventh most abundant element in the human body, and the sulphur-containing amino acids, cysteine and methionine, being required in our diet, sulphur is often overlooked. If I were to mention that we are talking about:

- cancer prevention
- proper functioning of the immune system
- slowed progression of cardiovascular disease

… you would recognise these as all desirable, and yes, we are talking about sulphur having a role in them. Now the challenge: sulphur is involved in the production of several metabolites that are not so easily recognised. Once we start hearing terms like allyl sulphur compounds, glucosinolates and isothiocyanates, most of us loose familiarity, but these items are fundamental to human health and the sulphur we get in our diet helps to assure their production.

A balanced diet of meat, vegetables and fruit can meet the requirements, but the situation is much different in many parts of the world, for example, in the developing world where a diet of largely cereals can result in insufficient methionine and cysteine.

Garlic and onions

Sulphur compounds found in garlic and onions, as examples, provide a protective role battling bacteria, fungi, and animals (Jones et. al., 2004). Crush a garlic glove and you release the precursors for the production of allyl sulphur. This compound is thought to have potential value as an anti-cancer and anti-thrombotic agent; an anti-thrombotic agent reduces the formation of blood clots (Milner, 2001).

Depressed levels of tumour cells, linked to such cancers as breast, colon, skin and others, have been attributed to allyl sulphur compounds (Milner, 2001). Research indicates that the pathway may be related to the way in which allyl sulphur compounds affect a variety of metabolic processes. Suspected carcinogens and potential environmental factors in the formation of cancers, such as nitrosamines, are repressed by allyl sulphur compounds (Brown, 1999; Ferguson, 1999).

Broccoli

Plants such as broccoli, cabbage, cauliflower and kale are all members of the brassicaceae family. These common items are part of a family that includes about 3000 species. They contain the sulphur-containing chemicals glucosinolates and their related isothiocynates. Over 120 glucosinolates and isothiocyanates are known (Fahey et al., 2001). Upon activation, these chemicals function in a fungicidal, bacterial, and nematicidal manner (Jez and Fukagawa, 2008). Glucosinolates are converted to isothiocyanates. These compounds have been shown to have cancer preventative properties (Jez and Fukagawa, 2008). Laboratory animals and cell culture research has demonstrated that isothiocyanates modify metabolism of carcinogens (Hecht, 1999; Bianchini and Vainio, 2004). Excretion of products of this process alleviates the cancer-causing effects.

In conclusion, there is a lot of research illustrating that sulphur-containing foodstuffs are important to the diet, although in some cases the mechanism may not be completely understood. Once again we are reminded of the importance of a balanced diet, which is not available to many throughout the world. Thus, the growing interest in sulphur, not only for its potential to improve yields, but for the quality of the crops produced.

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The global market for sulphur

Sulphur has re-entered a period of surplus after the commissioning of several large sour oil and gas projects.

Above: The return of stockpiling? Sulphur blocks at Fort McMurray, Alberta, Canada.

World production of sulphur reached 59.5 million tonnes in 2015. Roughly half of this (28.7 million t/a) comes from oil and oil sands refining, and the other half (29.5 million t/a) from natural gas processing, with the last two operational sulphur mines, at Siarkopol in Poland and Jaltipan in Mexico, contributing only a further 680,000 tonnes of the total, or just over 1% (and 95% of this mined total comes from Siarkopol alone).

Refinery output

Refinery output of sulphur is continuing to grow steadily. According to the US Energy Information Agency (EIA), global liquid fuel production increased from 93.4 million barrels/d (bbl/d) in 2014 to 95.8 million bbl/d in 2015, and it is forecast to increase to 97 million bbl/d by 2017. This in turn is a result of greater car use, especially in Asia; new consumption in China has added about half of all new fuels demand over the past five years. Increased consumption from these sources has so far more than offset savings in consumption which have come especially in the developed world, via greater fuel efficiency in vehicles and a slow but steady switch towards alternative fuels and power trains such as ethanol, methanol, hybrid and electric vehicles. At present there seems to be no sign that the trend towards increasing gasoline and diesel consumption will not continue.

At the same time, regulations on the sulphur content of hydrocarbon fuels is continuing to tighten around the world. While North America, Europe, Japan, Korea and Australasia all operate at 10-15 parts per million (ppm) sulphur content, and there is little room for extra sulphur from tightening regulations here, some of the fastest-growing economies are moving rapidly to reduce sulphur content of fuels. China has already moved to a 50ppm standard, and India is in the process of doing so. Nor is the tightening of standards confined solely to road vehicle fuels – as we note in the Editorial this issue, the International Maritime Organisation has decided to move to a global cap of 0.5% sulphur (5,000ppm) in all marine fuels by 2020. While the total volume of marine fuel is relatively small – only around 2 million bbl/d of the 95 million bbl/d total – the percentages of sulphur involved are all the larger and hence the move could be

a significant one for the sulphur industry. A move from 3 or 3.5% sulphur to 0.5% sulphur for 2 million bbl/d could represent an additional 5 million t/a of sulphur being extracted from fuels, assuming no large-scale switch towards alternative fuels such as LNG or methanol or the widespread adoption of emissions scrubbing technology (at present only around 200 out of the estimated 50,000 operational merchant vessels have such technology installed).

These two trends are also boosted by a third, which is the move towards processing of higher sulphur crudes. Over the past 30 years, the average sulphur content of crude processed by US refineries has increased from 0.9% to 1.44%. While the past few years have seen something of a plateau, the relative cheapness of sourer crudes has also led to additional investment in sulphur recovery in refineries around the world, especially Asia and the Middle East, where most new refinery capacity is being built. The slow switch of Canadian crude production from lighter, sweeter crudes towards more output from oil sands production, which tends to be heavier and sourer, is also a factor boosting sulphur content to US refiners, although it has been balanced by greater use of domestic shale-derived oil and natural gas liquids, which tend to have much lower sulphur content, and the recent run of low oil prices has also affected investment in new syncrude capacity in Canada, while the blocking of the cross-border Keystone XL pipeline also makes it harder for this syncrude to find a market in the US.

Nevertheless, overall these three factors mean that the steady increase in sulphur output from refineries is projected to continue for the foreseeable future, from 28.7 million tonnes in 2015 to 33.1 million tonnes in 2020, according to Integer Resources.

Natural gas

Use of natural gas is also rising steadily around the globe, mainly for power production. Global gas consumption has risen from 2.77 trillion cubic metres in 2005 to 3.47 trillion cubic metres in 2015, according to BP figures. This growth has been strongest in Asia, which accounted for about half of that increase, but there has also been considerable growth in the Middle East, where rapidly rising populations and demand for electricity in fast-growing cities like Dubai and Abu Dhabi have also pushed growth, and there has also been significant demand growth in North America, as gas begins to replace coal as a power generation fuel. Part of this has been due to the perception of gas as a lower carbon source of electricity than coal or heavy oil, but in North America the shale gas boom has also lowered prices and made gas much more competitive with coal as a feedstock for power and chemical production. Gas consumption worldwide increased by 1.7 % in 2015, up from the relatively low figure for 2014 and back towards its longer term average of 2.2-2.3% growth, but consumption growth was 6.1% in the Middle East last year. The US EIA forecasts global gas consumption to rise by a further 280 billion cubic metres from 2015 to 2020, which would take consumption to 3.75 tcm.

Unconventional gas

Production of gas from so-called 'unconventional' sources is growing particularly quickly. In North America this is of course shale gas, the story of which is now a well-worn one, but growth in production from coalbed methane, especially in countries like Australia, China and India, has also been a significant phenomenon. The beginnings of export of shale gas as LNG from the United States earlier this year was a key marker of how important the industry has become, and most of new LNG capacity that will come on-stream over the next few years will be represented by either US shale gas or Australian coalbed methane.

The shale gas boom has had a significant impact on sulphur availability in North America, as it has undercut the production of sour gas in the US and Canada, while the shale gas itself is mainly fairly sweet. The effect has been to remove up to 5 million t/a of sulphur production from North American sour gas over the past decade. It remains an open question as to whether the success of US shale gas production can be repeated elsewhere around the world, however. In Europe hydraulic fracturing faces what seem to be insuperable barriers in the form of national bans (in France and Germany) or entrenched local opposition (in the UK), while China, which is keen on developing shale capacity, faces the issue of lack of water availability for fracking, and so far there seems no reason to predict that shale gas will further crimp global sulphur supply in the near future beyond what has already happened.

Sour gas

With sweet, conventional gas in short supply, producers in some regions have turned to sour gas production, which is producing considerable new volumes of sulphur worldwide. While sour gas production is falling in North America, three main regions are rapidly increasing their sour gas production; China, Central Asia, and the Middle East.

China is now producing sulphur from its Puguang gas plant, which came onstream in 2010, and Yuanba, which became operational in 2015. Chuangdongbei began production earlier this year. When all three are at capacity, they will represent 4.2 million t/a of sulphur production. In the Middle East, Abu Dhabi's huge Shah sour gas project began producing in 2015, and will be responsible for 3 million t/a of sulphur at capacity. Qatar is about to start production from Barzan, with 1.5 million t/a of sulphur output at capacity, and Saudi Arabia, which is already producing from the Wasit gas plant, is planning start-up for the Fadhili plant in 2019. Iran is steadily ramping up production from its South Pars developments, and there are new sour gas projects planned in Oman. Finally, in Central Asia, South Yolotan/Galkynysh in Turkmenistan came on-stream at the start of this year, and the North Caspian Operating Company recently announced that the massive Kashagan field in the Caspian Sea had begun producing oil again planned, although the status of the gas processing plant remains unclear at present.

All of these developments taken together are responsible for a major increase in sulphur production from sour gas, which is projected to rise from 29.5 million t/a in 2015 to 41.0 million t/a in 2020.

Sulphur consumption

Most sulphur – around 85-90% - is consumed as sulphuric acid. Sulphuric acid is the most widely used industrial chemical, with a market size of more than 250 million t/a. Agricultural uses predominate, with single superphosphate, ammonium sulphate and phosphoric acid for phosphate fertilizer production accounting for about 60% of this. Metallurgical uses are a smaller (10%) but growing sector, and a variety of other industrial processes, from caprolactam to titanium dioxide production, accounting for the remainder. Industrial demand is continuing to increase rapidly, especially in China and Russia.

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Phosphates

Just over half of all sulphur consumption (in all forms) depends upon phosphate fertilizer production. In spite of some new capacity in Brazil and elsewhere, single superphosphate (SSP) use is on a long-term decline, and production fell from 6.7 million t/a in 2005 to 5.8 million t/a in 2010 (tonnes P_2O_5) and about 4.5 million t/a in 2015. However, other phosphate fertilizers, particularly mono- and di-ammonium phosphates (MAP/DAP), are on a seemingly inexorable rise, reaching 28 million t/a P_2O_5 in 2015. China in particular has rapidly expanded its MAP/DAP capacity, to the point of severe overcapacity, and has come to represent half of all MAP/DAP production, becoming a major net exporter in the process, at almost 5 million tonnes (P_2O_5) in 2015.

New phosphate production over the next few years will come from Ma'aden in Saudi Arabia, which is due to come on-stream in 2017, requiring 1.5 million t/a of sulphur, and a few other producers worldwide, but the major additions to Chinese capacity that have been seen in the past do not look likely to continue, as China is now focusing on capping fertilizer use by 2020. An overhang of projects may account for another 1 million t/a of sulphur demand there, but the vast bulk of new phosphate investment over the next few years, and hence sulphur demand, is coming from the huge expansions taking place in Morocco. By 2020, OCP is projected to account for 20% of all phosphate capacity in the world, and its capacity additions to that time represent just under 3 million t/a P_2O_5 – equivalent to nearly 9 million tonnes of sulphuric acid or 3 million tonnes of sulphur.

Metal leaching

Sulphur demand for sulphuric acid for metal leaching operations amounts to about 8.6 million tonnes S (in all forms – about 3.4 million tonnes S as solid sulphur). Copper leaching, particularly in Chile (there is also some copper leaching capacity in Peru and the United States) has been the major factor in this; about 70% of copper leaching currently occurs in Chile, but leaching is in decline there, and new capacity is coming from places like Africa. Leaching of nickel had been a major growth area, and there is also some acid use for leaching of uranium, rare earths and some other metals. However, the slowdown in the Chinese economy has led to a slump in demand for base metals at the same time that mines and production projects have been gearing up around the world, leading to overcapacity and low prices, and there have been production cutbacks and some new projects have been postponed or cancelled. Particularly hard hit have been copper leaching projects, with Freeport cutting output at El Abra in Chile and Miami, Tyrone and Sierrita in the US, and Glencore cutting back at Mopani and Katanga in Africa and Collahausi in Chile. While there is some incremental demand coming in uranium mining, nickel production is turning to other sources than the relatively expensive and temperamental high pressure acid leach process, and overall any demand increases from this area look to be relatively modest over the next few years.

Table 1: **Major sulphur exporters and importers, 2010 and 2015,** million t/a

Exporters	**2010**	**2015**
Canada	3.6	4.8
United States	1.5	1.7
Abu Dhabi	1.8	3.0
Iran	1.2	1.8
Qatar	1.2	2.2
Saudi Arabia	3.4	2.8
Kazakhstan	3.8	2.8
Russia	5.0	3.1
Importers		
China	10.5	11.9
Brazil	1.9	2.0
Morocco	3.9	4.7
Tunisia	1.8	1.0
India	0.9	1.4
United States	3.0	2.1
Australia	0.5	0.9

Sources: Fertecon, Integer, IFA, USGS

Supply/demand balance

In spite of the continuing investment in new phosphate capacity, the rapid growth in sour gas production has pushed the sulphur market into surplus for the time being. CRU estimates that the sulphur market went into slight surplus last year, but will have an excess of 2.2 million t/a in 2016, rising to 3.3 million t/a in 2018-19, before new phosphate capacity additions and slowing growth in sour gas production begin to bring the surplus down again.

Total elemental sulphur trade is around 32 million t/a, or just over half of all sulphur that is produced. As shown in Table 1, the major exporting areas, where sulphur production is in considerable surplus, are western Canada, southern Russia and Kazakhstan (the 2010 figures for these are inflated by major destocking which was occurring at the time), some of the major refiners in the Far East such as Japan, Singapore, Taiwan and South Korea, and Middle East oil and gas producers like Saudi Arabia and other Gulf countries such as Iran, Abu Dhabi etc. Major consumers are some of the world's major phosphate fertilizer producers, especially China, but also Brazil, India and North African countries like Morocco, Algeria and Tunisia, as well as Jordan. The US also imports sulphur on its east coast, particularly for phosphate producers in Florida. However, the difference between the 2010 and 2015 figures also clearly shows the increase in production in the Middle Eastern countries, apart from Saudi Arabia, where the first Ma'aden phosphate project has absorbed some of the production that used to be exported.

Stockpiling

With sulphur likely to spend a few years in surplus, and prices depressed – down to $75-80/t f.o.b. Middle East at time of writing – the question then becomes who will be forced into stockpiling over the next few years? Oil refiners tend to be one of the most involuntary of involuntary suppliers; keeping the refinery running requires the sulphur to continue being removed, and most refineries have little space for large scale stocks and so must sell sulphur whatever the market conditions. So it is among the sour gas producers that stockpiling is most likely to occur. The highest cost producers, in terms of reaching end-use markets, are those furthest from ports, and that tends to mean producers in Central Asia and northern Alberta. Canada already has 10 million tonnes of sulphur in storage at its oil sands production sites near Fort McMurray, but has room for more if need be. Kazakhstan did have a major stockpile of sulphur at the Tengiz TCO site, but was forced to sell it due to environmental concerns, and it remains to be seen how that might play with Kazakh authorities going forward. However, it seems a foregone conclusion that someone is going to be stockpiling over the next few years. ■

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A coke oven, one of the major sources of AS.

Ammonium sulphate production

Ammonium sulphate has had something of a resurgence in recent years, due to the move of caprolactam production to China and its utility as a sulphur-containing fertilizer.

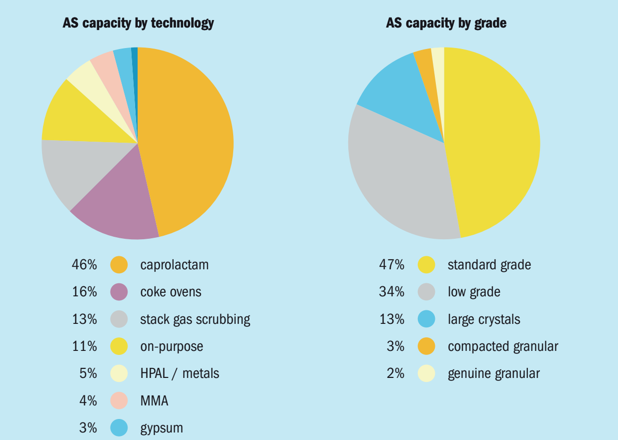
Ammonium sulphate (AS) was historically the first synthetic fertilizer to be used on a large scale, produced in Western Europe and North America as a by-product from the treatment of coke oven gas by sulphuric acid to remove ammonia. Initially valued only for its nitrogen content, its relative use diminished and was overtaken by the rise of other nitrogenous fertilizers with a higher N content; first ammonium nitrate (33%N compared to 21% for AS), and then more recently urea (46%N). However, as sulphur deficiencies in soil become a growing concern worldwide, use of AS continues to rise, aided by its increased supply as a by-product from a number of industrial processes where the AS becomes a 'sink' for the sulphur component of the reaction.

Production

Production of ammonium sulphate comes from a variety of different processes. The original, as noted above, and still a major source of AS today, is from neutralisation of ammonia in coke oven gas using sulphuric acid. But it can also come from acid neutralisation of ammonia in other industrial processes, including scrubbing of emissions from coal-fired power stations, now another major source. It can also come in the reverse case, where ammonia is used to neutralise excess sulphuric acid, such as in the high pressure acid leach (HPAL) processing of nickel ores, as well as other similar metallurgical leaching uses, or where ammonia is used itself directly as a leaching agent in sulphur/sulphate-containing rocks.

Finally, it can also come as a by-product from sulphuric acid reactions with other nitrogen-containing chemicals, including cyclohexanoxime, an intermediate in the production of caprolactam, itself the main precursor to nylon-6/polyamide-6 in fibre manufacture. Figure 1 shows the relative amount of ammonium sulphate produced from each process, and as can be seen, production from caprolactam manufacture has come to be the dominant source of the compound. There is also some on-purpose production from the reaction of ammonia and sulphuric acid, or treatment of gypsum with ammonia – shortage of AS in some key markets due to the lack of AS from industrial sources, and local cheap availability of ammonia led to increasing on-purpose production in some countries during the 1990s, but the rise of the caprolactam industry over the past two decades has reduced the impetus for on-purpose production.

Fig 1: Ammonium sulphate capacity by supply source and product grade



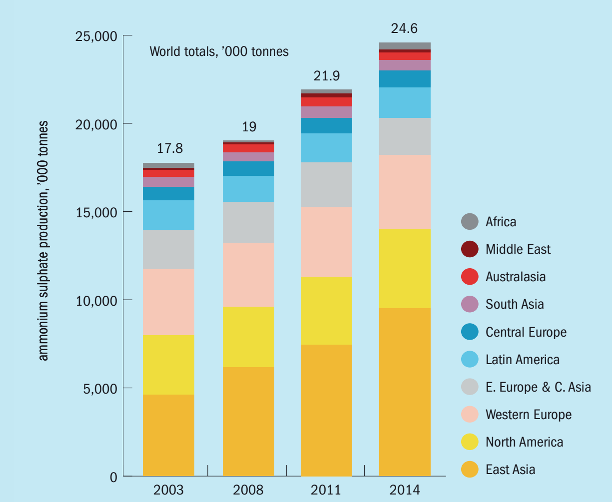
Source: Integer

Product quality

Grades of ammonium sulphate tend to vary according to source. As Figure 1 shows, the standard grade, derived from caprolactam manufacture, is the largest market segment, comprising small white or slightly yellowish crystals with few impurities. Ammonium sulphate derived from HPAL, stack gas scrubbing, acrylonitrile and cyanuric acid manufacture, as well as some on-purpose AS synthesis also all tend to produce 'standard' grade AS. This standard grade can be compacted to produce a pseudo-granule which is used in NPK blends and some fertilizer grades, and for which a slight premium can be charged. Slow drying can also lead to larger crystal formation, and this grade is also used in NPK blends and direct application. It is also possible to add a 'proper' granulation section, which often happens in on-purpose production. These are the most expensive, premium grade, for better quality fertilizer production. Lower grade, brownish and 'sticky' crystals meanwhile come from coke oven gas, methyl methacrylate manufacture and gypsum processing. These poorer quality crystals have a tendency to cake or crumble and are generally cheaper.

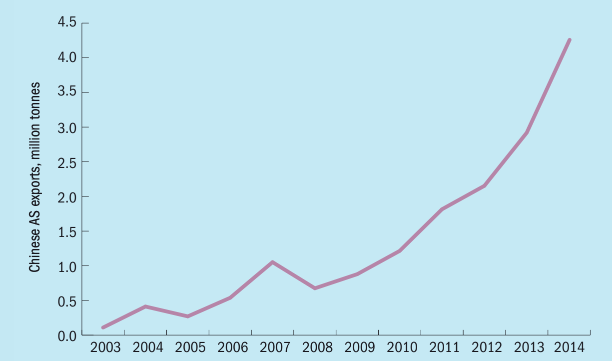
The premiums are often market-specific, however, with North America, Japan and Brazil tending to pay more for larger crystals/granules, and places like southeast Asia being much less concerned about the distinctions.

Fig 2: World ammonium sulphate production by region



Source: IFA

Fig 2: Chinese ammonium sulphate exports



Source: IFA

The rise of China

Until the late 2000s, AS production was still dominated by long-established caprolactam capacity in the industrial economies of North America, Western Europe and East Asia. These key global suppliers produced AS to meet domestic demand, but also relied on the important Asian export market, particularly China. However, the market has gone through a dramatic shift as China has industrialised, and as can be seen in Figure 2, the global balance of ammonium sulphate production has shifted inexorably eastwards away from legacy producers in Europe, the US and former Soviet Union. China's additional capacity came initially from coke oven gas production, and

Over the past five or six years, however, there has been an additional boost due to China's push for caprolactam production. Caprolactam demand is driven by the market for polyamide fibres for textiles, as well as resins and films manufacture, and as with many industrial commodities, incremental demand in these sectors has come almost entirely from China in the past few years. Demand for caprolactam has increased and is projected to increase by around 3-4% out to 2020.

There are various production processes for caprolactam, including HPO (hydroxylamine phosphate oxime) and HSO (hydroxylammonium ammonium sulphate oximation) – both licensed by DSM, and BASF's HSNO process, as well as ammoximation. The amount of ammonium sulphate by-product each process produces is dependent on the route, with HSO producing 4.4 tonnes of AS per tonne of caprolactam, HSNO 2.5 tonnes per tonne of caprolactam, and HPO+ (the latest iteration of DSM's HPO technology) and ammoximation 1.5 and 1.6 tonnes AS per tonne of caprolactam respectively. China has focused on ammoximation and HPO+ in its caprolactam production, so generating only relatively modest amounts of ammonium

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sulphate compared to other routes. Even so, however, such has been the volume of installed new caprolactam capacity that Chinese ammonium sulphate production quintupled in the decade from 2003-2014, from 1.2 million t/a to 6.2 million t/a, and China has now come to represent one quarter of all production around the world.

As with many other industrial commodities, China has over-invested in capacity, and utilisation rates have fallen, while Chinese domestic production now runs considerably ahead of domestic demand for AS. The upshot of this has been to increasingly push Chinese AS production onto the world market. Figure 3 shows the continuing rise of Chinese exports, now coming to represent 34% of all traded AS. The effect has been to push down production rates in other parts of the world correspondingly. However, in spite of this market shake-up, the premium pricing of high grade products continues to make ammonium sulphate supply an attractive proposition in some regions.

Consumption

The main use for ammonium sulphate is as a fertilizer, though there is some sparing use as an acidity regulator in foods and breads, and as a herbicide, as well as in leather tanning, textile dyeing, cellulose and fiberglass insulation, fire extinguisher chemicals, and fermentation. Its use as a fertilizer has been boosted by two factors – firstly for alkaline soils it can be an important way of bringing soil pH back up. Secondly, sulphur is increasingly been seen as a plant nutrient which needs to be applied deliberately in the same way as nitrogen, phosphorus and potassium. This has come about through the depletion of sulphur in soils as global measures to control sulphur dioxide emissions, initially from power stations and smelters (via 'acid rain') and more recently from vehicle exhausts due to the sulphur content of vehicle fuels, have led to progressively lower levels of SO_2 being emitted to atmosphere and hence lower levels of sulphur being deposited to soils. While there are many potential sulphur-containing fertilizers, ammonium sulphate is seen as a cheap and relatively easily available one.

Table 1: **Major consumers of ammonium sulphate, 2014** ('000 t/a)

Europe	
France	560
Germany	785
Spain	530
Poland	385
Turkey	1,070
Russia	520
Americas	
Brazil	2,425
Canada	1,070
Mexico	1,590
United States	2,300
East Asia	
China	1,890
Japan	605
Taiwan	680
Southeast Asia	
Indonesia	1,600
Malaysia	850
Philippines	585
Thailand	970
India	680
Total	**24,590**

Source: IFA

There is a relatively concentrated geographical pattern to ammonium sulphate consumption. The eighteen countries in Table 1 represent nearly 80% of all global consumption, and the top five represent half of this. While it is not unusual to see major fertilizer consumers like India, China and the United States on the list, some countries, like Brazil, Mexico, Turkey and Indonesia seem to be relatively over-represented. In Mexico, AS consumption actually represents 20% of all nitrogen fertilizer application.

Global demand for AS as a fertilizer is expected to grow in response to low-quality land expansions in Brazil, and the rising cultivation of sulphur-intensive crops in the US, South East Asia and Oceania. Overall global consumption is projected to increase at 2.3% annually this decade. Still, the market for ammonium sulphate tends to be supply driven because, unlike other nitrogen fertilizers, it is mostly derived as a by-product, with large volumes arising as a consequence of involuntary production.

New capacity

East Asia and North America have been the focus of global ammonium sulphate capacity additions over the last five years, responsible for 2.7 million t/a (57%) and 1.0 million t/a (20%), respectively, to the extra 4.8 million t/a of world AS capacity added between 2010 and 2015. China's overinvestment in caprolactam capacity means that additional volumes from this source are likely to slow over the coming years. However, according to the China National Fertilizer Industry Association, an increased focus on dealing with emissions from the coal-based power industry, which is by far the predominant source of China's electrical power, are leading to considerable new additions in stack gas scrubbing, and consequentially much Chinese AS capacity in the next few years will come from ammonia-based desulphurisation of coal emissions. Chinese producers are also beginning to take steps to improve product quality in order to better compete on the international market, as product quality issues have held back Chinese AS in some markets.

Elsewhere, KuibyshevAzot is engaged in a joint venture with Trammo to build a $12.8 million 140,000 t/a granular AS plant in Togliatti. Construction is due to be completed in 2017. German company GEA Messo has also signed a contract with PhosAgro to design and build a new 300,000 t/a crystalline AS production line at its PhosAgro-Cherepovets site. PhosAgro will use the high-grade output from the $400 million plant to replace AS currently sourced from chemical and metallurgical plants. The new AS production line will consume ammonia and sulphuric acid produced on-site and is also expected to be commissioned in 2017. PhosAgro is currently Russia's largest AS consumer due to the demand from NPK and NPKS blends.

Acid demand

Because of the variety of industrial processes which can produce it, it is difficult to estimate the amount of sulphuric acid consumed by the production of ammonium sulphate, except stoichiometrically, and even this is complicated by processing of gypsum and coal power station stack gas scrubbing. However, removing these two production routes from consideration still leaves 83% of all AS production, and taking that on a stoichiometric equivalent basis, each tonne of ammonium sulphate should account for 0.74 tonnes of sulphuric acid (100% acid basis), production of ammonium sulphate from sulphuric acid – by one route or another – can be calculate to account for around 15 million t/a of sulphuric acid, or about 6% of all acid consumption, and at present growth rates should represent another 1.4 million t/a of acid demand out to 2020. ■

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Sulphur and sulphuric acid in North America

Sulphur reports on the Argus North American Sulphur and Sulphuric Acid Seminar in Houston in September, where the focus was on market developments in the US and Canada.

The conference began with a morning on the sulphur industry. Rene Gonzales, a consultant to Argus, outlined his own forecast for global sulphur consumption. East Asia is the dominant sulphur consumer, and the growing Chinese market represents 80% of that. Global sulphur consumption is forecast to grow from 66 million t/a in 2016 to 71 million t/a in 2020, with most of that growth coming from East Asia, the Middle East and North Africa – the latter coming from Morocco's major expansion programme at Jorf Lasfar. Saudi Arabia and Jordan's phosphate expansions represent the main incremental demand in the Middle East, but this will level off after 2017. South Asian consumption is forecast to remain at around 3.5 million t/a, mostly (96%) represented by India. Consumption in Europe and Central Asia is relatively flat, likewise North America, but Latin American consumption will grow to support phosphate consumption.

David Tonyan of Argus narrowed the focus to the North American market. Supply had been tightened due to the wildfires affecting the Canadian oil sands region, increasing Vancouver prices slightly, but imports to the US were also down 30% and prices were on a downward trend all year. US sulphur production for 2015 was 8.9 million tonnes, of which 7.9 million t/a came from refining. The figure was about 140,000 t/a down on the previous year, but 1H 2016 figures showed a 130,000 t/a increase on 1H 2015, due to increased refinery production over and above continuing declines in sour gas sulphur output. Overall production is forecast to be relatively flat to 2020. US demand of 9.2 million t/a leaves a slight deficit, while Canadian demand of 725,000 t/a leaves Canada with a 4.5 million t/a surplus. About 1.9 million t/a of that is exported to the US. The US net surplus goes offshore from the Gulf, where most US production is concentrated. US consumption is of course concentrated (ca 65%) in the Florida phosphate belt. Canadian production is forecast to decline slightly to 2020, with falls in gas processing not quite offset by increases in oil sands sulphur output. Canadian inventories still top 10 million tonnes, with less than 800,000 t of that at gas plants. Canadian rail shipments to the US are forecast to decline, with more US imports from overseas into Mosaic's sulphur melter, and this in turn is leading to new Canadian investment in forming capacity.

Sulphur forming and melting

On the technology side, Mark Gilbreath of Devco reprised the motivations for and technology behind Mosaic's new 1 million t/a sulphur melter at New Wales, Florida. A fuller description of the plant and process can be found in *Sulphur* 365, Jul/Aug 2016, pages 22-24. Casey Metheral of Sandvik meanwhile described the drum granulation process offered by his company, using external seed generation in a single pass, as operated by the Beaumont sulphur facility in Texas. Some slightly contentious comparisons with other processes followed, which provoked lively discussion from other process suppliers…

Environmental strategies

Jeff Cooke of IPAC/Power Chemicals Ltd reviewed sulphur's well known environmental risks – fire, dust and acid generation – and looked at how companies can develop an environmental strategy to be a good 'corporate citizen' and neighbour. The problems can be interlinked – sulphur dust can collect on metal spars and supports and produce corrosion (as well as a potential fire/explosion hazard). Sulphur acidity means potential damage to ships holds and greater use of lime and neutralisation agents in transit and at the other end. Under these circumstances it is important to use an acidity control agent, he said, to reduce the activity of bacteria and prevent pH drop. The approach to dust suppression depends on how the dust is generated – via moving sulphur on a conveyor or during transfer, or from a static pile. Dust can be treated after formation, via a water curtain/mist, but a better approach is to prevent dust formation by treating the sulphur with a dust suppressant as it is formed, as well as at transfer points. Accurate measurement is required for precise dosing of dust suppressant agents, however.

Ethanol demand

Argus' Zander Coprozolla updated delegates on the ethanol blending situation in the US; on the one hand a competitor for gasoline as a blendstock and sulphur extraction from refineries, but on the other a boost to demand for phosphates and other fertilizers and some intrinsic acid use in ethanol production – a small but significant source of acid demand. Ethanol blended into fuel in the US runs at around 940,000 bbl/d – a record level has been achieved in 2016. Even so, stocks remain at historically high levels – over 20 million bbl. Canadian demand for ethanol has slackened this year from the 2015 figure of 6 million barrels, but this has been compensated for by record exports to Asia – China alone imported 3 million barrels in the first half of 2016, and exports to Asia, India, Mexico and Brazil are all on course to surpass their values for 2015.

Almost all of US demand is dominated by ethanol blending into regular gasoline – higher blends of ethanol (e.g. E85) remain a marginal factor in the market, as sales of flexible fuel vehicles – while rising – remain small (less than 25,000 vehicles total). Overall levels of ethanol blending into gasoline in the US are at about 9.5% in 2016, down slightly from 2015.

Phosphate markets

Phosphate processing is the key use for sulphuric acid in the US and elsewhere, and Wayne Welter of J.R. Simplot summarised global and North American phosphate markets. Production continues to come onstream in Morocco – a 1 million t/a facility started up in July. India's DAP imports are down slightly on last year but consistent with the average of the last five years, at 5 million tonnes to August. China's MAP and DAP exports are however down 35% for 1H 2016 compared to the comparable figure for last year. Russia is producing at full rates and expanding production due to a favourable cost situation due to the low rouble. There is also optimism for additional Brazilian demand in 2H 2016. For the moment however the market remains relatively oversupplied.

In North America, domestic phosphate production continues its long slow decline, down 13% in 2015-16 compared to 2010-11. The merger of Agrium and PCS has left just three major producers, and PotashCorp has clearly been the weaker, with lower production and operating rates compared to Agrium and Mosaic. The strong dollar has boosted imports over the past couple of years, especially from Russia and Morocco, and to a lesser extent China, and overseas producers like PhosAgro and Ma'aden enjoy far more favourable margins than North American producers. Global capacity additions continue apace, although world phosphate demand is forecast to rise from 40.9 million nutrient tonnes in 2015-16 to 44.7 million tonnes P_2O_5 in 2019-20. In the US phosphate applications are likely to be around the same for 2016 as 2015, although La Nina has given crop prices a slight boost due to dry conditions. Farm incomes and phosphate affordability are slightly down this year, and pricing favours more potash use.

US acid markets

In his North American sulphuric acid presentation, David Tonyan of Argus noted that low commodity prices had kept a ceiling on demand while lower sulphur prices had brought down acid prices. Corn, copper and DAP prices are all down, showing the weakness in demand. The sulphur burning plants starting up in Cuba and loss of demand in Chile had also lengthened the international market, while more supply is expected soon from Mississippi Power's gasification plant, and expansions of smelter capacity at Miami Arizona, but North American acid production was down by 4 million t/a in 2015 as compared to 2014 due to closures of sulphur burning plants. Overall North American production is forecast to rise by 1.7 million t/a to 2020, in spite of declines in Canadian smelter acid output, with a similar increase in demand, for fertilizer and industrial uses in the US.

> "Sulphur produced in North America, mainly molten, is effectively 'captive' to the North American market."

That demand for sulphuric acid in the US for industrial uses was next described by Ted Threadgill of Shrieve Chemical Co. Chemical synthesis, covering water treatment, plastics, pigments, dyes, paints, coatings and pharmaceuticals, amongst others, is the largest growth sector. Metallurgical uses in copper, zinc, nickel and lead processing are in decline, as is use in the pulp and paper industry. In the ethanol industry, where acid is used primarily for water treatment, demand is driven by government mandates, but low fuel prices and the end of government subsidies is leading to a shakeout among producers. Overall industrial consumption in North America is 12.2 million t/a, of which 11.4 million t/a is represented by the US. The North American total is forecast to grow to 13.1 million t/a by 2020.

Gene Meyer of Jones-Hamilton Co looked at the business of buying and selling acid in North America. Smelters, needless to say, focus on their metals production and keeping their acid tanks dry, while burners have a wider focus than just acid, including downstream products and generally higher margins. Gene estimated some acid production costs for different routes – estimating your supplier's costs is a key tool in negotiation. The price structure of the market has changed, he said. Prior to 2008 it was generally based on long term, firm prices. Now smelter operators have firm prices but shorter terms, while sulphur burners tend to operate at annually adjusted base price plus a quarterly adjusted sulphur surcharge. Sulphur produced in North America, mainly molten, is effectively 'captive' to the North American market, but prillers and melters allow access to the global market and have reduced price volatility.

Metals markets

Richard Hands, Editor of *Sulphur* magazine, looked at global metal markets and the future for smelter acid production. The copper industry was in the doldrums due to declining demand from China, and while there had been cutbacks in copper output, and some delays and deferments to new production, there are still a number of new copper projects coming onto the market over the next couple of years. Most of the capacity additions are in smelter/concentrate production, while the cutbacks have focused primarily on higher cost SX/EW capacity, with a net increase in acid production. China still has a deficit in smelter capacity, and 70% of new smelter capacity will be in China, possibly turning the country into a net acid exporter. In nickel, Indonesia's ban on ore exports and Philippine production cutbacks have pushed the market back into deficit and prices are rising, but most new nickel capacity is focused on nickel pig iron and ferronickel. Lead markets are down, but after some production cutbacks zinc appears to be back in deficit. The future of China's economy is likely to be the key determinant of how these markets move over the next few years, however.

Refinery acid

Livia Lorens of Haldor Topsoe looked at the use of Topsoe's WSA (Wet gas Sulphuric Acid) process as an alternative to a Claus plant in a refinery, gas treatment or gasification plant, with or without the addition of a feed from a sour water stripper, and highlighted the modular condenser which converts SO_3 to H_2SO_4. Topsoe now has 145 references for the technology, from 4 t/d to 1,150 t/d, and ranging from refineries to cokers, gasifiers, viscose plants and in metallurgical applications. ■

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The 3rd Middle East Sulphur Plant Operations Network Forum (MESPON 2016), organised by UniverSUL Consulting and supported by GASCO and Al Hosn Gas, took place 9-11 October in Abu Dhabi, UAE. Attracting more than 200 delegates, this annual event has developed into an important sulphur forum for sour gas and sulphur plant operators across the Middle East to share technical knowledge and operating experiences and to gain access to the expertise and resources of the wider global sulphur community.

With the recent start-ups of the Habshan 5 and Shah Gas facilities, the UAE has become the world's largest sulphur exporter and a major contributor to the Middle East's position as the world's largest sulphur producing region. With several other large sour gas development projects underway, the UAE is on track to becoming the world's largest sulphur producing nation in the near future, and is therefore a notable location for a conference focused on gas sweetening and sulphur recovery operations.

This year, the three day agenda for MESPON 2016 featured over 15 technical presentations and multiple panel sessions focusing on the design and operational challenges and considerations for amine plants, SRUs, TGTUs and sulphur handling facilities in the Middle East. In light of the current low oil price climate, there was a special session devoted to strategies for achieving operational excellence via energy efficiency improvements and optimisation of turnarounds. The conference culminated with a facilitated and interactive roundtable workshop providing delegates with a further opportunity to ask questions, exchange ideas and engage in open dialogue about their operating experiences.

Day one of the conference started off with welcome remarks from the executive chairman Hassan Al Hosani of GASCO and a welcome address by Angie Slavens of UniverSUL Consulting. The technical presentations on the first day provided the big picture for sour gas production in the UAE and strategies for operational excellence and included:

- How the UAE became the world's largest sulphur exporter – a timeline from 1976 to 2016 (UniverSUL Consulting, GASCO and Al Hosn Gas);
- Historical sulphur developments in Canada – sulphur and block storage of excess production (ASRL);
- Overview of a typical sour gas and sulphur plant (UniverSUL Consulting);
- Shah Gas Development – 110% capacity demonstration (Al Hosn Gas);
- Elemental sulphur corrosion in sour gas and Claus sulphur recovery systems (ASRL) – a live experiment was also set up in the conference auditorium demonstrating wet sulphur contact corrosion of carbon steel;
- A holistic approach to energy efficient improvement – Initiatives and emerging challenges (GASCO);
- Successful turnarounds for AGRUs and SRUs (Q-Chem).

Day two of the conference focused on amine treating, SRUs and TGTUs, including:

- Amine plant energy requirements and items impacting the SRU (GASCO);
- Minimising amine system failures in sour plants (Amine Experts);
- Habshan operational challenges (GASCO and UniverSUL Consulting);
- Unlocking the potential of existing brownfield gas processing assets by solvent swaps (Shell);
- The future for SRUs 50/51 at Habshan (Jacobs and GASCO);
- Intelligent design and prediction of end-of-run SRU/TGTU performance (Optimized Gas Treating);
- Design fundamentals and case study for TGT amine units (BASF).

Day three of the conference focused on the importance of the details from design to operation and featured presentations on the following:

- Corrosion in Habshan CBA units and its mitigation (GASCO);
- WHB tube sheet thermal protection (Porter McGuffie);
- Common causes of catalyst deactivation (Euro Support);
- Sulphur recovery and tail gas treating analysers – the normal, the abnormal and the paranormal (AMETEK Process Instruments and GASCO);
- Sulphur block pouring – an overview (Sandvik Process Systems).

Peter Clark of ASRL provided the closing address which discussed alternative energy, the transition to a low carbon economy and the importance of not compromising the supply of vital commodities such as sulphur, ammonia and many others that are currently produced or energised through the use of coal, oil and natural gas. ■

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An offshore wind farm – but what are the consequences of the move to renewables for the sulphur industry?

Alternative energy: the inconvenient reality for sulphur

P.D. Clark, Director of Research, Alberta Sulphur Research Ltd. and Professor Emeritus of Chemistry, University of Calgary, looks at whether it is possible to move to a low carbon economy and still have enough sulphur.

The transition to a low carbon economy must ensure that supply of vital commodities, now produced or energised through use of coal, oil and natural gas, is not compromised. Some of the more important commodities are sulphur, ammonia, fertilizer, steel, cement and base petrochemicals. Sulphur and ammonia are particularly important because high intensity agriculture relies on these products. At present, they are supplied almost exclusively through oil and gas. Sulphur, produced in almost equal amounts via sour natural gas and heavy oils, is used to make phosphate fertilizers. Other ways of making phosphate fertilizer are much more expensive and rely on petroleum coke or H_2 as reducing agents. One such non-sulphur route to soluble phosphate requires nitric acid which, in turn is manufactured by oxidation of ammonia. The hydrogen needed for ammonia synthesis is made by steam reforming of methane or liquid hydrocarbons, so, again, phosphate supply would be reliant on hydrocarbon. All alternative routes to phosphate fertilizer require fossil fuel and produce CO_2 as a by-product and in larger quantities than when using sulphur derived from oil and gas.

Mechanisation of agriculture and food distribution is also dependent on fossil fuel, so our entire food production system would be compromised without fossil hydrocarbon. Energy production by the so-called alternative methods of wind, solar and nuclear fission does not produce materials to manufacture fertilizer for agriculture. Biomass production, like any other agricultural activity, requires fertilizer, so its adoption as a supply of energy or for chemicals at levels now met by oil, gas and coal would overwhelm nutritional needs for a population moving towards 9 billion.

Replacement of coal-fired electricity generation by natural gas-based systems would largely solve the world's CO_2 emission problem. Adoption of less efficient means for production of vital commodities and in energy production would lead to increased atmospheric CO_2 levels. For example, production of sulphur from native deposits or its replacement, nitric acid, would lead to increased CO_2 emission per tonne of fertilizer produced, not less. Replacement of coke by wood charcoal in steel making would result in massive CO_2 emission increases as well as devastating the world's forests.

Contrary to popular opinion, heavy oil and bitumen should be the preferred way of supplying liquid fuels in a lower carbon economy because these resources would also supply sulphur, fertilizer, asphalt and coke for steel and cement manufacture. Overall, I suggest that our economy and industrialised systems on which we depend cannot be fully decarbonised. A balance between alternative energy supply (wind, solar, nuclear, hydro-electricity) and use of certain types of crude oil and natural gas will have to be struck for the near-term (1,000 years?). Beyond that period reduction in energy and material use, with intensive recycle, will be needed, hopefully in concert with a much reduced population.

Sulphur

This article discusses the transition to alternative energy supply and its impact on materials important to an industrialised economy. Of those materials, elemental sulphur is one of the most important as it underpins high intensity agriculture as well as many other key industrial processes. Today, fossil fuel supplies >95 % of all of the elemental sulphur made and consumed (ca. 58 million t/a)[1]. It is obtained as a by-product from desulphurisation of natural gas and crude oil. More sulphur, in the form of SO_2 which is converted to sulphuric acid, is recovered as a by-product of copper, nickel and other metal sulphide ore smelting. That source amounts to another 24 million t/a equivalent of elemental sulphur. Sulphur supply is summarised in Table 1[1].

It is clear that energy supply must eventually change from fossil fuels because they are finite resources.

Table 1: **Worldwide production of sulphur in all forms (2014), t/a**

Sour natural gas	25.0
Sour crude oil	27.4
Oil sands bitumen	2.3
Metallurgical ore smelting	24 (as H_2SO_4)

Moreover, limiting their use is desirable as it is projected that increasing levels of atmospheric CO_2 will cause significant changes in climate and the global environment. Perhaps the most critical of these changes could be significant rise of sea levels causing loss of some coastal cities and associated port infrastructure. However, we must be cognisant of the fact that we have built an economic system supporting the modern world which relies almost totally on fossil fuel. Most importantly, our agriculture relies on fossil fuel to supply fertilizer and also to enable its mechanisation and for distribution of food. Hydrocarbons and coal are also crucial for manufacture of polymers, steel, concrete, glass and asphalt, all vital components of an industrialised economy. It is ironic that a modern wind turbine cannot be made without the products (steel, fibre glass, polymers and concrete) energised by fossil fuel. Neither can a nuclear power plant or a solar cell. Most significantly, it has been calculated that steel and concrete manufacture, at least at the scale of current production, cannot be accomplished without coal or other hydrocarbon sources[2]. Without steel and concrete, public transit systems, electric cars, bicycles and much essential infrastructure cannot be built.

In part, I am presenting this analysis to contribute to a rational discussion of how to make the transition from fossil fuel to a lower carbon economy. This transition must, above all else, actually be feasible, especially avoiding options that will take us further into an uncertain environmental future. Large scale introduction of biomass is probably a bad option because of the wide spread environmental destruction that would result from production of liquid bio-fuels at the required scale while maintaining food output. Replacement of hydrocarbons and coal by biomass liquids and wood is not achievable because of the scale of the extra biomass needed and, so, in my opinion, will not happen to any significant extent. But we could do a lot of damage trying.

Carbon dioxide sequestration is also of very limited utility because the rate at which injection facilities could be built is insufficient to make an impact on atmospheric CO_2 levels. To date, we have constructed only a handful of CO_2 injection facilities, most of which were built with government subsidy. But at least 10,000 plants must be operational within 10 years to stabilise atmospheric CO_2 levels. It is doubtful that the materials and engineers required for this effort can be mobilised in such a short time. For 10,000 plants with an injection rate of 3,000 t/d per facility, this amounts to almost 11 billion t/a, approximately one third of current industrial emissions. This amount of reduction is calculated to be the quantity required to stabilise CO_2 levels to 450 ppmv[3], although 450 must be viewed as an approximate figure given our incomplete understanding of CO_2 cycling through the geosphere. Furthermore, the only means of removal of CO_2 from flue gases at large scale requires ammonia and monethanolamine (MEA), both products being made using hydrocarbon input (methane and ethylene respectively). In fact, very large expansion of MEA and NH_3 manufacture would be required to support CO_2 sequestration. A major problem with CO_2 sequestration is that it is difficult, if not impossible, to do it profitably. Having said all of this, it still makes sense to sequester CO_2 wherever possible.

Climate specialists inform us that build-up of CO_2 in the atmosphere is the problem. Obviously, any change to energy sources must reduce these emissions. My concern is that some of the suggested alternatives will actually make things worse, principally because of adoption of low efficiency alternatives which requires massive infrastructure which is very CO_2-intensive.

The carbon-sulphur cycle

This is a complex subject, but we only need to address one aspect of it. Evolution of replicating molecular systems, life as we commonly term it, some 3.8 billion years ago, lead to life forms that could absorb light, using the energy so gained to reduce CO_2 to complex organic materials that formed the structure of new replicating molecular forms. Oxygen is the by-product of photosynthesis which, over a very long period, accumulated in the Earth's atmosphere, eventually reaching 21 vol. %. One of the original sinks for O_2 was metallic sulphides, the oxidation of which resulted in water soluble sulphates. This process still continues today as surface sulphides are replenished through geological action. The major impact of sustained photosynthetic activity was to make O_2 abundant enough in the atmosphere to engender evolution of oxidative metabolic pathways and to radically alter the composition of the world's oceans, principally loading it with soluble sulphate salts. Oxidative metabolic pathways allowed proliferation of plants and animals

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SULPHUR AND RENEWABLES

on both land and in the seas during the Cambrian period (ca. 500 million years before present). Over the last 400 million years, the remains of these and other organisms were sequestered in sedimentary deposits along with calcium sulphate which precipitated from evaporating seas and lakes by virtue of its low solubility product.

The hydrocarbons which were formed from the organic material were thus intermingled with calcium sulphate which, together, were subjected to ever increasing temperatures and pressures by burial under sediments. Equilibrium calculations show that hydrocarbons will be oxidised by sulphate yielding H_2S and CO_2, some of which leads to the production of calcium carbonate. This seemingly improbable reaction is thermodynamically favoured at all reservoir conditions. In most hydrocarbon forming reservoirs, there is insufficient calcium sulphate to react away all of the hydrocarbons such that a typical gas reservoir contains CH_4, H_2S and CO_2 in a carbonate-containing matrix. H_2S levels in natural gas vary from a few parts per million all the way to 90% by volume, being dependent on the amount of calcium sulphate that was laid down with the organic material. This process proceeds through elemental sulphur leaving sulphur as a trace component in some gas reservoirs[4]. In oil reservoirs, the sulphur may oxidise C-H bonds and form C-S bonds, the net result of which is that many oil reservoirs contain liquid hydrocarbons in a mixture with organo-sulphur compounds and an associated gas cap containing H_2S. The overall consequence is that oil and gas, as well as some coals, has become the world's main supply of accessible sulphur (H_2S and reduced organo-sulphur compounds). It is accessible because of the high chemical free energy of these reduced sulphur species, a consequence of the initial adsorption of light energy by photosynthesizing organisms with release of O_2.

Utilisation of these oil and gas accumulations in ever increasing quantities has, thus, lead to ample supply of sulphur but also a rapid re-release of CO_2 to the atmosphere. Although the behaviour of non-equilibrium systems such as the Earth's atmosphere and climate are difficult if not impossible to predict accurately, current modelling suggests a significant change in global climate patterns if CO_2 levels rise too much further. So it would seem sensible to reduce the rate of accumulation of CO_2 and other greenhouse gases. The question is how to accomplish this feat without damaging the global economy to a point where it cannot function, in particular addressing the fact that fossil fuel not only supplies energy, but also commodities vital to an industrialised economy. Moreover, as already suggested, any change must be made with technology that can actually achieve the end goal: slowing release of CO_2 to the atmosphere.

Table 2: **Population, energy and commodity production**

	1951	1969	2000	2020
Population, billion	2.2	3.6	6.0	7.8
Energy consumption (10^{18} joule/year)	~100	~280	~480	~600
Sulphur production/consumption, million t/a	6	25	40	75
NH_3 production, (million t/a)	5	40	100	160

Fossil fuel and agriculture

Without design, we have constructed an agricultural and base economy in which fossil fuel is indispensable at today's scale of industrial and agricultural operations. N, P and K are the vital nutrients of plant growth, but we elemental sulphur, also an important nutrient in its own right, is needed for production of soluble phosphate fertilizer. Sulphur, recovered as a by-product from oil and gas, is converted to sulphuric acid which is used to digest insoluble calcium phosphates with the resultant phosphoric acid being neutralised by NH_3 to produce a variety of soluble, fast-acting fertilizers. Soluble phosphate fertilizers are vital to agriculture as the insoluble phosphates available in most soils cannot be taken up at rates high enough to support high intensity cropping. Overall, a complex chain of large scale industrial processes, all starting with oil and gas, produce ammonium phosphates mixed with other synthetic fertilizers such as urea, ammonium nitrate and ammonium sulphate. As far as I can see, sulphur is not obtainable at the current output from any source other than oil and gas. In a later section of this article, I will examine alternative means of producing sulphur and processes for manufacture of phosphoric acid which do not use sulphur.

Clearly, a rapid withdrawal from fossil fuel is not desirable. Fortunately, at least from the commodity viewpoint, reduction in oil and gas consumption will not happen quickly because of the power requirement to sustain our highly industrialised societies. Again, this is not to say that we do not need to wean ourselves from a fossil fuel driven system. Simply, such withdrawal must be done in a way that does not undermine civil and organised society.

Sulphur – the vital commodity

Sulphur is not like most commodities. It is produced as a by-product of oil and gas processing and, generally, is sold below its real value because refiners and gas processors do not want to be stuck with thousands of tonnes per day piling up at their plants. Obviously, if we reduce consumption of fossil fuel, we will reach a point where sulphur supply cannot keep up with demand. Traditional sources of sulphur; mining or Frasch production of native deposits, have been almost completely discontinued. Importantly, sulphur production from native deposits has never exceeded 15 million t/a, so if we were to attempt to return to this source, we would fall well short of the 60 million t/a now needed to support agriculture and industry. Moreover, Frasch production of native sulphur deposits relies on fossil fuel to heat water to 160C, injection of pressurised water into the reservoir to liquefy the sulphur and air lift to bring the dense liquid sulphur to the surface.

Given the central importance of sulphur to the world economy, and agriculture in particular, we should look more closely at its production and how we might overcome loss of sulphur in a decarbonised economy. As already mentioned, >95 % of our sulphur is a by-product of sour natural gas and crude oil processing. Sulphur production from sour gas in western Canada has declined steeply since 2005 from almost 7 to 2 million t/a because of the introduction of shale gas which is virtually H_2S-free. In recent years, much of the sulphur exported from Canada was purchased for phosphoric acid production in China and North Africa. In addition to gas processing, crude oil refining in the USA and, to a lesser extent, in Canada made North America more than self-sufficient in sulphur, with as much as 5 million t/a exported from Canada prior to 2010. Sulphur production in the USA has not increased significantly over the last decade because oil consumption has remained more or less static, at least in comparison to the 1990 – 2005 timeframe. The expansion of the Chinese economy and the expectation of higher protein diets by its urbanising population have required that China import up to 12 million t/a sulphur to support agriculture, in particular. Much of the sulphur bought by China came from Western Canada but lower Canadian sour gas production can no longer support this market. China now imports sulphur from the Middle East, Kazakhstan and many other countries as well as trying to develop its own sour gas fields.

Shale oil produced in the USA has very low sulphur content, but to date, introduction of 4 million b/d of shale oil in to US refineries since 2010 has not affected sulphur production because of an equivalent reduction in import of light, sweet crude oil from the Middle East. Most of the sulphur produced in the USA originates from heavy crude oil and bitumen imported from Canada, Mexico, Venezuela and the Middle East. In the near term, sulphur availability in the USA and Canada is sufficient because of Alberta bitumen and heavy crude refining. However, continued introduction of H_2S-free shale natural gas, low sulphur content shale oil and reduced development in Alberta's oil sands will require import of sulphur or phosphate fertilizer into North America at some future time. This change will be accelerated by government policy on increased vehicle efficiency and deliberate attempts to control CO_2 emissions in the transportation sector which will, eventually, lead to lower oil consumption. In the future, trucks and other large machines used in agriculture, for example, could be fuelled by compressed shale natural gas rather than diesel, so depressing sulphur production from refining of heavy crude oil.

For North America, it seems counterproductive to slow down Alberta oil sands or other heavy oil developments because this policy will eventually (I am guessing 20-30 years) make the continent reliant on other regions either for sulphur or phosphate fertilizer directly. Moreover, heavy oils provide asphalt for road construction and also petroleum coke for cement manufacture (the SO_2 would be sequestered as part of the cement). Light oil, as produced from shale formations, does not provide or support production of any of these commodities. I do not argue with the premise of reducing total fossil fuel use, but I contend that in refining sweet shale oil, we are choosing the wrong oils to process. I will return to this point later.

In the very near future (ca. 2020), sulphur for export will only be available from the Middle East, principally Abu Dhabi, Saudi Arabia, Qatar and Iran as these countries exploit their sour gas reserves. The only other major sources will be Russia and Kazakhstan although most of that production will be sought by China, India, Morocco and Tunisia to support phosphoric acid manufacture. Morocco, the world's largest exporter of phosphate fertilizer, will be joined by Saudi Arabia as the main suppliers on international markets.

Sulphur from non-fossil fuel sources

As already noted, sulphuric acid is a by-product of metals smelting and, presumably, that production would continue into the future. However, the amount of sulphuric acid made by this route is only about 30% of the world's needs and some of it is of insufficient purity for fertilizer production. So we need to address whether other sources of sulphur might be available. Native sulphur deposits, as mentioned, once supplied around 15 million t/a, but that industry became uneconomic as greater quantities of cheaper fossil fuel derived sulphur became available. The last major Frasch sulphur complex in the USA closed in 1999 along with most facilities in Mexico, Ukraine, Iraq and Poland. This production could be reintroduced, but it is an energy-intensive industry requiring high pressure hot water produced using natural gas fired boilers. It is unlikely that the Frasch industry can be rejuvenated at the scale of sulphur production from fossil fuel (now close to 60 million t/a sulphur). CO_2 emissions from hot water generation using methane would be another problem. Moving away from heavy oil does not mean that CO_2 emissions will decrease if the replacement technology produces more CO_2. Such an outcome could well be the case for sulphur as in Frasch sulphur recovery pressurised hot water must be injected to increase the sulphur bearing reservoir temperature to >130°C. This entails heating all of the reservoir minerals as well as the sulphur dispersed amongst the minerals. Since the energy needed to raise the water temperature would be produced through methane combustion, CO_2 production arising from sulphur obtained by the Frasch method could exceed that of sulphur production from oil sands bitumen.

Specifically, production of 1 t of sulphur by the Frasch process requires 4-50 t of water heated to 160°C[5]. This wide range in water requirement is a result of variation in the mineral/sulphur ratio in the reserve. Using an average hot water requirement of 27 t, the energy demand to heat the water to 160°C is approximately 15.8 GJ per tonne of sulphur produced, ignoring all other energy needs for running a Frasch sulphur mining complex. If all sulphur needed for the world economy, say 60 million t/a, was to be produced by the Frasch process (this is probably impossible because of limited reserves), 948 PJ would be required. Assuming natural gas would be used to supply that energy requirement, close to 100 million t/a CO_2 would be released to the atmosphere per year. Given that total emissions in 2014 were around 35 billion t, CO_2 emission from Frasch technology would be significant. This emission would be new CO_2 as it can be argued that the 60 million t/a sulphur currently supplied by oil and gas is currently produced without emission (H_2S to sulphur by the Claus process is exothermic). Of course, there is energy consumption to produce the 30 million t/a of H_2S from desulphurisation of crude oil because of the need for H_2 in that process. However, the conclusion is clear: loss of sulphur from oil and gas does not lead to reduction in CO_2 emissions; on the contrary, that change would result is a substantial increase in CO_2 emissions just for sulphur production. CO_2 emission from whatever "fuel" would be used to replace oil products would also have to be taken into account, remembering that wind and solar electricity do not come without emission.

Gypsum, $CaSO_4$, contaminated with many other minerals, is the by-product of phosphoric acid production using sulphuric acid digestion of calcium phosphate. In fact, a large part of all of the sulphur ever produced (ca. 60%) is now in the form of gypsum waste. Because it is largely insoluble in water and is impure, it is of little use. Numerous studies have been conducted as to how to recycle gypsum to sulphur or SO_2 but all methods require chemical reduction using coal, petroleum coke or another carbon source. All attempts to recycle gypsum by these methods have failed because of complications in the technology and because the processes are not deemed economically viable today. Such an industry would be a very large CO_2

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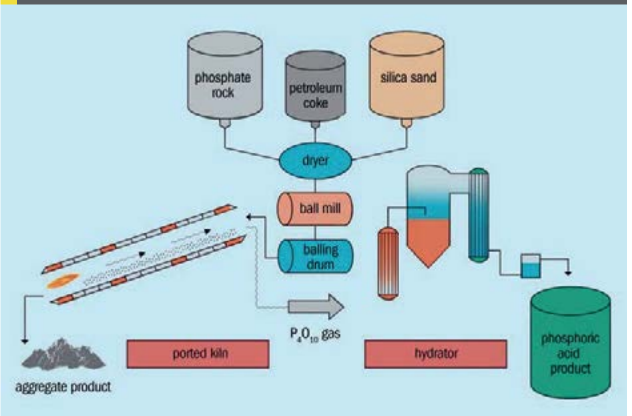
Fig 1: **Improved Hard process**



emission source if it was based on reduction by carbon. To my knowledge, no one has yet examined gypsum recycle using reduction with H_2 or H_2S. Of course, both reducing agents are only available today from oil and gas. Nevertheless, the H_2S route could be the basis of recovery of sulphur from gypsum waste while we continue to use fossil fuel and have H_2S at our disposal. To my knowledge this potential technology has not been examined. Of course, there are obvious complications in design of the process in addition to needing to transport the gypsum to the source of the H_2S.

The world's largest quantifiable repository of sulphur is as sodium sulphate dissolved in seawater. The energy requirement to separate it from water and all of the other salts in seawater likely make this source of sulphur inaccessible. Moreover, even if recovered, the sulphate must still be reduced chemically using carbon (coal), fossil fuel or H_2.

The bottom line conclusion is that today there is no viable source of elemental sulphur without fossil fuel so, in a fully decarbonised economy, we would have to do without it. This requires re-tooling of many of the world's industries as well as its most important, agriculture. Is this change possible?

Alternative routes to phosphoric acid

The need for phosphoric acid in agriculture will continue although, undoubtedly, its use could be reduced with better farming practices and some recycle. So, how would we make it if sulphur was not available? One approach, which predates the use of sulphuric acid, employs reduction of phosphate ore with petroleum coke to produce elemental phosphorus followed by oxidation to phosphoric acid[6]. Its prime application today is to make elemental white phosphorus (P_4) which is used for a number of phosphorus derivatives. It is a very energy-intensive process involving heating of a mixture of dried calcium phosphate ore with petroleum coke and sand in a carbon lined electric arc furnace. The electric arc generates a temperature of 1,400-1,500°C with the silica reacting to sequester the calcium in the ore as calcium silicate slag. The phosphate undergoes reduction by coke to phosphorus and CO with the phosphorus (as P_4) being captured in a water condenser and CO being used to generate some of the electricity for the arc furnace. Some 12-14 MWh is required to produce 1 t of elemental phosphorus. Phosphoric acid is generated by burning the phosphorus in air and dissolving the product P_2O_5/P_4O_{10} in water. It is estimated that phosphoric acid made by this route is more than twice as expensive as product produced by wet sulphuric acid method. Of course, the P_4 route to phosphoric acid also requires coal or petroleum coke and gives rise to CO_2 emissions. Primarily, this route is used to make high quality phosphoric acid, used in food additives for example, and for other phosphorus derivatives such as PCl_3[6].

In the early 1980's Hard and Megy at Occidental Research Corporation developed a rotary kiln process, replacing the electric arc. In their modification, all energy is provided internally by in situ production of phosphorus oxides and CO_2 from CO (Figure 1). Pre-formed balls of phosphate ore, silica and petroleum coke are fed to a rotary kiln with a counter-flow of pre-heated air through the kiln[7]. Thus, as elemental phosphorus is produced, its oxidation and that of the by-product CO provides the energy needed to engender reaction between carbon (coke) and phosphate. The phosphorus oxides are then passed through water, producing phosphoric acid. In many ways, the Hard-Megy process is similar to the electric arc production of elemental phosphorus but with increased energy efficiency. However, this method still relies on the use of hydrocarbon sourced coke and would have a large CO_2 emission. Thus, although, it is yet to be commercialised, it is debatable whether such technology would be acceptable in a low carbon world.

At present, world production of elemental phosphorus by the electric arc process stands at 1.3 million t/a compared to phosphoric acid production by the wet sulphuric acid route at 78.8 million t/a, equivalent to ca. 25 million t/a phosphorus[6]. If the sulphuric acid route becomes compromised because of lack of sulphur, the phosphorus industry will have to be increased by around 25 times. Of course, it must be remembered that all non-sulphur routes to phosphorus and phosphoric acid rely on coke produced from coal or petroleum. So, simply reducing use of sour gas and oil, with a concomitant reduction in sulphur output, will not necessarily result in a reduction in CO_2 production associated with phosphate fertilizer production if alternative methods have to be used.

Replacement of sulphur with nitric acid

Another means of producing soluble phosphate fertilizer was introduced in 1927 by the Norwegian Erling Johnson[8]. This process consists of acidifying insoluble calcium phosphate ore with nitric acid. One of the attractive features of this process is that it converts phosphate ores to two useable fertilizers, calcium nitrate and phosphoric acid with much reduced solid waste. Calcium nitrate can be isolated by crystallization at low temperature or a composite fertilizer can be made by neutralisation of the product mixture with NH_3.

The potential advantage of this process is that it does not produce insoluble gypsum waste or require sulphuric acid. This technology then provides phosphate fertilizer in

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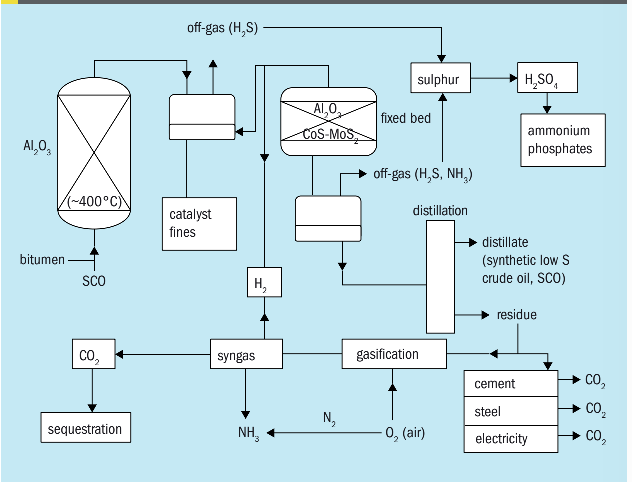
a post-hydrocarbon world. Well, not so fast; H_2 is needed. Nitric acid is, of course, a product of the fossil fuel industry because large amounts of H_2 are required to make NH_3 which is subsequently oxidised to nitric acid using the Ostwald process. All of the H_2 needed for ammonia synthesis comes from steam reforming of CH_4 so nitrophosphates also depend on fossil fuels. A non-hydrocarbon route to NH_3 is possible via water electrolysis and air separation but it would be entirely dependent on electricity from renewable sources in a non-hydrocarbon world.

In order to obtain some assessment as to the feasibility of the nitrophosphate route to soluble phosphate fertilizer at the scale required to replace phosphate produced using sulphur/sulphuric acid it is useful to examine the ammonia and nitric acid industries in quantitative terms. World phosphoric acid production from the wet sulphuric acid route is almost 79 million t/a. If the nitric acid route was used, 155 million t/a nitric acid would be required, equivalent to 41.8 million t/a NH_3. Since the ammonia used for production of nitric acid would be an additional NH_3 requirement, its global production would have to be expanded by about 25%. This is an approximate figure because of by-product N_2O formation in nitric acid production and because the co-produced calcium nitrate of the nitrophosphate process would replace some N-fertilizer needs. In addition, since current nitric acid production stands at 55 million t/a, its production would need to be tripled. When it is remembered that all of the hydrogen needed to support this technology would come from electrolysis of water in a decarbonised world, electricity production will have be expanded very significantly to replace the energy which at present is provided through fossil fuel. All of this electricity would, apparently, be produced using much lower power density methods (wind, solar).

One aspect of nitric acid production that needs to be considered carefully is that it is one of the world's prime sources of emission of N_2O[9], a greenhouse gas 298 times more powerful than CO_2 and with a long atmospheric lifetime. It is already considered to be the third most potent greenhouse gas, so expansion of nitric acid manufacture would have to be done under very strict emission limits. Very large scale H_2 manufacture using renewable electricity to support increased NH_3 and nitric acid production would contribute to increased CO_2 emission. Quite possibly, we are in a closed loop from which there is no escape using current technology and economic strategies.

Fig 2: **Upgrading of oil sands bitumen**



One conclusion from this analysis is that H_2 manufacture by different methods could assume increased importance in a lower carbon economy, but exactly how it would be made and what the environmental consequences would be is unclear.

Reduction of phosphate use

It is always better to reduce use of a commodity rather than try to re-capture it in some type of recycle scheme. This statement is true from a common sense perspective but particularly so when analysed from an energy consumption viewpoint. Thus, the most feasible method for reducing sulphur consumption in a decarbonizing world is simply to use less phosphate fertilizer. Since vast quantities of water-soluble fertilizers, including phosphates, are lost to rivers and oceans, improved application methods are clearly the real solution along with reduction in food wastage, now said to be as much as 35% of all harvested material. Improved agricultural practice and food management is vital.

Nevertheless, considerable effort is being expended on phosphate recycling technology; much of it is wasted effort in terms of reduction in CO_2 emission. It is proposed[10] that phosphate would be captured as struvite (NH_4MgPO_4) from water processed in sewage plants. Obviously, this material is a very useful fertilizer as it provides N, P and Mg, the latter element being the central component of chlorophyll. But, since the magnesium is mined as some form of carbonate (dolomite for example) which must be processed at high temperature to produce the soluble magnesium salts needed for capture of phosphate as struvite, phosphate recycling would come at the cost of an increase in CO_2 emission relative to production of new phosphate using sulphuric acid, which produces minimal CO_2. Obviously, capture of phosphate as struvite is very useful in terms of phosphorus conservation, but from an energy and CO_2 emissions viewpoint, it is much better to simply use less in the first place.

The case for oil sands bitumen

Suggestions to eliminate hydrocarbon and coal use by 2050 or 2100 are short-sighted, if not impossible to actually implement. Doing so would actually preclude construction of wind turbines, solar cells, nuclear power stations and all other infrastructure, in current forms. Public transit systems using steel and concrete would not be possible. That means no new trains, buses or electric cars using steel or any petroleum based polymer.

So why choose heavy oils and bitumen over light shale oils now produced in the USA, Canada and other parts of the world? As is already probably clear, sulphur, asphalt, petroleum coke, steel and concrete are valuable, if not indispensable in an industrialised society. Light shale oil does not contain sulphur compounds and has no significant residuum content and, hence, is of little use to augment asphalt (roads), concrete, steel manufacture and, most importantly, to provide sulphur for agriculture. I am not suggesting business as usual in the way of ever-increasing hydrocarbon consumption, but use of some fossil fuel to support vital sectors of the economy seems to be necessary until very different technology is identified. Actually, I do not know what these different technologies might be for most commodities. We need to limit CO_2 emissions in other ways and I will make some suggestion later.

Even if bitumen and heavy oil are important to our energy and commodity future, I would contend that we need to utilise these hydrocarbons in improved ways. Currently, synthetic crude oil is made by a combination of coking and hydro-treating technologies. In particular, coking is wasteful of resource as it produces coke (ca. 15% of the input bitumen) containing ca. 7 wt % combined sulphur. This product cannot be used directly for steel making (too high sulphur content) or used for power generation without expensive SO_2 control measures.

The bitumen processing scheme suggested in Figure 2 overcomes these limitations and, while undoubtedly may be more expensive just from the oil product point of view, it may be more economic when other commodities manufactured as part of the integrated scheme (steel, fertilizer, cement) are taken into account. Importantly, the combined suite of technologies could be developed with less or zero CO_2 emissions when considered as an integrated system. Detailed engineering and economic evaluations need to be conducted but it seems obvious that integrating vital technologies into central locations is preferred because it enables collection of CO_2 produced by all processes.

The first stage envisages primary upgrading of bitumen with synthetic crude oil over a fixed solid bed (alumina) designed to accommodate some carbon lay-down and for removal of vanadium and nickel sulphides. This technology has already been examined in our laboratories for bitumen transportation and is currently under investigation at the pilot scale. After removal of solid fines, the entire product would be upgraded further to oil containing <0.5 weight % combined sulphur. The amount of liquid cracking would be controlled in both units to provide oil containing enough low sulphur content residuum for syngas production to support H_2 and NH_3 production as well as for cement and steel manufacture on-site. Alternatively, oil residua could be used for power generation. Off-gases would be treated in the usual way with H_2S converted to elemental sulphur.

The overall design of this plant would integrate all technologies in a self-sufficient way. Thus, all H_2 needed for bitumen upgrading could be made using gasification of bitumen residua. The air separation plant would utilise syngas (combustion, electricity generation) as a source of energy required for air compression. N_2 from air separation would be used for NH_3 synthesis, which, in turn, would use sulphuric acid made from sulphur produced on site to support ammonium phosphate production. Furthermore, the bitumen upgrading process would be such so as to produce a low sulphur residuum that can be used directly in steel and cement manufacture (after coking).

All of the technology encompassed in Figure 2, bar production of sulphur, produces CO_2. Because these technologies would be conducted on adjacent sites, this CO_2 could be collected and either used in production of urea using some of the NH_3 produced on-site or disposed of by injection into suitable reservoirs. The last point would suggest that such an integrated facility for Alberta bitumen use should be built in either the Edmonton or Lloydminster regions as reservoirs for CO_2 injection are close by. Alberta bitumen would now be the cleanest oil on Earth with zero CO_2 emissions for oil production and the associated cement, steel, electricity, sulphur and fertilizer, a first anywhere in the world. The synthetic crude oil produced in this complex can be used internally in Canada or exported as per market needs. Such an integrated scheme could be a major boost to the Canadian economy and be entirely "green". In particular, local production of steel would reduce CO_2 emissions elsewhere. Preferably, the fertilizer generated would be used in Western Canada and the immediate USA to enhance agricultural output. This strategy amounts to a de-globalization of the world economy with overall improvement in industrial operation efficiency.

Conclusions

The transition to a zero carbon economy is impossible because alternative energy production methods rely on fossil carbon to enable these technologies. Moreover, a complete transition is undesirable because fossil carbon use produces the vital commodities fertilizer, and hence food. Steel and cement, the ubiquitous materials of construction in a modern World, amongst many other commodities, cannot be produced without some fossil fuel.

Quite possibly, alternative technology for energy and materials is not possible without fossil fuel. But, the ratio of non-carbon energy to fossil fuel derived energy can be changed slowly to reduce carbon emissions. However, the rate of change could be slower than projected because of the low power density of alternative energy technologies. Importantly, such technology should be examined carefully to ensure that it will actually lower CO_2 emission.

The long-term solution to energy and materials requirement is population reduction but, given that significant reduction is unachievable in the near term, improved energy efficiency, materials recycling and de-globalization of the world economy, particularly for food production and key commodities (steel, cement, fertilizers) would be good first steps.

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How to measure temperature in the Claus furnace

D. Ducharme of LumaSense Technologies discusses different methods to measure the temperature of the Claus reaction furnace, including the new generation Pulsar 4 infrared temperature measurement pyrometer system.

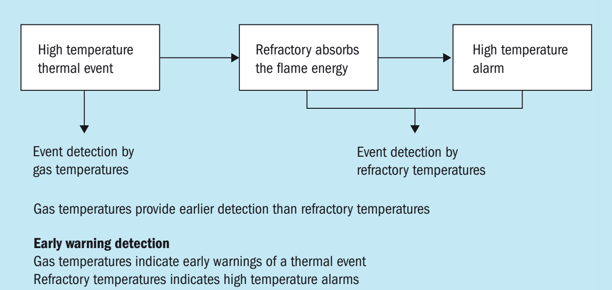
There are two schools of thought on temperature measurement in the Claus reaction furnace. One is typical of the gas plant where the concentration of H_2S is known and is constant. Why measure the temperature when there is no control over it? Constant flow with sufficient air to burn one-third of the H_2S will produce a constant reproducible temperature, and as long as the mixture ratio remains constant, there is no need to know the temperature.

The other school of thought is in the refinery or gas plant that receives its feed gas from a variety of different sources. The operator has to constantly monitor the composition of the feed gas, adjust the mixture ratios accordingly and watch for refractory damaging temperature excursions resulting from unexpected feed loads. The implementation of O_2 enrichment increases operating temperatures making reliable temperature measurements a critical requirement.

There are two critical temperatures required for the safe and efficient operation of a sulphur furnace:

- Refractory temperature is critical for furnace high temperature alarms and automated shutdown systems. This temperature represents the infrastructure temperature and the high temperature limits are specified by the engineering design. However, using only refractory measurements for furnace control offers no early warning of a high temperature excursions.
- Combustion flame (gas) temperatures offer the operators process temperature information and early warning of temperature excursions before they are absorbed by the refractory and create a refractory temperature excursion that eventually trigger a high temperature alarm or shutdowns. The ability to provide an accurate combustion temperature measurement provides an early warning of a critical temperature event that is critical for control in the higher operating temperature in an oxygen-enriched environment.

Fig 1: **High temperature thermal event timeline**



Source: Lumasense

High temperature thermal events have a process that starts with an increase in the flame or gas temperature. The energy from the flame is absorbed by the refractory causing an increase in the refractory temperatures over time and eventually reaching the high temperature alarm or system shutdown limits. The early indication of a high temperature event starting in the flame or gas temperature measurement provides a substantial early warning to a systems operator allowing for actions to be taken before a thermal event would be detected by a refractory measurement and trigger a high temperature alarm or shutdown limit. Using gas or flame temperature measurements with a refractory measurement for safety systems is the best practice for high temperature furnace operations (Fig. 1).

Temperature measurement in Claus plants is the norm and non-temperature monitoring is very rare.

Temperature measurement methods for the Claus furnace

The "eyeball" method

The most common is the "eyeball" method. The experienced operator simply looks into a viewport and observes the colour of the combustion process. Surprisingly, some operators can estimate the temperatures within ± 50°C. LumaSense publishes a colour/temperature pocket card (Fig. 2). Some will scoff at the "eyeball" method, but it has saved many a reactor from potential destruction under the watchful eye of an alert operator.

Thermocouples

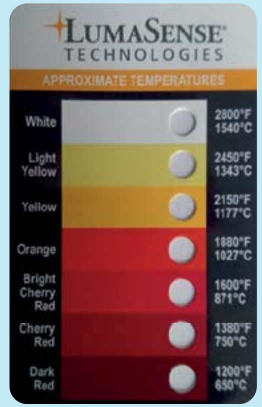
The most widely used instrument in the Claus furnace is the thermocouple. In most installations, thermocouples (and other resistance temperature devices) do not stand up under the rigours of the Claus harsh environment. Highly corrosive H_2S at 1,315°C (2,400°F) combined with combustion vibration and thermal shock are just too much for most thermocouple installations. Fast response, thin wall ceramic thermowells (metal won't hold up at these temperatures) prove too brittle to endure thermal shock and combustion vibration. Very thick thermowells react too slowly and only offer refractory measurements.

One area where thermocouples are successful is when they are embedded just below the refractory surface. This type of installation is useful for refractory protection.

Infrared thermometer

The infrared thermometer can be mounted outside the environment of the combustion process sighting through a viewport into the Claus furnace. They offer wide range temperature spans, fast response times, and selectable wavelengths with which to view the combustion process temperature and refractory temperatures.

Fig 2: **Lumasense colour/temperature pocket card**



Typical industrial pyrometers measure single temperatures and are subject to flame transparency changes in the furnace as feed changes accrue.

Having a pyrometer with two separate detectors with separate filters specific to refractory and gas (combustion) measurements with separate analogue and digital signal outputs is preferred over individual installations of single wavelength pyrometers requiring two separate pyrometer installations at a high installation and maintenance cost.

The second benefit of having two separate detectors filtered for refractory and gas measurements is the capability to apply flame transparency algorithms to the output to reduce flame impingement on refractory measurements and flame transparency in the combustion (gas) measurements.

Typical industrial pyrometers have errors when measuring flames (gas) or through flames (gas). When clean burning, the flame can become partially transparent to the gas wavelength being used. This transparency will allow some refractory to be seen and the refractory temperature to be included in the pyrometer measurement resulting in a lower measurement for the gas temperature than is actually occurring. In the case of a dirty or larger flame, the refractory wavelength measurement will have elements of the flame temperature due to low flame transparency. In this case, the lack of transparency of the flame will add components of the flame temperature to the refractory measurement, creating a higher IR refractory measurement than is actually occurring. The issue is also enhanced by changing flame transparency as feedstocks change over time, creating a variable error in a typical single wavelength pyrometer.

Note: By two wavelength pyrometer we are not referring to two colour pyrometers that use comparative wavelengths to compensate for dust and other attenuating applications. The two wavelengths referred to here are separate refractory and gas (flame/combustion) detectors and filters.

By using both a refractory measurement and gas (flame/combustion) measurement and applying the LumaSense (FMA) flame measurement algorithm that compensates for flame transparency, errors due to varying flame transparency can be removed and corrected in the individual refractory and gas measurement outputs of the pyrometer.

LumaSense has combined the two wavelengths for refractory and gas measurements into a single pyrometer that limits the installation and maintenance cost. By combining this pyrometer with the proprietary FMA, Lumasense has produced the Pulsar 4 advanced next generation SRU and sulphur burner infrared temperature measurement pyrometer system (See Fig. 3).

Fig 3: **Lumasense Pulsar 4 installation**

PHOTO: LUMASENSE

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Pyrometer verification and calibration methods

It is possible for infrared pyrometers in service on a Claus thermal reactor to read incorrect values due to miscalibration or misalignment. **T. Keys** of Delta Controls Corporation discusses the advantages and drawbacks of different options for pyrometer verification and calibration, including both in place calibration and uninstalled calibration.

Infrared pyrometers in service on a Claus thermal reactor are in an extreme environment. It is possible for the pyrometer to read incorrect values for a number of reasons including miscalibration or misalignment. Miscalibration can be caused by slight drift of the electronics among other factors. If the accuracy of the unit is in question, action must first be taken to verify that the optical sight path is not occluded by the build-up of material and that the lens of the pyrometer is not obscured. Subsequently, the optical alignment of the pyrometer must be verified to be concentric with the bore. The pyrometer can become misaligned due to severe vibration, improper installation or mishandling. Once actions have been taken to verify the alignment and optical sight path, the calibration of the unit must be verified. A number of options exist for pyrometer verification and calibration including both in place calibration and uninstalled calibration, each with both advantages and drawbacks.

Calibration methods

Prior to removal of any component of a Claus reactor pyrometer, an assessment must be made as to the ability of the nozzle block valve to provide a gas tight seal when closed. A malfunctioning or leaking valve, usually due to build-up of solid sulphur, will limit the choices of calibration methods to comparison of other permanently installed temperature measurement devices or the use of a handheld pyrometer.

Factory calibration

The pyrometer can be sent to the factory for recalibration and recertification. This option can be costly due to the time required to uninstall the unit, shipping/handling, calibration costs, and having a standby instrument on hand. The advantage is that the factory can accurately recalibrate the pyrometer in a blackbody calibrator traceable to a NIST standard.

Black body calibrator

Commercially available black body calibrators (Fig. 1) can be maintained in an instrument shop for calibration. The pyrometer would be removed from service, brought to the shop and calibrated using the black body. The black body calibrators that can reach the high temperatures used in Claus thermal reactors are extremely expensive, finicky, and require training to operate and maintain making this a less than ideal option.

Outside contractor

Contractors can be employed to periodically perform calibrations on-site. This can be costly and the pyrometer may have to be removed for calibration. Also, the effectiveness of the calibration method must be evaluated.

Insertion thermocouple

A specially designed insertion thermocouple can be temporarily mounted in place of the pyrometer's lens assembly. Using a sliding gland seal fixture, a stainless steel sheathed thermocouple is inserted into the pyrometer nozzle to the closed block valve. The sealing gland is then tightened to minimise leakage but permits the thermocouple to be inserted to a pre-determined distance to measure the temperature just beyond the refractory hot face (see Fig. 2). This method has some distinct disadvantages. The temperature that is measured at this point may not accurately represent the temperature measured by the pyrometer. This is due to the pyrometer measuring infrared light from the far side of the thermal reactor, as well as other reflected light from within the reactor. This causes the pyrometer to read a more average temperature as opposed to the point temperature measurement obtained by the inserted thermocouple. This is explained in more detail below. There are also safety considerations when carrying out this operation. Due to the sliding seal, slight leakage of reactor gases is possible, normally requiring that the operation be carried out under supplied air. Another consideration is that many Claus thermal reactors operate at a temperature higher than

Fig 1: **Commercially available blackbody calibrator**

Source: Delta Controls

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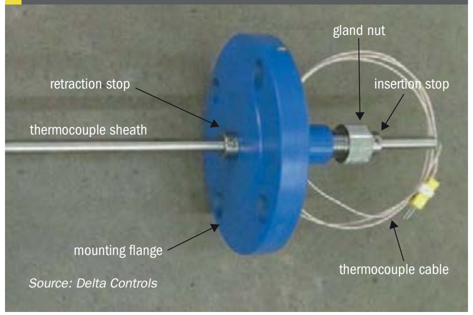
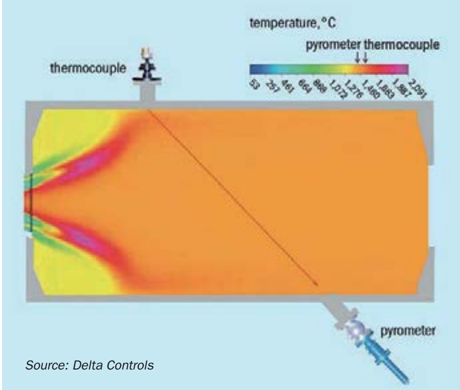
Fig 2: **Insertion thermocouple**



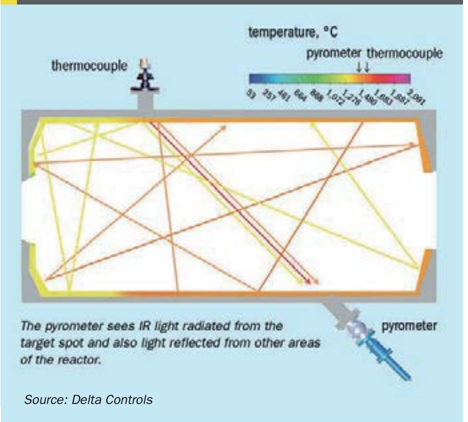
Source: Delta Controls

Fig 3: **CFD model: the burner zone of a Claus thermal reactor with the pyrometer aimed directly at the thermocouple**



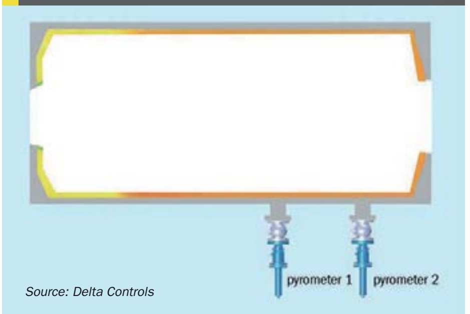
Source: Delta Controls

Fig 4: **IR light detected by the pyrometer**



Source: Delta Controls

Fig 5: **Side by side pyrometer calibration**



Source: Delta Controls

a stainless steel thermocouple sheath can withstand. At high temperature the stainless steel sheath can become deformed to the point that it cannot be withdrawn from the thermal reactor through the sliding gland to the point where the block valve can be closed. After the thermocouple measurement is taken, the thermocouple is then removed and the pyrometer adjusted to the thermocouple's measured value. All factors considered, using an insertion thermocouple to verify the accuracy of the infrared pyrometer should only be performed when no better options are available.

In place calibration

It is possible to calibrate the pyrometer in place without removing it from service. These methods use other instruments on the thermal reactor as references for calibration. Some options are as follows.

Calibrate using the nearest permanent thermocouple

If the thermal reactor has a nearby permanently installed thermocouple, it can be used to verify or calibrate the pyrometer. This is an improvement over the insertion thermocouple, since there is no risk of leakage, overheating, or extraction problems.

A disadvantage of this method is that the thermocouple may not be located in the same area as the pyrometer and will not read the same temperature. In fact, even if the pyrometer were pointed directly at the thermocouple, the two instruments might read different values.

Fig. 3 depicts a typical temperature profile of the front section of a Claus thermal reactor. This profile was created via computational fluid dynamics (CFD). A thermocouple is positioned close to the burner and a pyrometer further down the reactor is aimed directly at the thermocouple. Note the elevated temperature at the thermocouple created by the burner flame while the rest of the downstream thermal reactor section temperature is uniform.

In this example the pyrometer is aimed directly at the thermocouple. The hot infrared energy around the area of the thermocouple is easily viewed by the pyrometer and one would expect the two instruments to read about the same temperature. However, this would not be incorrect. The thermocouple measures the temperature of the refractory hot face at one small point. In this model, the spot temperature at the tip of the thermocouple is considerably above the average temperature of the refractory due to the direct impingement of hot combustion gases.

The pyrometer detects the hot radiated energy from the area around the thermocouple, but due to the relatively low emissivity and high reflectivity of the refractory brick, between 50% and 80% of the light detected by the pyrometer is actually reflected light radiated from surrounding surfaces, as noted in Fig. 4. In Fig. 3, the nearby surfaces are considerably cooler than the target spot of the pyrometer; the pyrometer will therefore report a temperature less than the temperature of the thermocouple.

Calibrate using a nearby permanently installed pyrometer

Some thermal reactor installations have multiple pyrometers mounted in the same zone for redundancy (see Fig. 5). In this case, it may be possible to use one pyrometer to calibrate the other.

This is only possible if the following conditions are met:

- both pyrometers are looking at the same area of the thermal reactor;
- the pyrometer being used as a reference is known to be in good working condition.

Calibrate using a handheld pyrometer

The foremost recommended method to calibrate a pyrometer is with a handheld Claus reactor pyrometer. The process pyrometer is temporarily removed and replaced with a portable pyrometer that has matching optical characteristics. After reading the thermal reactor temperature, the process pyrometer is placed back in service and adjusted to match the portable pyrometer reading. In many cases, nearby viewports may be used instead of removing the process pyrometer.

Note that the portable pyrometer must be one that is specifically designed for the Claus thermal reactor. A general purpose portable infrared pyrometer typically has too wide a viewing angle to accurately see down the narrow aperture of the valve, nozzle, and borehole into the thermal reactor. It is very likely that a general purpose portable infrared pyrometer may detect wavelengths that are sensitive to changes in the composition of the process gases, causing erroneous readings. Such an instrument may also be sensitive to attenuation by coatings on the viewing window or partial occlusions in the bore.

Fig 6: **Delta Controls model HIP handheld pyrometer**

Source: Delta Controls

A portable pyrometer designed for use in a Claus thermal reactor (Fig. 6) will have the appropriate narrow field of view, will detect the same wavelengths of light as the permanent pyrometer, and will ignore the attenuation of the window or any partial bore occlusion.

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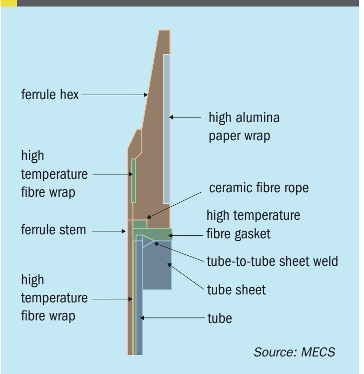
Rapid WHB retubing at IPL Mount Isa site

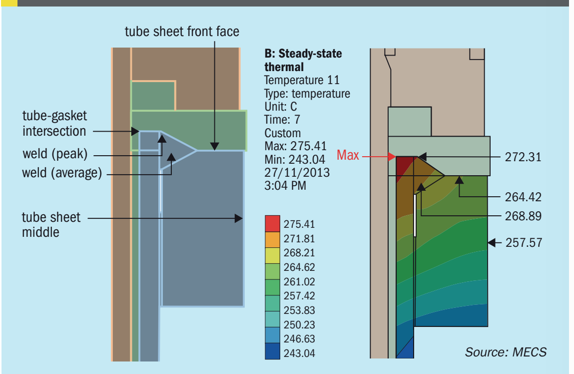
Energy recovery is a critical driver of sulphuric acid plant economics and the ability to properly design, operate, and maintain energy recovery equipment is critical to the successful operation of a sulphuric acid plant. Properly maintaining an acid plant waste heat boiler involves the right skill, expertise, and at times, creative solutions to balance the various needs of a plant. The IPL Mount Isa boiler retubing project, described here by **B. Lamb** of MECS, **M. Donaghue** and **R. Gosling** of RCR Energy and **L. Leonforte** of Incitec Pivot, provides a great example of this.

Fig 1: **Finite element model configuration**



Source: MECS

Fig 2: **Finite element model temperature results**



Source: MECS

Effective energy recovery in sulphuric acid plants can drive the economics of the plant every bit as much as the actual production of sulphuric acid. As such, many technologies have been used over the years to effectively recover energy. Examples include:

- waste heat boilers (WHBs) for recovering heat from the oxidation of sulphur into sulphur dioxide in the furnace;
- economisers, superheaters, and gas to gas heat exchangers for recovering heat from the catalytic conversion of sulphur dioxide to sulphur trioxide in the converter;
- boiler feedwater preheaters to cool strong acid by heating treated water that is fed to the deaerator;
- recovery of the heat generated from the absorption of SO_3 into sulphuric acid, such as MECS® HRS™
- latest generation, integrated technologies for optimising energy conversion across an entire plant, such as MECS® MAX3™

As energy recovery plays such a crucial role in overall plant economics, the reliable operation of energy recovery systems and the associated equipment is critical to the successful operation of a sulphuric acid plant. In the case of acid plant WHBs, ensuring reliable operation includes aspects such as proper design, operation, and maintenance.

Challenges for IPL Mount Isa

In the case of the IPL Mount Isa sulphuric acid plant, 2014 presented some very serious challenges associated with maintaining the site's 16 year old No. 1 waste heat boiler (WHB1).

WHB1 is a horizontal tube sheet boiler with 859 tubes, 70 mm diameter x 9,000 mm long. The boiler shell is 3,410 mm ID and 45 mm thick. Process gas from the sulphur burner directly upstream, enters a refractory-lined plenum and enters the tubes at 951°C, producing 2,400 kPa(g) steam in the boiler shell. The hot end tube sheet had circular ceramic ferrules consolidated with 100 mm of high alumina refractory held on with "cowhorn" anchors.

IPL had recent experience with tube to tube sheet failures in their No.2 waste heat boiler (WHB2), which was re-tubed under priority conditions by RCR Energy, including a redesigned tube to tube sheet joint. The original tube to tube sheet joint had a large root gap and a large "V" at the back of the tube hole, which seemed intended to wash the crevice and cool the tube welds. However, IPL preferred a conventional hole with face welding followed by expansion, although this configuration had the potential to increase the tube tip temperature. Whilst there was no refractory in WHB2, the methodology formed a basis for retubing WHB1.

Ultimately, it was the pitting corrosion found in the tubes of WHB2, attributed to water chemistry that led to the decision to re-tube WHB1.

With WHB1, there was concern that the tube tips may be experiencing high temperatures under the hot face refractory. Excessive tip temperatures can lead to sulphidising and hence weld failure. IPL identified that a new hot face design, incorporating HexPro™ ferrules manufactured by Blasch Precision Ceramics (Fig. 1), provided time savings during re-tubing and afforded better inspection and repair options in the future. RCR Energy performed thermal calculations on the boiler and had Aurecon carry out thermal finite element analysis (FEA) of the redesigned tube to tube sheet joint, inclusive of the HexPro™ ferrules (see Fig. 2). Comparative analysis was carried out up to 1,200°C and it was found that the HexPro™ ferrules provided excellent protection of the tube ends with slight improvement in temperatures at the tube sheet.

In addition to the capital cost of a new boiler; the likelihood of removing and replacing a new boiler and its infrastructure during a three week shutdown is remote. With tubing unlikely to last another four year campaign, the decision was made to re-tube WHB1, including new tube sheets and hot face refractory.

Fig 3: **Cutting WHB cold end vestibule (left) and tube sheet (right)**

Fig 4: **Hot end tube cutting**

Fig 5: **Insertion (left) and cutting (right) of new tubes**

Fig 6: **Marking out hand holes prior to complete removal**

PHOTOS: MECS

Retubing considerations

A major time constraint identified was gaining access to the hot end, where the plenum has three layers of interlocking refractory brick. As personnel and tools could access the hot end through the sulphur burner openings, it was decided that the three layer system would not be disturbed, and the hot end tube sheet would be brought through the boiler shell from the cold end. The tube supports would be sectioned to allow the tube sheet to pass through from the cold to the hot end. This necessitated pre-determining a tube sheet diameter that was accessible from the hot end and compatible with the refractory design. RCR Energy designed a rail system that could support the tube sheet in its optimal orientation during insertion.

Note: It was not possible to simply cut the tube sheet and "pull" the bundle as steam risers and down comers projected inside the shell. Further, impingement plates and tube support plates (baffles) were welded to the shell and support plates were not connected to either tube sheet with tie rods.

To commence repairs, access was gained from the cold end plenum by cold cutting the dished end from the plenum cylinder, as shown in Fig. 3.

After removal of the hot face refractory, tubes were released from behind the hot end tube sheet and the hot end tube sheet removed in sections, as shown in Fig. 4. This allowed the tubes to be withdrawn from the cold end.

After the new tube sheet was installed in the hot end, openings in the tube support plates were restored. As there were

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no manways in the boiler shell, RCR Energy removed hand holes (in their entirety) to provide the access necessary to reinstate and inspect tube supports and guide tubes during insertion. The cold end tube sheet was installed and tubes were loaded, tacked, trimmed and welded, as shown in Fig. 5.

Re-welding of the complete hand holes was carried out with temper bead welding to avoid stress relieving of the boiler shell, as shown in Fig. 6. This technique was a success with weld hardness limits met throughput.

Reinstatement of the cold end dished end, combined with progressive non-destructive testing of welds and final hydrostatic testing of the shell allowed WHB1 to be returned to service in the allotted time.

Refractory Considerations

Another consideration for minimising plant downtime was the refractory work to be done on the WHB tube sheet. Conventional boiler designs utilise cylindrical ceramic ferrules, as shown in Fig. 7. Although inexpensive, the installation of conventional round ferrules can be quite time consuming, requiring the packing of monolithic refractory between the ferrules themselves, as well as a careful, lengthy curing and subsequent dry out of the refractory in order to ensure that, first, a ceramic bond is formed, and second, that all free and chemically combined water is removed from the lining prior to start-up. Failure to do this can have catastrophic consequences for the refractory.

To make matters worse, this labour-intensive and time-consuming technique for protecting the WHB tube sheet often causes other adverse effects. The monolithic refractory structure that is created on the tube sheet is prone to cracking when the boiler is cycled from ambient temperature up to operating temperature, as shown in Fig. 8.

To better understand this concept of thermal cycling, it is convenient to picture concrete pavements. Pavements often have expansion gaps every one metre in order to allow the concrete to expand and contract when the temperature cycles between day time and night time temperature (perhaps a temperature difference of 20°C). Pavements without expansion gaps can develop cracks, as shown in Fig. 9. Thus it is no surprise that when a boiler cycles by thousands of degrees, the tube sheet refractory can crack if it is not engineered with the capability to expand and contract.

Fig 7: **Conventional waste heat boiler ferrules**

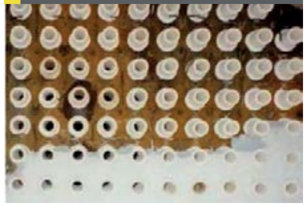

Fig 8: **Cracks in tube sheet refractory**

Fig 9: **Pavement with expansion gaps (left) vs pavement without expansion gaps (right)**

Fig 10: **IPL Mount Isa ferrule installation with HexPro™ ferrules**

Fig 11: **HexPro™ ferrules with tapered inlet for lower pressure drop**

PHOTOS: MECS

In order to provide adequate tube sheet protection for the long run, avoid refractory cracking due to thermal cycling, and provide a solution that could be installed as quickly as possible, IPL management employed the use of MECS® HexPro™ WHB ferrules manufactured by Blasch Precision Ceramics. In contrast to conventional ferrules, HexPro™ ferrules utilise hexagonal heads so that no mortar is required in between the ferrules. Thus the ferrules can simply be put into the tube sheet, as shown in Fig. 10. The result is a 67% reduction in ferrule installation time. In the case of the IPL Mount Isa boiler retube project, this time proved to be very valuable; thus the higher material cost for the ferrules was justified by the speed of installation.

Furthermore, the HexPro™ ferrules offered IPL the opportunity to face lower future maintenance costs. This is because the ferrules are engineered to expand when the boiler heats up and contract during cool down. Since there is no mortar in between the ferrules, the ferrules can grow and shrink without cracking.

As an added bonus, the ferrules selected by IPL Mount Isa also had a lower pressure drop compared to conventional cylindrical ferrules because the hexagonal ferrule heads allowed for the use of a tapered inlet, as shown in Fig. 11.

Putting it all together

Working with the right team of experts, the team at IPL Mount Isa were able to successfully retube their boiler before it failed, execute the work during a tight turnaround, and take advantage of modern technologies such as thermal modelling, finite element analysis, temper bead welding, and HexPro™ ferrules that will lead to improved operation, longer service life, and reduced maintenance costs down the road. ■

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Waste heat boiler design, operation and reliability

Waste heat boilers (WHBs) are very important components of the sulphur recovery unit (SRU) for the recovery of useful byproduct energy. In the past, WHBs generated low pressure steam but modern designs generate much higher pressure steam, thus presenting mechanical design and operating challenges. As a result, WHB failures are more common.

The purpose of this article is to identify the key design and operating considerations for the SRU WHB. The primary intention is to raise awareness of the importance of the WHB so that good design and operating practices will be engaged and SRU reliability will be improved.

In recent years the frequency and severity of WHB problems have increased. It is suggested that the increase and severity of these problems are related in large part to the following items:

- Higher pressure steam generation.
- Increased oxygen-enriched SRU implementation.
- Utilities are not instrumented to the same degree as the primary process.
- DCS system has reduced field surveillance.
- High turnover/inexperienced operating staff.
- Lower staffing of operating and technical support roles.
- Limited SRU design experience in operating companies.
- Lack of feedback from operating performance to engineering design team

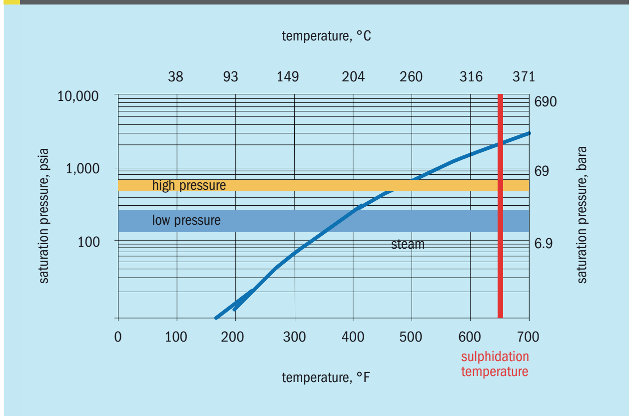
SRU start-ups and shutdowns are less frequent as the industry has moved towards longer run-times between scheduled shutdowns. In the past biannual turnarounds were common, today scheduled turnarounds are typically three to four years apart. Several gas plants and refineries are targeting five years between scheduled turnarounds. This change in turnaround philosophy has resulted in the start-up, shutdown and utility systems being less familiar to operating staff. It is also more likely that the operating staff has changed, and thus experience with start-up and shutdown activities has been lost since the last turnaround. Furthermore, the extended run-time increases the possibility that the WHB mechanical integrity and associated utility systems could be compromised since the last inspection.

A major change in the industry in the last 15 years is the trend of replacing satellite control rooms, necessitated by pneumatic control systems, with central remote located control rooms utilising electrically based DCS control systems. In itself the DCS systems have provided terrific advancements in control strategies, process variable data tracking, overall system component tracking (i.e. control valves, rotating equipment, motors, etc.), allowing for statistical data analysis on both the process and utility side. However, with remotely located control rooms fewer operating staff are available in the plant, with less surveillance of the field equipment.

The safety and control features of the single remote control room based on a DCS/PLC system are very beneficial. For many locations, an unfortunate casualty of this "advancement" is that field check-out is not as common. It is not unusual to spend an entire day in a refinery SRU and not see an operator. There was an era in which a routine walk through the "metal forest" would provide a feel for the operating condition of the unit on the basis of sound, sight (i.e. sulphur rundowns, steam leaks, etc.), smell and touch. This notion may seem nostalgic, but the current modern DCS/PLC systems do not completely replace the human senses. At one time the limited amount of data provided by the control system was supplemented and complemented by the database accumulated by the human element. It is suggested that there may be too much reliance placed exclusively on the data provided by the DCS system. The intermittent blowdown requires operator intervention. Instrumentation systems have not been extended to certain critical items such as the WHB continuous and intermittent blowdown. This is especially true for the very critical WHB intermittent blowdown system, and this means verification and tracking cannot be provided by the DCS system.

The lack of experience has been aggravated by the industry shortage of both operating and technical support personnel. Thus, it is typical for operating staffs to be inexperienced and also overworked. It is common to hear that the operating and technical staff are working only to put out "brush fires" which leaves no time for learning or optimising the units. This becomes a significant problem for items related to the WHB operation in particular.

Fig 1: **WHB operating regime vs. carbon steel sulphidation temperature**



Waste heat boiler design and operating considerations

Operating regime

Sulphur recovery units generate two products, sulphur and steam. In many cases the steam is more valuable than the sulphur. Steam is generated as a way of usefully transferring the significant amount of energy generated by the Claus process in both the thermal and catalytic stages. WHB high pressure steam can be utilised for SRU catalytic indirect reheat, feed stream preheat and to drive a turbine on the combustion air blower. The steam generated in an SRU can also be utilised outside the SRU, e.g. the excess can be exported for heating (amine reboiler, sour water stripper boiler, steam tracing etc.) or to spin a turbine.

In the past the WHB generated low pressure steam but modern designs generate much higher pressure steam thus presenting mechanical design and operating challenges. As a result, WHB failures are more common.

With older SRU designs, typical of the pre-1990 era, the WHB was designed as follows:

- Pressure range: 10 to 17 barg (150 to 250 psig)
- Steam temperature: 179 to 204°C (354 to 399°F)

Modern designs of the last 20 years are typically designed as follows:

- Pressure range: 31 to 41 barg (450 to 600 psig)
- Steam temperature: 236 to 251°C (457 to 484°F).

The material of construction of a WHB is carbon steel. The attack of carbon steel by H_2S (sulphidation) has an onset temperature of 343°C (650°F). Thus, in comparing the operating temperatures of low pressure steam generation and the modern high pressure steam generation there is a smaller margin between the shell side operating temperature and the sulphidation temperature (Fig. 1). The higher operating temperature of the WHB steam side presents new challenges to the WHB design and operation. There is a smaller margin for error which places greater importance on the tube sheet/ferrule system design and the operation of the SRU thermal stage. This is especially true for elevated operating temperatures associated with oxygen-enriched SRU operation and also for natural gas start-up and shutdown.

Excessive temperature, rapid process temperature changes and thermal cycling associated with start-ups and shutdowns affect the reliability of the WHB by degrading the tube sheet system (refractory/ferrules/tube sheet/tube-to-tube sheet joint/tubes). Thermal cycling is detrimental to the WHB tube sheet system longevity and reliability. The reaction furnace/WHB can have a thermal-cycle life expectancy (a limited number of cycles) of as long as 20 years, in well-designed, operated and maintained systems, and as short as two or three years for inadequate designs. Damage to the tube sheet protection system results in unscheduled outages and impacts SRU reliability.

WHB mechanical considerations

Most modern plants implement a single pass configuration, and as outlined in the previous section tend to generate high pressure steam. The steam side configuration can be natural convection with an external drum or kettle type drum, the latter being used for most units smaller than 100 long t/d. Regardless of the configuration, the steam side of the WHB is normally built in accordance with ASME Section 1 code or Section VIII, determined by local permitting jurisdiction and owner requirements. The material of construction for waste heat boilers includes the primary components of the shell, tubes and tube sheets, all of which have been of carbon steel regardless of the configuration or actual SRU application.

Older WHB designs were commonly "two-pass fold back" configurations that allowed implementation of hot-gas bypass (HGBP) for the SRU first stage catalytic heating. The HGBP configuration allowed a slip stream of hot process gas to be taken from the first pass outlet and to be mixed with the No. 1 reactor inlet gas. This system has proven to be unsatisfactory from a maintenance and operating perspective, especially at SRU turndown operation.

Normal design practice is to limit cooling in the WHB such that the temperature remains above the sulphur dew point. During low flow operations, excessive cooling can occur within the WHB, and sulphur can condense within the waste heat boiler. Some method is required to remove the liquid sulphur. This can be accomplished by having process piping self draining to a thermal condenser (preferred) or by having a sulphur rundown line to the sulphur pit (not preferred). The WHB should slope one to two percent downward towards the process outlet for drainage of liquid sulphur. This slope also promotes the movement of sludge in the bottom of the water section.

Field experience has shown that thermosyphon boilers are less vulnerable to failure than kettle type steam generators. For high temperature applications, properly designed thermosyphon boilers provide the advantage of high water recirculation rates with the benefit of better water distribution and a smaller temperature gradient across the tube sheet. The kettle boiler must be designed with an adequate disengaging space in order to minimise the steam side back pressure and boiler water entrainment with the steam.

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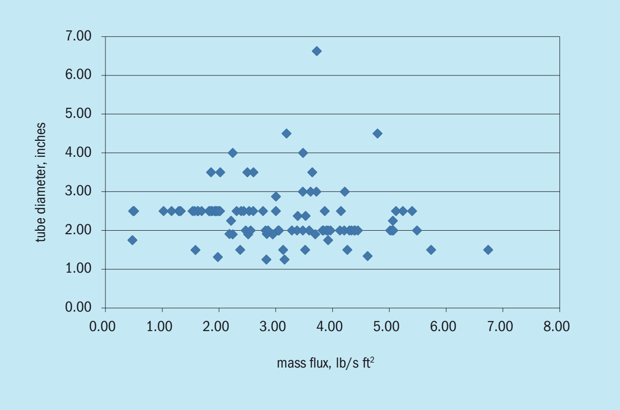
Fig 2: **Industry survey of SRU mass flux values vs boiler tube diameter**



Tube sizes used in industry for the WHB are typically 50 to 75 mm (2 to 3 inch) diameter and range from 37 to 150 mm (1.5 to 6 inch). There has been a practice in recent years to use smaller diameter tubes, less than 50 mm (2 inch) O.D.; the perceived benefit is to "quench" the H_2 + sulphur reaction, and thus reduce the re-association to H_2S with the intention of maximising the thermal stage sulphur recovery. In practice, some units have experienced fouling problems associated with the smaller diameter but from a mechanical perspective the smaller tubes have been made to work.

In side-by-side comparison at multi train installations, larger diameter tubes, greater than 50 mm (2 inch) O.D. with minimum 10 BWG (3.4 mm or 0.134 inch) wall thickness, have proven to be the preferred choice in most applications. The choice of WHB tube diameter is a function of initial capital cost and plot space availability; smaller diameter tubes require less tube length than larger diameter tubes in order to satisfy the WHB surface area requirements.

In all tube size and layout considerations, the recommended tube pitch is 1.5 times the tube O.D. dimension. Tube field layout should ensure good water circulation and distribution and avoid vapour aggregation within the tube bundle to prevent vapour blanketing tubes. Rotated square pitch is strongly preferred as it has been demonstrated to be the most resilient configuration. The WHB tube length is normally set to provide sufficient heat transfer surface area to meet the duty requirements while allowing for 0.02 to 0.03 bar (0.3 to 0.4 psi) process side pressure drop.

The tube side heat transfer coefficient (or process gas heat transfer coefficient) is a function of the tube diameter, mass flux, tube wall thickness and fouling. Gas composition affects heat transfer properties; although not so different over a broad range of process conditions, this should be considered for high CO_2 gas or high level oxygen enrichment. Water side coefficient should be based on submerged nucleate boiling.

Vapour blanketing on the steam side of the WHB represents the principal limitation in the design and operation of the WHB. This requires appropriate tube field layout and limiting heat flux. The tube pitch arrangement is very important and square pitch rotated at 45° should be used. This type of layout creates less back pressure on the steam side of the tube bundle which results in easier vapour disengagement and thus less chance of vapour engulfing tubes and leading to blanketing. These considerations are vital for high temperature thermal stage operation, such as straight through ammonia destruction or oxygen-enriched operation, where temperatures are in excess of 1,260°C (2,300°F), and the LMTD can be high. This directly correlates to high flux rates at the tube entrance with approximately 50% of the steam generated in the first 25% of the boiler tube length.

Heat flux is determined by the radiant contribution plus tube side (process gas) convective heat transfer coefficient, tube wall conductance and water side heat transfer coefficient. The primary variable driving heat flux is the process-to-water temperature difference, which varies by a factor of ten over the length of the tube. The radiation component can add approximately 20% to heat flux but is of no real significance below approximately 538°C (1,000°F).

Avoiding conditions of steam blanketing on the boiler tubes is important. The heat flux rates over the entire tube length of the WHB should be evaluated, especially the turbulent entrance area near the end of the ferrule. The heat flux should not exceed 50% of maximum nucleate flux at design, and 65% for maximum service conditions. These limits will keep the tube wall within 10°C (18°F) of the water boiling temperature at design, well below the 30-40°C (55-70°F) break-over to Leidenfrost film boiling, which occurs when the critical maximum nucleate flux is exceeded. The in-service, fouled condition will be a substantially lower heat flux than maximum clean condition although tube wall metal temperatures are substantial higher.

A conservative nucleate boiling coefficient and attendant design heat flux and mass flux should be set to assure reliability. Water flow patterns influence this transition. Higher coefficients are acceptable for an external steam drum configuration as they have forced convection, in comparison to natural convection in kettle type WHB. At very high steam flux rates (greater than 1 x 10^6 W/m² (0.3 x 10^6 Btu/hr/ft²)) there is substantial risk in exceeding maximum nucleate boiling flux and entering Leidenfrost boiling region. When this occurs the external tube is dry, covered by a film of vapour, and the heat transfer coefficient drops dramatically to about one-half or one-third of nucleate boiling. Tube wall temperature increases radically, by 100°C or more, putting the tube wall at risk of collapse.

Appropriate temperature and mass flux operating conditions can be established to provide reliable service for a specific WHB. The limitations of heat flux in the high temperature, turbulent, entrance region at the end of the ferrule can be assessed in detail for specific situations. In all cases the tube sheet protection system must be designed to maintain suitable metal temperatures. The effect of the burner flame pattern and the resulting refractory and tube sheet protection system ferrule temperatures require an effective high intensity recirculating burner type. A long or poorly

SRU WASTE HEAT BOILERS

Fig 3: **Low pressure steam generation: option for seal weld procedure**

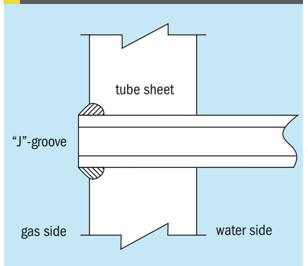
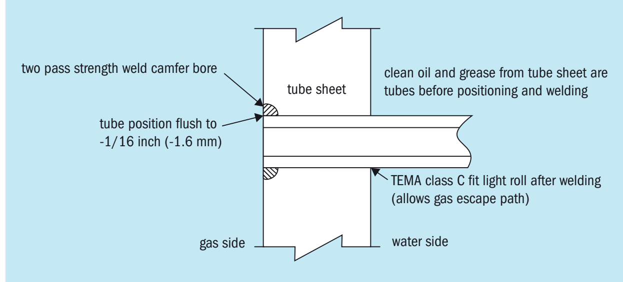


Fig 4: **High pressure steam generation: option for strength weld procedure**



mixed flame can impinge on the tube sheet or create hot spots that cause excessive ferrule temperatures. A minimum length of the reaction furnace of 4.5 m (15 ft) is needed to avoid excessive temperatures in the tube sheet protections system.

A recent industry survey gathered data on more than 100 operating WHB units that have successfully operated for greater than ten years (Fig. 2). This summary represents a cross section of industry with respect to SRU plant design and configurations, including refinery and gas plant, split flow, by-pass, oxygen enriched, ammonia, BTX, SWS operation etc., from different process licensors, with different flow rates, tube sizes, tube sheet diameters and duties. The survey has correlated the metric of tube size and mass flux. The initial results indicate that for WHB units that meet the criteria of successful operation of 10 plus years, 80% of the units operate in the tube mass flux range of 10 to 20 kg/(s·m²) (2.0 to 4.0 lb/(s·ft²)). Note, that there has been successful 10+ year operation both above and below this range, thus providing evidence that while the mass flux metric is important, it is only one factor in the determination of successful WHB operation.

Emphasis is placed on the importance of proper design of the boiler feed water, steam connections and intermittent blowdown connections. It is imperative that the correct amount of boiler feed water is directed to the critical inlet tube sheet location. From an operational perspective, intermittent blowdown is a critical operating procedure that will protect the tubes, especially in the location of the highest steam flux near the inlet tube sheet. Intermittent blowdown is done manually and is necessary for long-term reliable operation of the WHB, regardless of whether or not continuous blowdown is employed.

The benefit of thin tube sheets versus thick tube sheets is strongly supported by field experience. Taking into consideration all design and operating factors, there have been more failures with thick tube sheet units, especially with regard to tube-end and tube sheet hot face corrosion. Thermal modelling, using tools such as computational fluid dynamics (CFD) in conjunction with finite element analysis, supports the calculations that there is a higher temperature gradient across thick tube sheets. The higher temperature gradient results in more tube-to-tube sheet weld failures as well as tube sheet stress cracking. Typically the preferred tube sheet thickness should be limited to 38 mm (1.5 inch).

Tube-to-tube sheet weld procedures

A principle consideration in the design and repair of SRU heat exchangers is the tube-to-tube sheet weld procedure. For low pressure heat exchangers, such as the condensers, a seal weld procedure is acceptable. A field proven example of a seal weld procedure is provided in Fig. 3, although service history will be better with strength welding here also. However, for high pressure heat exchangers, such as the waste heat boiler, a strength weld procedure must be utilised. A field proven example of a strength weld procedure is provided in Fig. 4. Other viable alternatives also exist. The proper strength weld procedure is mandatory but is too often neglected especially in field repairs.

Industry experience has shown that the tube-to tube sheet weld can be porous with resultant water leaks and early failure unless special procedures are applied for fit up and welding. WHB failures are not identified until water leakage occurs and result in unscheduled shutdowns.

Measures to improve WHB tube-to-tube sheet strength weld reliability include the following:

- The tube sheet should be drilled to TEMA Class C, for a tighter tolerance between the tube and tube sheet.
- Preferably, but not mandatory, tube ends should be flush to minus 1.6 mm (1/16 inch); any extension past the tube sheet can be severely heated and subject to sulphide attack.
- The tube sheet should be chamfered to a depth of twice the thickness of the tube wall (or J-groove profile).
- Tubes and tube sheet must be cleaned to remove oil and grease from machining operation prior to welding. This is in order to prevent porous welds caused by generating of gases during welding which must pass through the weldment.
- The tubes should be welded to the tube sheet with a two pass strength weld, before rolling of the tubes.
- An inspection is needed after the first weld pass with repair of any deficient welds. A second weld pass is then made and inspected.

After welding, mild rolling should be done to stress relieve the weld and seal the tube to the tube sheet to prevent crevice corrosion. Rolling the tubes prior to welding aggravates the problem of trapping gases, which must escape through the weldment.

WHB start-up/shutdown procedures

Boilers and steam systems contain an air atmosphere prior to start-up. A very important requirement of getting any steam system operating efficiently is the removal of air. Air is a poor conductor of heat and thus mixtures of steam and air, for a given steam pressure, have less heat content than steam alone. Furthermore, air allowed

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to accumulate in a condensing steam heat exchanger will substantially reduce the steam side temperature gradient as the air (non-condensables) reduces the steam vapour fraction. With higher pressure boilers, the feed water is often passed through a deaerator before it is pumped to the boiler. The best deaerators can reduce oxygen levels to 3 parts per million (ppm) in water. This residual oxygen can then be dealt with by chemical treatment. However, this oxygen will be accompanied by about 6 ppm of nitrogen, which the chemical treatment ignores. The nitrogen will accumulate over time with a significant effect on heat transfer if not removed from the system.

Non-condensable gases, specifically carbon dioxide, oxygen and nitrogen, are present in steam systems. At 80°C (180°F) water can dissolve about 0.6% of its volume of air. The solubility of oxygen is roughly twice that of nitrogen, so air which dissolves in water contains nearly one part of oxygen to two of nitrogen rather than the one part to four parts in atmospheric air. Carbon dioxide has a higher solubility, roughly 30 times greater than oxygen. Free oxygen is a normal component of a water system but it is the agitation of boiling and temperature elevation that causes the carbonates in water to produce carbon dioxide. Both oxygen and carbon dioxide will cause corrosion in the entire steam/condensate system. An important feature of a properly designed steam system is the ability to purge these non-condensable gases from the steam system.

Corrosion is a given factor in a steam system. Corrosion attacks the boiler tubes and steam mains. The primary defence is to carefully monitor and maintain the boiler feed water treatment system and control the non-condensable gases (oxygen and carbon dioxide) that promote corrosion.

The shutdown procedure of the WHB is also critical. The WHB is a system with tube sheets attached to a pressure-bearing shell. In shutdown operation, the shell temperature, and thus pressure effects, will lag the tube sheet. In order to mechanically protect the tube sheet, industry guidelines typically recommend that the boiler should be cooled down at a rate no greater than 25 °C/hour (45 °F/hour).

Steam quality

As previously mentioned, sulphur recovery units generate two products, sulphur and steam. In many cases the steam is more valuable than the sulphur. Only part of the steam generated in an SRU can be utilised within the SRU, and the excess is exported to a steam header system. Depending on the steam pressure, SRU steam production is about 2,750 to 4,500 kg (6,000 to 10,000 lbs of steam) per long ton of sulphur recovered.

The SRU is a net producer of high pressure steam, even with high pressure steam being used as a heating medium for both preheaters and reheaters. Thus, depending on the end user, the steam quality can be a significant issue. Wet steam (vs saturated vs superheated) can damage steam turbines and has a lower heat content than dry saturated steam. For both thermosyphon and kettle style systems it is important to consider steam purification in the design phase. In thermosyphon systems, the external steam drum must be designed with the correct circulation rate, water holding time, surge capacity, make-up water temperature and correct separation internals to generate high quality steam with very low water entrainment. From an operating perspective, it is important to check the steam drum internals for mechanical integrity and to ensure that the operating conditions match the design basis. Frequently, the operating conditions do not match the original design and there is a resulting drop in steam quality. The steam drum design is vendor specific and it is recommended to have the vendor check the design versus the operation of the steam drum.

Kettle type boilers also warrant a full vendor review for operating conditions. The kettle must be large enough (have sufficient disengaging area for low vapour velocities) to prevent/minimise any liquid entrainment with the vapour outlet. The required area above the tube sheet is a function of the steam specific volume and steam flow rate. Fig. 5 shows a kettle sizing chart that has been successfully utilised for sulphur recovery units[1].

Boiler feed water/utility water/make-up water

The treatment of water for steam generation is one of the most difficult branches of water chemistry. The operating pressure and design of the boiler determine the quality of water required for steam generation. The recommended boiler water limits for drum type boilers is given in Table 1[3]. Boiler feed water quality must be commensurate with the level of steam service so that good operating efficiency and boiler reliability are economically achieved for the stated boiler water quality targets.

Deposits, particularly scale, can form on boiler tubes. Each contaminant has an established solubility in water and will precipitate when it is exceeded. At the high temperatures found in a WHB, deposits are a serious problem causing poor heat transfer and a potential for boiler tube failure. From a design perspective, it is important to design the heat exchanger with the appropriate fouling factor in order to ensure that the WHB is properly sized.

Table 1: **Recommended boiler water limits**

Drum pressure	Total dissolved solids boiler water maximum		Total alkalinity boiler water range	Suspended solids boiler water maximum	Boiler feed water hardness	Total dissolved solids steam range
psig	ppmw	Conductivity µS/cm	ppmw	ppmw	$CaCO_3$ ppm	ppm
0 - 300	3,500	7,000	140 - 700	15	0.300	0.2 - 1.0
301 - 450	3,000	6,000	120 - 600	10	0.300	0.2 - 1.0
451 - 600	2,500	5,000	100 - 500	8	0.200	0.2 - 1.0
601 - 750	2,000	4,000	80 - 400	6	0.200	0.2 - 1.0
751 - 900	1,500	3,000	60 - 300	4	0.100	0.2 - 1.0
901 - 1000	1,250	2,000	50 - 250	2	0.050	0.2 - 1.0

Fig 5: **Kettle sizing chart**

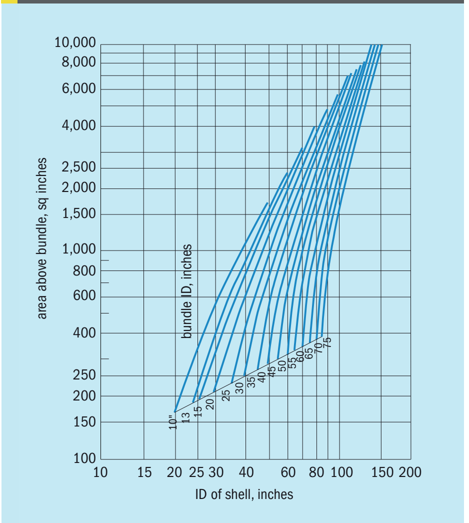
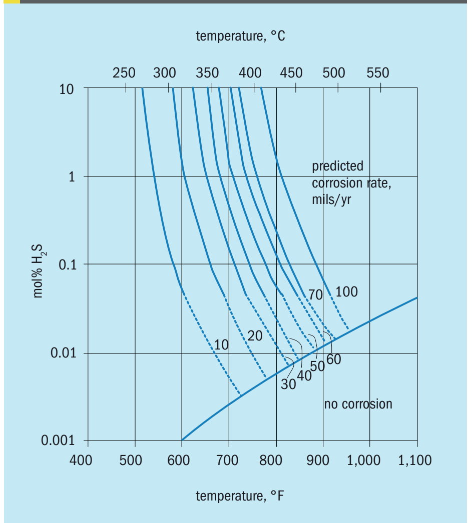


Fig 6: **Couper Gorman curve**



The recommended overall fouling factor for a WHB is 0.00018 (m²·°C)/W (0.001 (ft²·hr·°F)/Btu). Fouling increases tube wall metal temperature, the degree of which is dependent on the mass flux and heat flux.

Boiler water blowdown

The design and operation of the WHB boiler water blowdown is a critical component that is far too frequently overlooked. Boiler water blowdown is done to remove the impurities concentrated water from the boiler feed water in the WHB, and to do so while it is operating under pressure. The removed water containing suspended and dissolved solids is replaced with relatively pure treated boiler feed water. Regardless of the treating efficiency, none of the treatment processes in themselves are capable of removing all substances and a small amount of solids will be present in the boiler water. The solids become less soluble in the high temperature of the boiler water and as the water boils off as relatively pure steam, the remaining water becomes concentrated with either suspended or dissolved solids.

There are two principal types of blowdown: intermittent and continuous. Intermittent is done manually and is necessary for the operation of the boiler regardless of whether or not continuous blowdown is employed. Continuous blowdown is a continuous and automatic removal of concentrated boiler water to control dissolved solids. Both types of blowdown are necessary and work together to control scaling.

Internal chemical treatment, while not common, is based on water analysis and is used primarily to precipitate many of the solids and to maintain them as "sludge" in a fluid form. This sludge along with suspended solids that may be present must be removed by the intermittent blowdown process. If the concentration of sludge/solids is not lowered through blowdown, but rather accumulates, foaming will occur along with scale build-up and other harmful deposits.

The scale forming as salts tend to concentrate and crystallise on the heated surfaces. Scale has a low heat transfer value. It acts as an insulation barrier and lowers the heat transfer resulting in lower operating efficiency and presents the possibility of overheating the boiler metal. The result can be tube failures (collapse from external pressure), tube-to-tube sheet failures (sulphidation) or other WHB metal damage.

It was common for older WHB designs to have two or three intermittent blowdown connections and very common to include intermittent blowdown at both the hot inlet and the cold outlet end. However, despite the severity of higher operating pressure and temperature, many modern designs typically have only one intermittent blowdown. Since there is only one intermittent connection and typically the WHB is sloped, the intermittent connection is located at the cold end. This location will have the lowest steam flux rate, thus providing less tube protection than if an additional intermittent blowdown was located at the hot inlet tube sheet end of the WHB.

Intermittent blowdown

The manual blowdown valve and discharge lines are located at the bottom or low point of the boiler. This also provides a means of draining the boiler when it is not under pressure. The intermittent blowdown should be opened fully for a short duration (approximately 10 to 20 seconds) at least once per shift, thus ensuring proper removal of accumulated solids that have settled out in the bottom of the boiler.

A good intermittent blowdown design incorporates two manual valves. If two manual valves are utilised in the intermittent blowdown system, it is recommended that the blowdown valve nearest the boiler be opened first and closed last, with blowing down being accomplished by the valve furthest from the boiler. The sequence of operation once established should ensure that the valve last opened should be the first closed so that the other valve is saved from throttling service to ensure tight closing. The downstream

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valve should be cracked slightly to allow the discharge line to warm up, after which this valve is opened slowly. Quickly close the downstream valve tightly, and then close the valve next to the boiler. The frequency and amount of each blow should be determined by an actual water analysis.

Frequent short blowdowns are preferred to infrequent lengthy blowdowns. This is particularly true when the suspended solids content of the water is high. With the use of frequent short blowdowns, a more uniform concentration of the pressure vessel water is maintained. Blowing down is most effective when the generation of steam is at the lowest rate since the feed water input then is also low, providing a minimum dilution of the boiler water with low concentration feed water.

The water level should be observed during periods of intermittent blowdown. The blow-off valves should never be left open and the operator should never leave until the blowdown operation is completed and the valves are closed. It is necessary to ensure the valves are shut tightly.

Properly designed boilers have more than one blowdown connection. They permit blowdown from both ends of the bottom of the boiler. Blowdown connections are also needed on headers for draining and for removal of suspended solids which may accumulate and restrict circulation.

Continuous blowdown

The WHB is equipped with an internal continuous blowdown pipe. The collector pipe is located several inches below the normal water level, at a point where the most concentrated water is found. Periodic adjustments to the valve may be necessary setting to increase or decrease the amount of blowdown and water testing.

Proper monitoring and maintenance of appropriate water conditions in the boiler are mandatory to ensure long term integrity of the boiler. Boiler water conductivity is the principal measurement to monitor continuous blowdown effectiveness and to make control adjustments to keep within the target range. This should be monitored at least once per shift, and its trend helps in adjusting other boiler chemistry variables.

The amount of water lost through a continuous blowdown is usually the majority; considerably less water is lost through bottom blow-off in order to remove a given amount of suspended solids. The amount of blowdown depends upon the rate of evaporation and the amount of sludge forming material in the feed water.

The exact location of the continuous blowdown take-off line depends primarily on the water circulation pattern and the position must ensure the removal of boiler water where impurities are the most concentrated. The line must also be located so that boiler feed water or chemical feed solution does not flow directly into it. The size of the lines and control valves depends on the quantity of blowdown required.

The other significant water-related boiler problem is corrosion. Oxygen attack is accelerated by high temperature and low pH. Corrosive attack can occur at steam-blanketed boiler surfaces where restricted boiler water flow causes overheating. The level of contamination build-up is adjusted by utilising the correct level of blowdown, and obviously, correct treatment in the makeup treatment system. During turnarounds, the process side (inside of tubes) is normally scheduled for inspection and cleaning, but frequently the utility side (water/steam side) is neglected. The steam side must not be neglected if extended WHB operating times are to be achieved.

A problem that appears to have become more common is related to the design and the operational procedures associated with continuous and intermittent blow down. Normally the continuous blowdown nozzle is located at the elevation of the WHB normal liquid level. Poor water management can lead to external tube fouling and reduced heat transfer resulting in thermal stress of the WHB tubes, tube sheets and tube-to-tube sheet welds. The unfortunate result of inadequate use of the intermittent blowdown has resulted in more frequent tube failures due to high temperature failure. With proper practice and procedure good quality, reliable boiler operation is readily achieved.

WHB ceramic ferrules

The ceramic ferrule system is designed to thermally protect the tube sheet metallurgy from corrosive attack by the H_2S gas. High temperature sulphidation is a temperature driven phenomenon and corrosion rates are conservatively represented by the Couper Gorman Curve (Fig. 6).

At increasing temperatures the H_2S reacts with the carbon steel to form iron sulphide scale (typically referred to as sulphidation) according to the following equation:

$$H_2S + Fe \rightarrow FeS + H_2O$$

This reaction results in metal loss with maximum loss occurring at the tube weld which is furthest away from cooler WHB water/steam side and where the metal temperatures are the highest. Loss of the tube weld directly impacts reliability resulting in tube leaks, where high pressure steam enters the reaction furnace compromising the tube sheet lining.

It is critical to design the tube sheet protection system, specifically the ceramic ferrule, to keep metal temperatures to within allowable limits; below 340°C (645°F) to minimise and control the rates of sulphidation.

FEA (finite element analysis) and CFD (computational fluid dynamics) have proven to be a useful tool in predicting tube sheet temperatures and determining the thermal gradients within the ceramic. These models consider the actual design and/or plant operating data, as well as specific unit geometry as inputs and use them to determine the temperature profile across the lining. These simulations illustrate that the bulk of the heat transfer is not across the refractory thickness but due to conductive heat flow through the ferrule wall and into the boiler tube.

Even though refractory ceramics have low thermal conductivity, as the ferrule wall is very thin it tends to maintain a temperature close to the process gas. This is one of the reasons it is critical to have sufficient ceramic fibre insulation between the ceramic and the boiler tube/tube sheets. Ceramic fibre insulating papers have thermal conductivities which are an order of magnitude lower than the ceramic and play the key role in limiting metal temperatures. FEA/CFD can be used to determine the impact of the ceramic fibre insulation and the thickness of ceramic fibre that is required to produce the requisite temperature profile. Ceramic fibre insulation also provides a gas path seal to prevent process gas flow between the ferrule and the tube.

Fig. 7a illustrates the ideal temperature profile through a tube sheet protection system. The temperature within the ceramic remains uniform and the ceramic fibre insulation protects the boilers and tube sheet maintaining temperatures within allowable limits. Fig. 7b provides a close up of the tube weld temperature (with all other components hidden from the view).

Another feature of the ceramic fibre insulation and gasket is that these materials isolate the hot ceramic from the cooler metallurgy. Direct contact between the two will lead to localised temperature gradients across the wall of the ferrule resulting in thermal stress induced cracks. These cracks may manifest as either longitudinal or circumferential cracks depending on whether the maximum hoop strain or maximum axial strain is surpassed first. In all cases, however, the crack initiates at the hot (tensile) face. It is therefore imperative to minimise thermal gradients within the ferrule wall using adequate ceramic fibre insulation between the ferrule and both the boiler tubes and tube sheet.

CFD enables effective simulation of the metallurgy temperatures and thermal gradients within the ceramic for each set of process conditions. However, the reactions that occur in a WHB are quite complex, and successful interpretation of any computer modelling must also be coupled with empirical observation and experiences to ensure correct assumptions and input parameters.

Another important innovation in the design of insulation for WHB and SRU tube sheets has been the development of the hexagon (or square) style ferrule. Solid hexagon or square head ferrules are a cost-effective alternative to traditional castable tube sheet linings. Installation is generally very simple; the ferrules are simply inserted into the tube sheet and castable refractory is used to insulate the tube sheet around the outer periphery. The hexagon or square ferrule system has the advantage of allowing for easy removal enabling inspection of the tube sheet itself without dismantling of the total refractory face.

Although the solid hexagon (or square) style ferrule has been in service for more than 40 years, it was not until the advent of the hexagon (or square) ferrule that this style was used with any real success (Fig. 8).

Thermal modelling/CFD has allowed designers to determine the thermal and mechanical stress in these tube sheet protection systems. In the solid one-piece hexagon (or square) design the maximum mechanical load and thermal stress is concentrated at the shoulder where the insert (shank) is connected to the heavier head. These stress concentration issues have been minimised in the two-part hexagon (square) style ferrule. The shank and hexagon (square) head are two separate components which can expand and contract independently from each other, thereby minimising thermal expansion mismatch and evenly distributing the mechanical load along the entire ferrule insert. Moreover, this design permits the use of a ceramic fibre paper wrap over the entire ferrule insert, thereby creating an effective heat barrier, and reducing metal skin temperatures. The two-part system is also better able to accommodate thermal expansion mismatch, unusual thermo-mechanical load as well as tube sheet flexing, and is suited for use in SRUs with or without oxygen capability.

Fig 7a: **Ideal temperature profile through the ceramic ferrule**

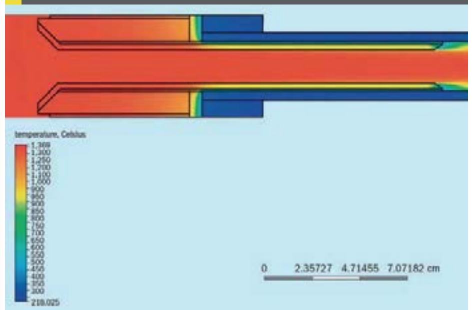

Fig 7b: **Close up of temperature profile at tube weld**

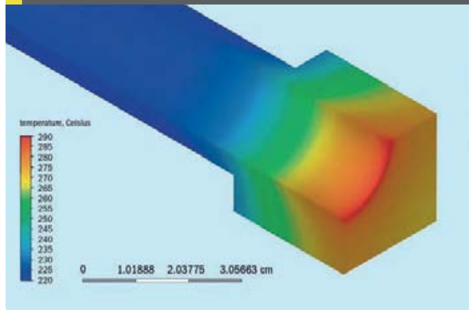

Fig 8: **Two part hexagon style ferrule drawing**

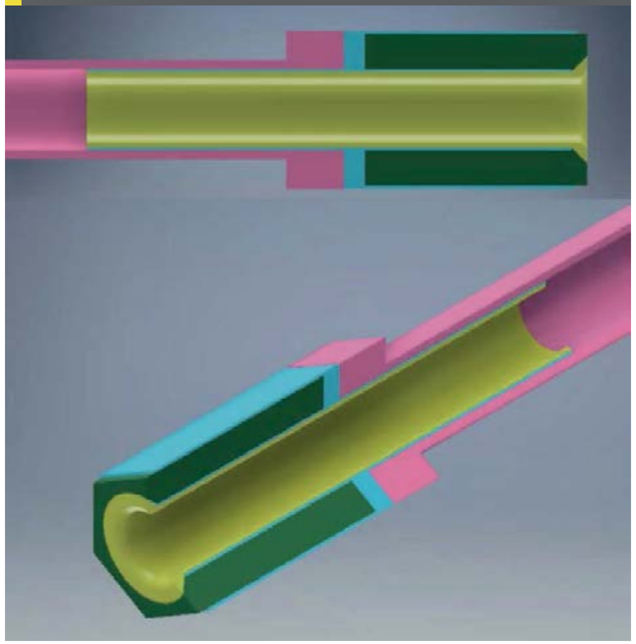

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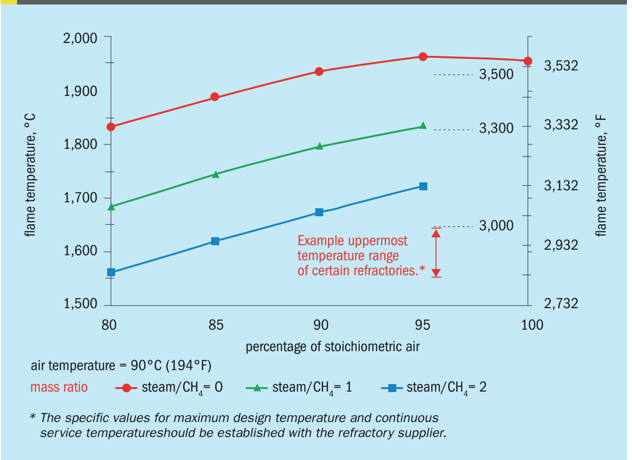
Fig 9: Flame temperature as a function of stoichiometric air and steam injection



Correct design of these "two-part" systems is critical to the performance and reliability. The shape and size of the refractory head is determined based on the tube pitch and orientation: square head for square or rotated-square pitches; hexagon head for triangular pitches. The thickness of insulating wraps will have a direct impact on the boiler tube and tube sheet temperatures. The ceramic ferrules insert (shank) is typically wrapped with one or more layers of ceramic fibre paper. This insulating material is an aluminum oxide or vitreous alumina-silicate fibre-based material with low thermal conductivity. As the thickness of the ceramic fibre paper increases, the ferrule inner diameter decreases, increasing both the pressure drop through the ferrule and the inlet gas velocities. Ultimately process design specifications will limit the allowable inner diameter of the ferrule.

The two-part design is a simple system to install and is routinely completed by normal refractory technicians. While there is more than one way to accommodate the method in which the heads fit together, designing an expansion allowance with a combination of ceramic fibre paper between the ferrule heads and a lower strength ceramic mortar grout is the approach preferred by the industry. This approach has proven to provide an effective radiant/heat barrier while addressing the real life installation and fit challenges often encountered in the field. This includes tube sheet configurations with small gauge tubes, as well as tube sheets with very tight or uneven tube pitches.

The two-part hexagon (or square) style ferrule has seen extensive use in high temperature oxygen enriched units and has proven to be a cost-effective alternative to traditional castable tube sheet linings, with the durability to withstand increasingly severe operating conditions as imposed by strict environmental regulations. By matching CFD modelling to empirical observation from a variety of applications and service conditions, the industry has developed an understanding of how to extend tube sheet reliability and minimise tube leaks due to high temperature corrosion.

Natural gas start-up/shutdown/hot standby considerations

Most sulphur recovery units use natural gas on a continuous basis for the incinerator, but 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. For all other cases and for the majority of natural gas firing, the burner must be fired at slightly sub-stoichiometric (air deficient) air conditions. This is necessary because any excess air will cause catalyst deactivation and may result in sulphur fires that can be very damaging to the catalyst and equipment.

The thermal stage is designed to operate with natural gas for start-up, shutdown and hot standby. Natural gas firing requires stoichiometric operation and the resulting flame temperature of 1,650+°C (3000+°F) can be damaging and thus natural gas firing requires flame moderation (Fig. 9)[2]. The tube sheet and ferrule system in the WHB must be designed for the elevated temperature of the natural gas operation.

There have been many cases of WHB damage during start-up and shutdown operation. The ceramic ferrules are vulnerable to thermal shock and thus the operating procedure must be carefully planned and executed. A less likely failure, but one that has occurred, is poor WHB water level maintenance during start-up and shutdown; the boiler must be operated with the proper water level and shutdown system in operation.

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 60°C (140°F) 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. Fig. 10 provides the steam rate versus natural gas rate to achieve the indicated flame temperatures of 1,500°F (815°C), 1,750°F (954°C), 2,000°F (1,093°C), 2,250°F (1,232°C) and 2,500°F (1,371°C), 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. Fig. 11 provides the nitrogen rate versus natural gas rate to achieve the indicated flame temperatures of 1,500°F (815°C), 1,750°F (954°C), 2,000°F (1,093°C), 2,250°F (1,232°C) and 2,500°F (1,371°C), respectively.

Nitrogen purge impact on the WHB

The nitrogen purge system can be triggered by an SRU trip and thus automatically opening of a nitrogen isolation valve. The nitrogen purge is required to protect the burner assembly from radiant heat damage back from the reaction furnace refractory in which the heat source can range from 1,050 to 1,550°C (1,900 to 2,800°F)

Fig 10: Low pressure steam requirement for flame moderation when firing natural gas at 95% stoichiometry

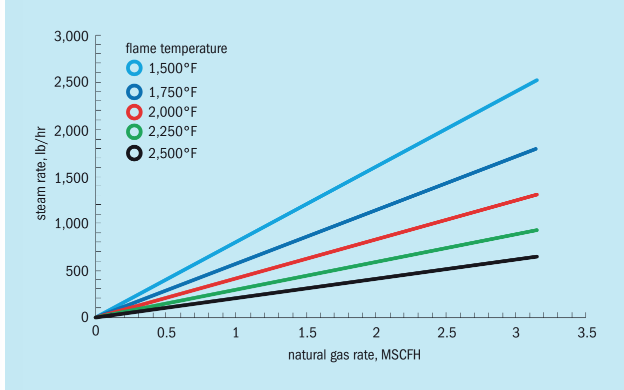
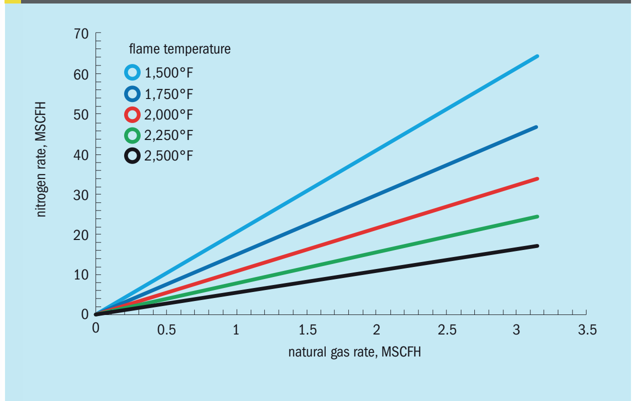


Fig 11: Nitrogen requirement for flame moderation when firing natural gas at 95% stoichiometry



and to prevent the migration back of corrosive thermal stage process gases into the burner assembly. The SRU trip nitrogen purge must be provided to both the combustion air and acid gas lines in order to protect the entire burner assembly. The nitrogen purge rates that will protect the burner should be set by the burner vendor.

Nitrogen has become a popular medium for accelerating cooling of the unit and eliminating the concerns for sulphur fires during shutdowns. One significant risk of utilising nitrogen in an attempt to accelerate the shutdown is the violation of the refractory vendors' recommended cool down rate. In order to avoid catastrophic damage to the tube sheet ferrules, the recommended time/temperature change gradients for cool down and start-up rates must be adhered to. Furthermore, use of large quantities of nitrogen for shutdowns is an intermittent operation, and thus it is imperative to ensure that nitrogen is in fact the material being utilised. There have been several bad experiences in purging with what was believed to be nitrogen and in fact a different unknown material was utilised. In one particular example, kerosene was inadvertently utilised in place of the intended nitrogen for the SRU purge! In another recent example of intermittent use, the nitrogen source was taken from upstream of the liquid nitrogen vaporiser and thus liquid nitrogen was fed to the SRU resulting in plugging of SRU equipment and damage to some of the front-end components.

For special nitrogen requirements, such as SRU start-up and accelerated cool downs industrial gas companies offer customised nitrogen services. This type of service provides a fast, flexible supply of high-quality nitrogen for planned or unplanned turnarounds, start-ups and maintenance activities. Such nitrogen supply is designed to safely and economically meet a plant's nitrogen needs over a wide range of pressures (up to 690 barg/10,000 psig), flow rates (14,000 m³/h/500,000+ std ft³/h per pump) and temperatures (-195°C to 370°C+/-320°F to 700+°F) thereby providing the entire nitrogen requirement or supplementing the plant's main nitrogen source.

Summary

There are many challenges associated with the WHB design and operation. This article has addressed the mechanical design, ferrule design, steam side considerations including water quality and steam flux rates and start-up/shutdown procedures. Adoption of good design and operating practices as presented here, and commitment to their practice, enables operating companies to reduce the risk of WHB failure from problems related to the water side or ferrule-tube sheet protection system. Improving WHB operation improves SRU reliability, enhances probability of achieving extended intervals between turnarounds, and reduces environmental emissions from unplanned shutdowns.

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Acknowledgement

This article is an updated version of the paper "Examining the impact of waste heat boiler design and operation on WHB reliability" by Elmo Nasato (Nasato Consulting Ltd), Domenica Misale-Lyttle and David Barrow (Industrial Ceramics Limited) and Michael A. Huffmaster (Consultant), presented at the Sulphur 2015 Conference in Toronto, Canada, 9-12 November 2015.

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