1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

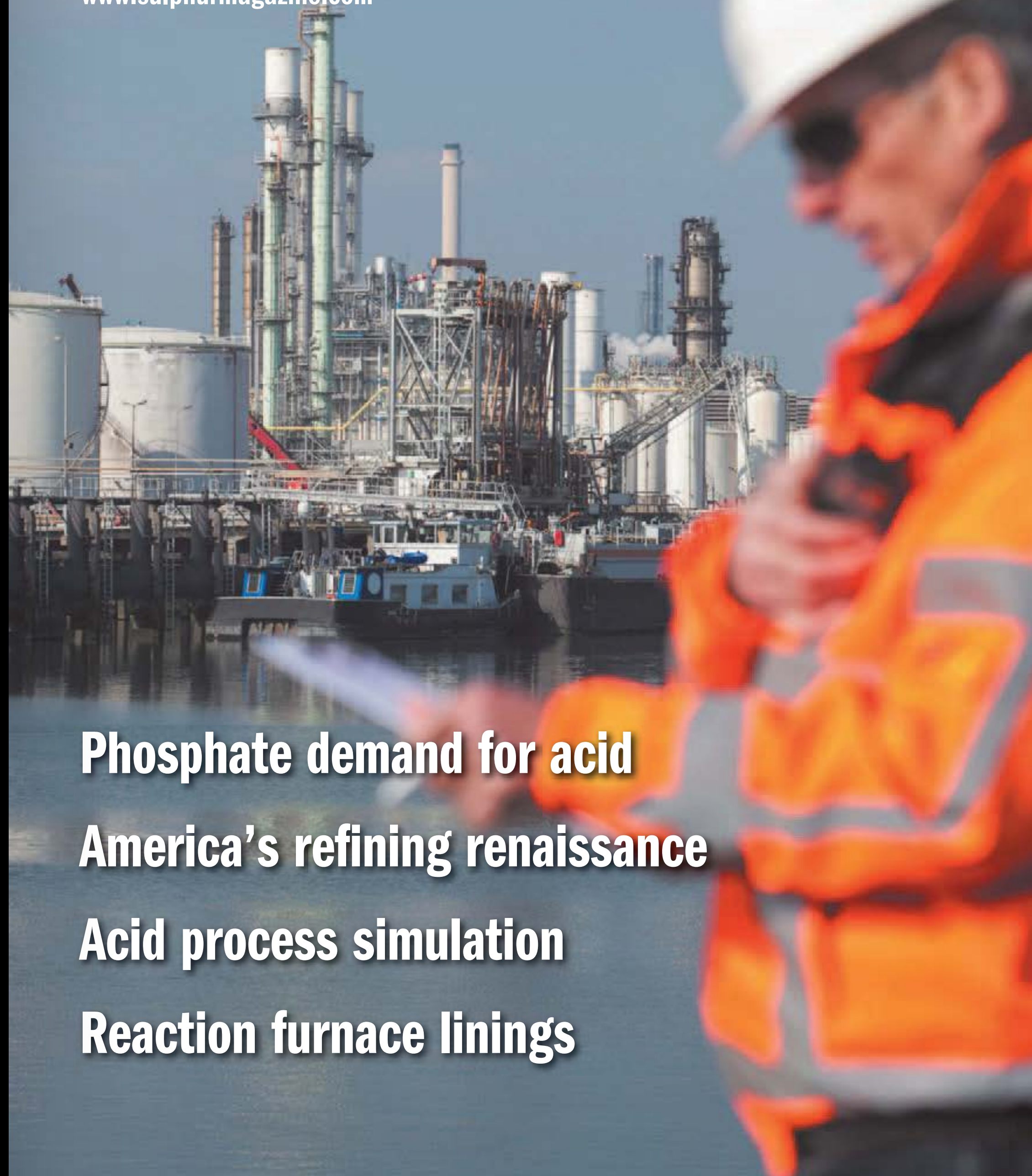
Welcome to our interactive version of Sulphur Issue 359

Please use either the buttons on the left or top right of the page to navigate your way around this interactive PDF

Number 359
July | August 2015

SULPHUR

www.sulphurmagazine.com



Phosphate demand for acid

America's refining renaissance

Acid process simulation

Reaction furnace linings

CONTENTS

SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

Cover: *Refinery operation.*
Olivier Lantzendorffer/iStockphoto.com

SULPHUR

www.sulphurmagazine.com

NUMBER 359 **JULY | AUGUST 2015**

CONTENTS

REGULARS

Phosphate demand
Still the key growth area for sulphuric acid.

Acid process modelling
The role of simulation tools in sulphuric acid plants.

Read this issue online at:
www.sulphurmagazine.com

Published by:
BCInsight

CONTENTS
What's in issue 359

COVER FEATURE 1
Phosphate demand for acid

COVER FEATURE 2
America's refining renaissance

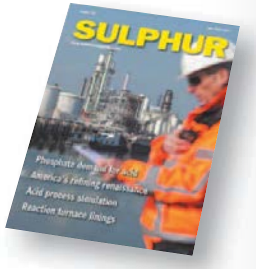
COVER FEATURE 3
Acid process simulation

COVER FEATURE 4
Reaction furnace linings

SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

After phosphorus



> "Could phosphate recycling replace the phosphate fertilizer industry?

The sulphuric acid industry has for decades been our main way of recovering usable phosphate from phosphate-bearing rocks, and hence helping to ensure global food security. Its extraction from phosphate rocks began in the late 19th century, as supplies of guano, often quarried from Pacific islands, began to run short as a supplement to traditional manuring as a way of getting phosphates back into the soil. Phosphate rock now accounts for 90% of the phosphate fertilizer that is applied to the soil (most of the rest comes from manures). Phosphorus is a key element for living creatures – Isaac Asimov once described it as "life's bottleneck". For a while a few years ago there was concern that the world might even be running out of phosphate – the so-called 'Peak Phosphate' debate, until revised estimates of global reserves showed that there were several hundred years at least of phosphate reserves, much of it in Morocco and western Sahara. Nevertheless, the concentration of phosphate reserves in a handful of countries has concerned some people about potential issues to do with security of supply – if Morocco were to face an 'Arab Spring'-style revolution, for example.

It is also true that we are in relative terms quite profligate with our phosphate resources. It is estimated that only around 20% of the phosphate actually applied to fields ends up in the food we eat. Phosphate leaching from fields into watercourses has been a major pollution issue for developed countries via eutrophication.

Last year we looked at the Improved Hard Process as a potential competitor for traditional wet process phosphate extraction, offering the possibility of making use of lower grade phosphate rocks and avoiding the production of phosphogypsum. But there is also increasing interest in another source of phosphate – recycling it from waste water.

Adult humans, it is reckoned, retain only about 2% of the phosphate that they eat, and the rest is excreted; on average about 1.3 grammes of P per person per day. To this can be added another 1.3-1.8 g P per person from other household and industrial sources (such as detergent) in urban waste water. Since this is, in most of the developed world, processed centrally at sewage treatment works, it provides an opportunity for recovery of the phosphate content of the water – up to 95% is potentially recoverable. The European Union has been at the forefront of moves to recover more phosphorus from waste water. In Sweden, 60% of wastewater phosphate must be recovered as of this year, and Germany is now moving in a similar direction. In case anyone thinks that these are trivial or niche applications, studies have shown that the total dissolved phosphorus in urban waste water in the EU is about 1.2 million t/a P_2O_5. When it is considered that EU phosphate fertilizer consumption was about 1.0 million t/a P_2O_5 in the 2011-12 growing season (down from 2.2 million t/a in 1985), then the potential becomes obvious.

At the moment phosphorus in EU waste water is recovered as stabilised sewage sludge or so-called 'biosolids', which are often then applied directly to fields. About 90% of the phosphorus in the water ends up in the biosolids, and about 20% of these biosolids then find their way into agriculture. Part of the reason for the fall in phosphate fertilizer application in Europe has been down to use of this recovered phosphate. In the US, about 4 million t/a of biosolids are applied to fields, with an average P_2O_5 content of 2.27%, or the equivalent of 90,000 t/a P_2O_5 of phosphate fertilizer. However, its potential contamination by heavy metals and other compounds is leading to a search for other ways of recovering the phosphate. The addition of magnesium chloride or hydroxide to the sewage sludge can precipitate the phosphorus as struvite (magnesium ammonium phosphate), a stable crystalline form suitable for agricultural use, for example, and over the past few years plants have been starting up across Europe to process sewage sludge into struvite.

So could phosphate recycling replace the phosphate fertilizer industry? Well no, of course not, and certainly not for decades, but it's worth noting that the Dutch government has signed up to a target of ending imports of mineral phosphorus by 2025, and if these technologies become scalable then other European countries are likely to follow suit. The European phosphate fertilizer market of 1.0 million t/a is, likewise, only a fraction out of a global phosphate industry of 45 million t/a P_2O_5. But China has said it is aiming to cap consumption levels of phosphate fertilizer at 2020 levels. For decades the sulphur industry has been able to count on phosphate extraction to eat up additional supplies of sulphur. Might there come a time, even a couple of decades hence, when this is no longer the case?

Richard Hands, Editor

SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

Price trends

MARKET INSIGHT

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

SULPHUR

Stable fundamentals

Middle East sulphur producers and Chinese end users appeared to reach a stalemate in June, as the gap in price ideas on each side widened. The downward trend in spot pricing has since reversed however, with a more bullish outlook championed by producers leading to upward price momentum for June and July. Reluctance from many buyers to commit to higher priced tonnage left some players waiting on the sidelines, although increased activity in China helped to stabilise pricing somewhat. However, the attitude in purchasing behaviour remains on a hand to mouth basis, reflected in the drop in sulphur inventory levels at key ports in China, dropping down to 800,000 tonnes in June. The disconnect between stock levels and prices has led to uncertainty over price direction for the remainder of the year. For the time being, Chinese sulphur imports remain stable on year ago levels, with Saudi Arabia ranking the number one supply source for the market, followed by Kazakhstan and South Korea. The expectation in the longer term is for China imports to dip, raising questions over trade flows from the Middle East as new supply is added to the balance.

The stable to firm tone in the market through June has set the stage for a more confident outlook following the downward price trend in the early part of the year. This is driven by the expectations on demand, and improvements in key markets. Spot prices in China are expected to rise further above $163/tonne CFR in July, before reaching a ceiling.

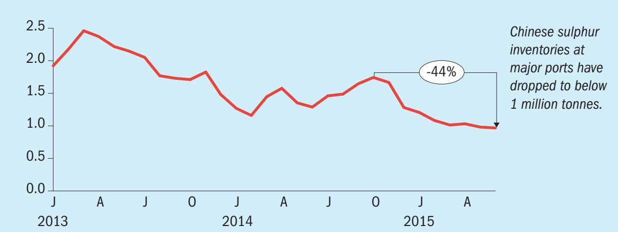
Middle East producer prices have moved up, highlighted by the sales tender awarded in Qatar by Tasweeq at $146-147/tonne f.o.b. Ras Laffan for July shipment. This was concluded above the June monthly price posted by the supplier at $141/tonne f.o.b. Meanwhile, in the UAE, Adnoc posted its June Official Selling Price (OSP) at $145/tonne f.o.b. Ruwais, up $5/tonne on May. Aramco Trading also increased its monthly price for June to a similar level, posted at $142/tonne f.o.b. Jubail. Intentions for the month of July were not clear at press time, but it was indicated prices would firm further based on the level of enquiries seen from end users. Middle East producer stock levels were also described as low or sold out in June, further heightening expectations of higher pricing.

The focus in the Middle East remains on the projects in the pipeline for the coming year. The Shah gas project in the UAE and Wasit gas plant in Saudi Arabia are key projects on the watch list for the coming months. In terms of exports from the Middle East, the Al Hosn Shah project will certainly impact trade flows, while sulphur produced at the Wasit gas project will be for consumption in the local market at the large scale Ma'aden phosphate project.

Over in Canada, producer Syncrude's month long turnaround was completed and sulphur shipments were reported to be healthy in June. Demand from the US was heard to be stable, although the question remains over how this trade route via rail will be impacted with the upcoming start-up of Mosaic's 1 million tonne per year remelter project towards the end of 2015. The first sulphur cargo is due to arrive during the summer from Kazakhstan to Tampa, for the purposes of testing and to begin commissioning the remelter. Sulphur is expected to be procured from a range of sources in the longer term, such as from the Middle East and FSU.

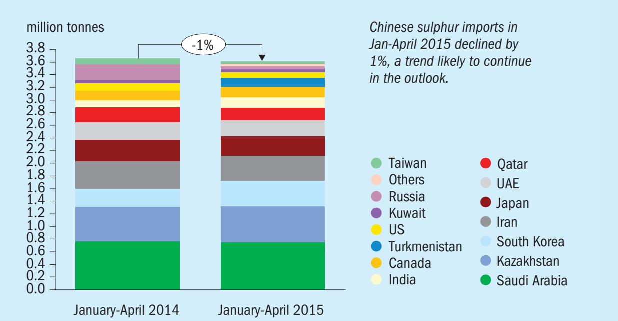
Sulphur production from gas plants in Canada continue to decline, with an 11% decrease in Q1 2015 on a year earlier. This trend is expected to continue in the outlook, as seen over recent years owing

Fig 1: Chinese sulphur inventories



Source: ICIS, Integer

Fig 2: Chinese sulphur imports



Source: Integer, GTIS

SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

to the depletion of gas wells and the economic conditions of the market.

Sulphur supply in the US market has remained healthy, with regular refinery utilisation rates reported. Sulphur moving from the US Gulf to Brazil and Morocco has been stable, although 1H 2015 exports from the Gulf have been pegged at 100,000 tonnes below the same period a year earlier. This is attributed to unplanned refinery maintenance, increased volumes of domestic sales within the US and lower carry over inventory from 2014.

Spot tenders in India through the end of May and into June tested the market. FACT's 25,000 tonne tender was awarded in the low/mid-$160s/tonne c.fr for June arrival. The buyer also issued a subsequent tender for July arrival. RCF and SPIC both closed tenders, with prices in the $160s/tonne c.fr range. Iffco is expected to receive 60,000 tonnes of sulphur in July following a spot deal. The origin in unclear, but speculated to be from the Middle East. The price range in 1H July in India was reviewed in the low/mid-$160s/tonne c.fr and expected to remain stable to firm in the outlook.

In the European market, demand in the downstream industrial sectors is expected to slow down due to seasonal demand patterns in markets such as caprolactam, paints and coatings shifting, on the back of summer maintenances. Prices for the third quarter continue to under discussion, although some deals were heard agreed at a rollover, as anticipated, on the second quarter. The molten sulphur market has been stable, although there is concern over the long term considerations for supply in the region, due to the decline of gas and oil based sulphur production.

SULPHURIC ACID

Stable trade

Exports from NW Europe have been stable through May and June, with prices hovering unchanged at $30-35/tonne f.o.b at the start of July. In terms of supply, producer Boliden underwent a turnaround at its Harjavalta, Finland smelter end May. A turnaround is also planned for September 2015 at its Ronnskar, Sweden smelter. Atlantic Copper also has a turnaround in September. Turnarounds will continue to support stable pricing in the outlook, particularly with a steady flow of export demand and stable domestic demand in NW Europe. Domestic acid contracts in the region settled at rollovers, pointing to a stable outlook.

The view for Chile in the second half of the year is healthy overall, with spot purchasing expected to increase as end users look to top up contract volumes for their requirements. The floods in March led to some improvement in acid trade. Since the disruption, the rail network has not been repaired, and logistics in the region are now running via road. This is expected to remain the norm, with the investment required to revive the rail network believed to be exponential. Indications spot demand may total 60,000-100,000 tonnes remain unconfirmed, but we expect to see an uptick in spot activity. First quarter acid shipments in Chile increased by 8% at 601,901 tonnes.

Brazilian spot demand has led pricing to around $90/tonne CFR through June. Demand in the coming weeks and months is expected to be healthy, with traditional buyers Mosaic, Yara, Timac and Petrobras expected to hold tenders for their requirements. Prices have the potential to rise in this market, based on expectations of smelter suppliers remaining in comfortable positions through the 2H 2015.

In Asia, Korea Zinc was due to complete its partial turnaround on 29 June. The plant had been running at 70% of capacity during the month long turnaround. Acid availability has been stable from South Korea however. Prices were heard in the mid/high-$20s/tonne FOB for Japanese tonnage in June. The Philippines remains crucial for exports from Japan since the start up of the Taganito nickel project. This is likely to remain strong through the remainder of 2015.

In terms of demand, AFT/Fertinal in Mexico is expected to run maintenances at its acid plants towards the end of 2015. Based on this, the need for acid imports are expected to increase, with around five spot cargoes required to cover AFT between October and December. Meanwhile OCP, Morocco is taking its usual acid quantities under contract, however, there has been limited indications of spot requirements and interest in June and early July. Acid imports are not expected to meet the levels seen in 2014, due to the ramp up of sulphuric acid plants which will in turn mean increased sulphur volumes imported.

Price indications

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

Cash equivalent	**January**	**February**	**March**	**April**	**May**
Sulphur, bulk ($/t)					
Vancouver f.o.b. spot	155-165	160-170	165-175	135-140	135
Adnoc monthly contract	170	180	140	140	150
China c.fr spot	175-190	170-190	150-160	130-160	155
Liquid sulphur ($/t)					
Tampa f.o.b. contract	147	147	145	132	132
NW Europe c.fr	170-200	170-200	170-200	170-200	185
Sulphuric acid ($/t)					
US Gulf spot	70-80	60-80	70-80	70-80	75

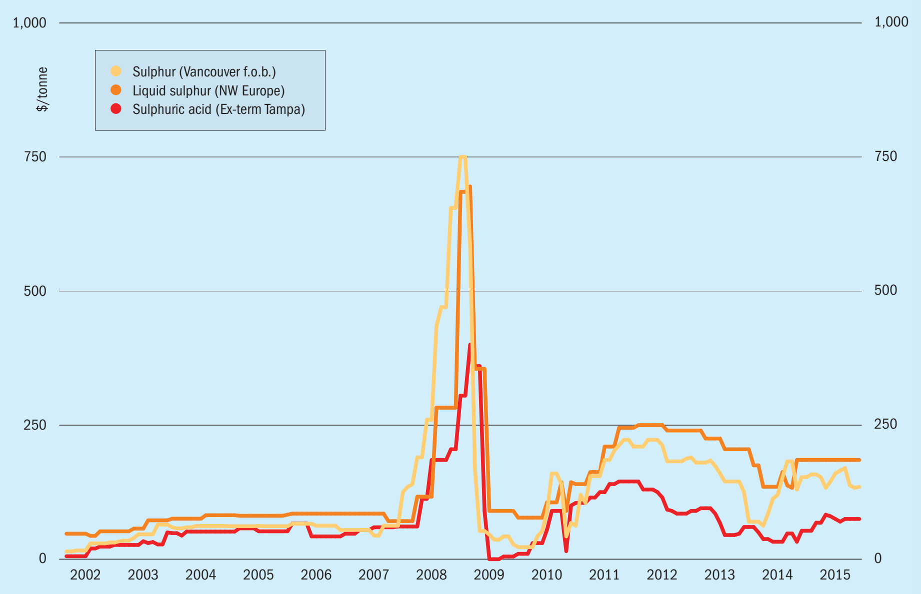
Source: CRU

SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

Historical price trends $/tonne



Source: BCInsight

SULPHUR

- Demand in China expected to remain stable through 2H 2015 due to the flat export tax system for fertilizers. Increased prices are a possibility, before reaching a ceiling, with the potential to stabilise or see a downward correction.
- Middle East producers are likely to increase prices for the month of July and August, based on a more bullish outlook in the 2H 2015 – expecting demand from key end markets Brazil, India and China.
- Sour gas projects in the Middle East remain the focus for expectations on trade of sulphur in the outlook – increased volumes from the UAE's Shah gas project will impact availability in the market, although contract agreements may alleviate some pressure on the spot market.
- US sulphur production to remain stable to healthy due to refinery operating rates, despite the drop in oil prices. Availability from the US Gulf in the medium term outlook is expected to rise, and lead to increased trade to Brazil and other markets.
- NW Europe continues to be stable and is likely to remain stable going into the latter part of the year. The slow down during the summer due to seasonal shifts is not expected to have a major impact on the market.
- **Outlook:** Prices are expected to reach a ceiling in Q3, with the potential to stabilise or to see some downward correction. However, with Chinese buyers remaining in a hand-to-mouth position, this is unlikely to lead to large drops in the pricing, based on the assumption of a healthy processed phosphates market in the second half of the year. Supply and exports remain the major focal point in discussions for the market outlook – with new supply impacting traditional trade routes and leading to increased diversification.

SULPHURIC ACID

- Exports from NW Europe to remain stable. Prices likely to be stable to firm – as smelters are comfortable and hold scheduled maintenance turnarounds.
- Moroccan acid imports may not meet the levels seen in 2014, as OCP progresses with its sulphuric acid plant and looks to increase sulphur volumes in its processed phosphates project.
- End user demand in Chile could support pricing in the market, although interest will supplement contract volumes.
- Turkey is expected to remain a key outlet for European acid producers, although there is a question mark over the volumes required by Meta Nikel's leaching project in 2015. The delay to the Toros acid plant continues to support trade to Turkey however.
- Asian acid prices to remain healthy in the outlook, as demand in South East Asia and Latin America looks to be stable in the second half of the year. Positive netbacks are anticipated for the coming months.
- **Outlook:** Prices for sulphuric acid remain robust in the forecast, owing to the comfortable position for many smelters. Key markets that could lead to shifts in pricing include Chile and Brazil. The level of demand from these markets could boost prices, or support stable pricing at least.

QATAR

Research collaboration on sour gas pipe corrosion

In early June at a ceremony at Qatar University, London's Imperial College signed an agreement with Qatar University and the Qatar Shell Research and Technology Centre (QSTRC) to conduct research and development work to prevent corrosion wet sour gas pipelines. Imperial hopes that its research on the subject will help to increase the lifetime of pipelines in Qatar. Qatar has recently faced the technical challenge of dealing with the corrosion of pipelines that transport sour oil and gas.

As part of the agreement, Qatar University will use its Centre for Advanced Materials to develop the capability to study pipeline corrosion. The university already provides assistance to local oil, gas and processing industries.

Speaking about the signing, Dr Hassan Al-Derham, vice president for research at Qatar University, said; "this agreement with Qatar Shell, which is focused on understanding scaling and corrosion in sour gas pipelines, aligns with QU's research priorities and is integral to Qatar's vision of becoming a knowledge-based society where research plays a vital role in resolving emerging issues, especially concerning the oil and gas industry, the country's main source of revenue for development."

Youssif Saleh, the General Manager of QSRTC, added; "in line with the Qatar National Vision 2030, Qatar Shell is committed to identifying research collaborations that address real challenges impacting our business, that bring together coalitions involving key local research institutions, and which offer the opportunity for direct applicability for the benefit of the State of Qatar. Shell is proud of the investments that we make in innovation and research, but we're also delighted that we can support Qatar's ambition to develop research capacity in the country."

Prof. Margaret Ryan of Imperial College said; "we are excited about this new research program to develop fundamental understanding of complex multi-scale systems in order to address real world technical challenges. We look forward to working with QU and QSRTC to develop a new approach towards delivering robust, innovative solutions to pipeline integrity issues facing the oil and gas industry in Qatar."

Start-up for acid gas removal unit

Prosernat has announced the successful testing, operation and handover of a 1.1 bcf acid gas removal unit (AGRU) for Qatargas at Ras Laffan Industrial City. This new AGRU is part of a major debottlenecking which is being performed for the Qatargas 1 LNG plant at Ras Laffan in order to maintain production at 10 million t/a LNG while coping with increased levels of H_2S and CO_2 in the feed gas. This project – the Plateau Maintenance Project (PMP) – involves the construction of an additional acid gas removal unit (AGRU) treating in a single train 1,100 MMscfd of natural gas, an associated sulphur recovery unit (SRU) and tail gas treatment unit (TGTU) within the minimum plot area allocated to the greenfield part of the project. The new AGRU has been designed by Prosernat based on AdvAmine™ MDEAmax technology using on open market MDEA solvent. This design fully integrates the acid gas removal unit, the acid gas enrichment section and the amine section of the TGTU.

OMAN

Petrofac awarded contract in Oman

UK-based Petrofac says that it has won a $900 million engineering and procurement contract from Petroleum Development Oman (PDO) to provide services for its Yibal Khuff sour oil and gas field, located around 350km southwest of Muscat. Petrofac will provide detailed engineering, and construction and commissioning management support services, as well as procurement on an incentivised pass-through basis for four and a half years. This will extend throughout construction and during start-up of the integrated oil and sour gas facility, according to the company.

The total contract value is around $900 million with one-quarter of the revenues relating to professional services (engineering, construction and commissioning management). The development of the field will add to PDO's future oil production while the associated gas will be utilised for power generation and enhanced oil recovery developments.

"This contract builds on the Rabab Harweel Integrated Project, which we are already executing alongside PDO and represents a further milestone in the development of our EPCm delivery strategy. Furthermore, it reinforces our presence in Oman where we have a number of ongoing projects and a local engineering office, and where this project will further complement our agenda for increasing in country value. We will continue to maintain a strong focus on this aspect of our delivery by accessing the local supply chain and recruitment of local resources, and we are very much looking forward to growing and strengthening the team working alongside PDO to deliver this project," said Craig Muir, managing director for Petrofac's Engineering and Consulting Services.

The gas at Yibal Khuff is around 3% H_2S, and the project is expected to yield significant tonnages of recovered sulphur.

UNITED STATES

Melter tank delivered to Mosaic project

In mid-May, Tampa Tank Inc.-Florida Structural Steel delivered the world's largest sulphur melter tank from its fabrication facility in Lakeland, Florida to the nearby project site. The tank has an outside diameter of 21.5' (6.55m), is 29.5' tall (9m) and weighs approximately 42.5st (38.6 tonnes). The 20-mile delivery took 12 hours over two nights, requiring teamwork among 12 different companies and 30 personnel with 21 vehicles.

Devco is supervising work on the sulphur melter, which when completed towards the end of 2015 will have a capacity of 1 million t/a of sulphur. Work is being conducted on behalf of the Mosaic Company, the world's largest supplier of phosphate and potash.

Port Arthur reports 'operational upset'

Total Petrochemicals & Refining USA Inc. reported an 'unexpected operational upset' at units within its 174,000 bbl/d refinery in Port Arthur, Texas. In a regulatory filing to the Texas Commission on

SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

Environmental Quality, the company said the operational problems resulted in flaring of gas, but said it implemented “acid gas shedding measures and switched acid gas to available sulphur recovery units to assist in minimising emissions.”

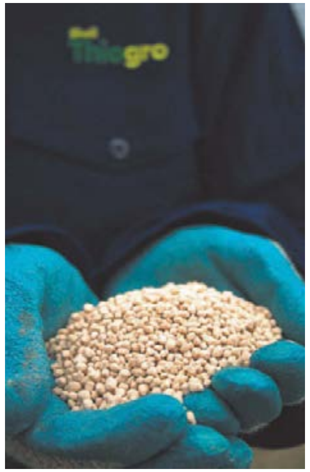
Permit review for Albany oil sands terminal

The New York state Department of Environmental Conservation (DEC) has decided to subject the application by Global Partners for an environmental operating permit to a full review. Global Partners had been planning to refit its existing Port of Albany facility to allow it to begin handling oil sands syncrude brought by rail from Alberta, including the installation of seven boilers to keep the oil sands warm while being moved from rail cars into storage tanks. The syncrude would be eventually taken by barge down the Hudson River to refineries in New Jersey, Delaware, and the Gulf Coast. The DEC originally ruled in November 2013 that the terminal refit would not have a significant environmental impact, but has decided to review the environmental permit following public comments and concerns expressed by the US Environmental Protection Agency (EPA), such as lack of emissions monitoring data for hydrogen sulphide. Refineries in New Jersey and Delaware have already been configured to use oil sands syncrude as a feed, and the Port of Albany has been seen as a potential gateway to dramatically increasing the quantity of oil sands refined on the East Coast, but this decision and the recent two-year delay for TransCanada's Energy East pipeline may scupper those plans in the short term.

UNITED KINGDOM

New sulphur enhanced urea technology

Shell has announced the development of *UreaPluS* technology, the second generation of its *Thiogro* sulphur-enhanced fertiliser technologies. *UreaPluS* technology for the first time enables fertiliser manufacturers to incorporate micronised sulphur particles into urea, producing a differentiated sulphur-enhanced urea product. “As Shell’s integrated sulphur management business, we are proud to be able to help meet the global demand for sulphur as a plant nutrient by launching a technology that can deliver sulphur to plants through the most widely-used nitrogen fertiliser in the world – urea,” said Mike Lumley, general manager of Shell Sulphur Solutions.



Shell’s Thiogro *sulphur-enhanced urea.*

Shell’s *Thiogro* team has already produced various high nutrient density grades of sulphur-enhanced urea, ranging from 7-18% elemental sulphur, over the course of two successful pilot runs at IFDC (the International Fertilizer Development Centre), in Muscle Shoals, Alabama. The team is now focused on testing this product in agronomic and scientific trials, and integrating the technology with various urea forming technologies. *UreaPluS* utilises Shell’s micronisation technology to emulsify the particles of elemental sulphur evenly throughout the urea, forming a homogeneous granule, in contrast to existing elemental sulphur-containing urea technologies, which typically coat urea in a layer of elemental sulphur. The microscopic size of the sulphur particles, at under 40 micrometres (µm), promotes the oxidation of the sulphur within the crop season. It is expected that the technology will also be able to incorporate micronutrients like zinc and boron into the granule, enabling urea manufacturers to produce customised grades that meet local needs.

Total fined for sulphur accident

The Total Lindsey Oil Refinery in North Lincolnshire has been fined after a worker suffered serious burns when he stepped into an open access cover and fell into the molten sulphur below. The tanker driver had just finished loading molten sulphur and was attempting to detach the loading lance from a loading arm when his foot went into the open lid and into the tanker. He managed to pull himself out but the 140°C molten sulphur caused serious burns to his right leg. The man was unable to work for three months and needed extensive skin grafts. The UK Health and Safety Executive (HSE) prosecuted the refinery, one of Britain’s largest, after an investigation following the incident, which occurred in October 2013. HSE told the court that Total had no effective safe system of work in place in relation to the attaching and detaching of the loading lance. The hazard of working on top of the tanker had not been adequately identified or assessed. It served an Improvement Notice on the company to make sure safety systems for loading were improved. Total then installed a new articulated loading arm on the unit loading area, meaning a loading lance no longer needs to be attached or detached during loading operations. Total was fined £20,000 ($36,000) plus court costs for a breach of the Health and Safety at Work Act 1974.

Vertical sulphur pumps

Amarinth, a company specialising in the design, application and manufacture of centrifugal pumps and associated equipment to oil, gas, petrochemical, chemical, industrial and renewable energy markets, has developed a new range of API 610 VS4 vertical sulphur pumps. Sulphur presents unique challenges for pumps because of the limited temperature range (approximately +/- 20°C) in which it is at a viscosity suitable to be pumped. At lower temperatures the liquid will start to revert to a solid and at higher temperatures its viscosity increases due to the formation of polymers, bringing maintenance and reliability issues for operators if the pump is merely a simple adaptation of a design used for other liquids.

Amarinth says that it has drawn on its experience in designing bespoke pumping solutions for the oil and gas industry to produce an API 610 VS4 vertical pump that could meet the challenge of reliably pumping molten sulphur. A survey of existing sulphur pump users reported high incidents of bearing failures, shaft problems and having to run significantly shorter maintenance periods to try and minimise failures, all of which resulted in increased downtime for the plants. To deliver a robust, reliable and easily maintainable pump, Amarinth then embarked on an 18 month design and test study. The result, the company says, is a pump which includes a new arrangement for the shaft bearings and lubrication film which reduces the previous bearing and shaft issues operators had reported. It also has a redesigned jacket to maintain the temperature of the molten sulphur and hence its viscosity, reducing the solidification of the sulphur around the pump, particularly when it is lifted for maintenance. A new design of impeller is optimised for the best efficiency for molten sulphur, and the company’s proven modular column design enables the rapid production of bespoke pump lengths and greatly simplifies maintenance and removal of the pump. Finally, the pump features improved access so that regular maintenance can be completed quickly and with less disruption to the associated pipework and plant.

Oliver Brigginshaw, managing director of Amarinth, commented: “We are delighted to add these sulphur pumps to our range of pumps for the oil and gas industry. Drawing on our many years of experience with vertical pumps it is the culmination of three years research and development by our team of dedicated engineers and we look forward to leveraging the technologies we have pioneered on this project into other products to deliver even more effective pumping solutions for other applications.”

RUSSIA

Lukoil commissions SRU train

A commissioning ceremony has been held at OSO Lukoil Permnefeorgsintez near Perm for the second gas and condensate processing train. Present were Lukoil president Vagit Alekperov, Mikhail Babich, presidential envoy to the Volga Federal District, and Viktor Basargin, Governor of Perm Territory. The new low-temperature condensation and fractionation unit for associated petroleum gas, involved revamping of existing facilities and the construction of 20 new main and auxiliary units, including a compressor unit with a gas-turbine drive, a dehydration block, a gas low-temperature absorption unit, a low-temperature condensation and fractionation unit, and a sulphur-recovery unit. The new train will enable the company to completely remove hydrogen sulphide from all the associated petroleum gas extracted in Perm Krai, as well as produce 3,600 t/a of liquid sulphur.

Lukoil president Vagit Alekperov commented; “the commissioning of the new unit in Perm is yet another significant step as part of [Lukoil’s] recent large-scale program to upgrade processing capacities. Not only will the program make it possible to raise the utilisation level of associated petroleum gas in Perm Krai to 95%, the program will unlock synergies for Lukoil in the territory through the production of associated petroleum gas, its processing and power generation.”

Tecnimont to build Gazprom refinery

JSC Gazprom Neft has awarded Maire Tecnimont SpA. an engineering, procurement and construction management services contract for the execution of the Combined Oil Refinery Unit (CORU) projectat Gazprom’s existing Moscow Refinery. Gazprom Neft is the third-largest oil

BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

company in Russia by refining volume and fourth largest in terms of production. The overall contract value to Tecnimont is approximately €480 million, on a multi-currency basis of euros and Russian roubles (the latter totalling approximately 30%). The contract has been awarded under a lump sum scheme for engineering and procurement and under a reimbursable scheme for construction management. The scope of the project encompasses the implementation of a new hydroskimming section with a set of process refining units, part of which are licensed by a major refining technology provider.

The project is mainly aimed at producing gasoline and diesel distillates under EURO 5 specifications. Tecnimont's scope also includes ancillary and new utilities units. A significant portion of materials and subcontracting activities will be supplied by local partners within the Russian Federation. Completion is expected within 36 months from the letter of intent.

Pierroberto Folgiero, Maire Tecnimont Chief Executive Officer, commented: "This contract represents an outstanding opportunity for Maire Tecnimont Group to start a long term collaboration with Gazprom Neft, one of the leading players in the refining market globally, leveraging Tecnimont's very well established presence in the Russian promising downstream business environment. We are therefore truly honoured to expand our refining references to such a prestigious world class client with this flagship project in Moscow."

Ammonium sulphate granulation plant

Trammo AG has signed an agreement with KuibyshevAzot to establish a new joint venture company to produce granular ammonium sulphate. The new company, Granifert LLC, will be a 50-50 joint venture between the two companies, with facility to be located at KuibyshevAzot's site at Togliatti. The plant's design capacity will be 140,000 t/a, with an estimated investment cost of 700 million roubles ($11.9 million) over the implementation period of 2015-2017.

KuibyshevAzot is one of the leading producers of ammonium sulphate in Russia and Eastern Europe, with a capacity of 450,000 t/a at Togliatti, including 90,000 t/a of granular AS production. The start-up of the granulation plant in 2012 marked the first Russian company to produce this product. The company says that granular AS has the advantage of improved physical and mechanical properties such as increased hardness of granules and lower friability, as well as better application and blending characteristics. Viktor I. Gerasimenko, chairman of KuibyshevAzot JSC said: "Implementation of the new project with Trammo will provide agricultural producers with advanced fertilizers and will also encourage job creation during the period of the plant construction and operation".

MEXICO

Cooperation agreement for oil and gas projects

A cooperation agreement has been signed by Arendal and Prosernat to mutually strengthen the two companies' capability to offer turnkey advanced technological solutions to the Mexican oil and gas market. The agreement covers; joint evaluation of the Mexican market and promotion of Prosernat technologies within it; identification and winning of joint business opportunities in Mexico where the joint partnership would make sense, using technologies in the Prosernat portfolio and modularisation of process units; and support for Arendal in their appraisal of setting up a facility in Mexico to supply the US market.

MALAYSIA

Axens selected for RAPID project

State oil and gas company Petronas has selected Axens as technology provider for the huge Refinery and Petrochemicals Integrated Development (RAPID) project, to be located in Pengerang, Johor. RAPID is part of the Pengerang Integrated Complex (PIC) development, which includes six major associated facilities; the Pengerang co-generation plant, re-gasification terminal 2, air separation unit, raw water supply project, liquid bulk terminal, as well as central and shared utilities and other facilities. Located on a 6,242 acre site in Pengerang, PIC forms part of the Johor State's Pengerang Integrated Petroleum Complex (PIPC), developed to establish new engines of growth for Malaysia whilst meeting future energy requirements and strengthening Petronas' position as a key player in the Asian chemicals market.. RAPID is estimated to cost $16 billion and is due for start-up by early 2019.

Axens performed the initial detailed feasibility study for RAPID in 2010, and has now been selected to provide several technologies for the project, including: naphtha hydrotreating to purify naphtha removing dienes, olefins compounds, sulphur and nitrogen species with a feed capacity of 21,000 bbl/d; *Octanizing*™ a continuous catalytic regenerative (CCR) reforming process for maximising the production of reformate from heavy hydrotreated naphtha , with a feed capacity of 14,000 bbl/d; – *Prime-K*™ a catalytic process achieving hydrotreatment of a kerosene cut, with smoke point improvement and deep desulphurisation, with a feed capacity of 30,000 bbl/d; and *R2R*™ a residue fluidised catalytic cracking (RFCC) process including a double regenerator to crack residue feedstock or vacuum gas-oil into lighter hydrocarbons. The 140,000 bbl/d RFCC unit also includes a propylene recovery section. Finally, Axens will supply a *Prime G+*™ catalytic process aiming at desulphurising FCC gasoline while minimising octane loss which includes a selective hydrogenation reactor/splitter and hydrodesulphurisation reactor/stabiliser with a capacity of 75,000 bbl/d.

INDIA

BPCL to press on with refinery expansion

Bharat Petroleum Corp Ltd (BPCL) says that it will continue with a$3.2 billion Phase II expansion of its Bina refinery in Madhya Pradesh in spite of unwillingness by its joint venture partner Oman Oil Company (OOC) to fund it. BPCL plans to raise capacity at Bina to 15 million t/a in two phases. The first phase will increase capacity from the current 6 million t./a to 7.8 million t/a, at a cost of $560 million, with a target completion date of 2018, and the second phase will add the remaining 7.2 million t/a of capacity at a cost of $3.2 billion by 2021. OOC, which holds a 26% stake in Bharat Oman Refineries Ltd, the joint venture owning company, says that it is willing to participate in the first phase expansion but not in the second phase.

Bharat Oman Refineries Ltd was founded as a 50-50 joint venture in 1993, but delays to the project implementation led to OOC freezing its investment at 2%. It bought back into the refinery project in 2009 and expanded its stake to the current 26%. BPCL owns 49% of the company, and the remaining 25% is held by a variety of financial institutions. BPCL also operates a 12 million t/a refinery at Mumbai and 9.5 million t/a refinery at Kochi unit. ■

Sulphuric Acid News

RUSSIA

CFIh buys Giprochim

CFI holding Ltd. (CFIh) has acquired Giprochim, a Russian company providing licences, technologies, engineering services, equipment supply and related services for the design of all types of sulphuric acid plant (using either solid sulphur or gases or residue containing sulphur). CFIh says that the acquisition will allow it to reinforce its position as a supplier of process and technologies to the fertilizer and chemical markets in Russia and the CIS as well as to better develop the worldwide market, and that its customers "will greatly benefit from the combination of CFIh's expertise and knowledge with those of Giprochim in the field of sulphuric acid and associated technologies such as sulphur melting, SO_2/SOx gas treatment, ammonium sulphate, potassium sulphate, SSP, etc."

"This acquisition of a sulphuric acid licensor is in line with CFI Group's strategy to enter into the acid business to offer its customers an entire package from acid to final product," said Julien Crispyn, CFIh Managing Director.

"CFI Group has created a sulphur pole to support its customers' needs around the monetisation of sulphur and derivative compounds."

MOROCCO

Symphos discusses acid emissions

On Wednesday, 20th May at OCP's annual Symphos phosphate symposium, Iliass ElFali, director of OCP's Safi site and Thierry Marin, DuPont MECS' Clean Technologies Director for Europe, Middle East and Africa jointly chaired a lively morning panel which discussed the challenges that the sulphuric acid industry is currently facing to cut emissions. The two industry specialists led a previous workshop examining global sulphur dioxide emission reductions at Sulphur 2014 in Paris last November. However, half a year later, the industry is facing new challenges; in a number of presentations, this session gave concrete examples of live sulphuric acid plant upgrades, discussed the latest developments in sulphuric acid catalysts and examined the risk inferior or ageing catalysts pose. The session also highlighted the benefits improved, sustainable SO_2 recovery can bring, from heat recovery to examples of increased production capacity.

"The OCP Group is committed to sustainable and eco-friendly agriculture. As part of our environmental focus, we also carefully consider the impact our sites and SO_2 emissions can have on the communities in which we operate," said Iliass ElFali. "The Symphos 2015 sulphuric acid panel discussion allowed members of the sulphuric acid industry to find out what the latest methods and practices are that can help them reduce emissions."

Thierry Marin said: "Innovation in the phosphate industry is critical. It is a strategic necessity. But it will only occur if we look further into the future; if we collaborate and if we continuously engage with stakeholders and customers."

EGYPT

Contract awarded for phosphoric acid plant

Egyptian chemical company Evergrow has contracted with Belgium's EcoPhos for setting up a 60,000 t/a dicalcium phosphate (DCP) plant, a 33,600 t/a 85% purified phosphoric acid (PPA) plant 85% and a 90,000 t/a granular anhydrous calcium chloride plant at El-Sadat City. EcoPhos will also have an exclusive offtake agreement for the DCP production. EcoPhos will provide the technology licence, basic and detailed engineering services, and supply proprietary and general equipment to Evergrow. The complex will use hydrochloric acid from potassium sulphate (SOP) furnaces and low grade phosphate rock as feedstocks, rather than sulphuric acid. The phosphoric acid will be used by Evergrow's animal feed phosphate business Aliphos.

Evergrow, established in 2006 by Mohamed El-Kheshen in the Abo Rawash Industrial Zone at Giza, is the first producer in Egypt of fully soluble potassium sulphate, mono-ammonium phosphate (MAP), mono potassium phosphate (MKP), urea phosphate, and solid and liquid NPK fertilizers, as well as calcium nitrate (crystal and liquid), copper sulphate, and calcium chloride. As demand has increased over the last few years, the company established a second production complex at the El Sadat Industrial zone to manufacture phosphoric, sulphuric and hydrochloric acids to increase its capacity of potassium sulphate, calcium nitrate, and calcium chloride.

NAMIBIA

Concerns over sulphuric acid transport

The former president of the Chamber of Mines of Namibia and managing director of Rössing Uranium, Werner Duvenhage, has called on the Namibian government to urgently review the capability for transport of sulphuric acid by state owned transport company TransNamib. Duvenhage was expressing concerns about the transport of the 340,000 t/a of acid which will be produced at the Tsumeb copper smelter when the new acid plant there comes on-stream in July. TransNamib is facing a shortage of locomotives amongst other things, and as TransNamib will not be able to carry the acid by rail, Rössing Uranium, which will be a major buyer of the acid, will be forced to use road tankers to move the offtake. The matter has become a particular cause for concern for Namibia in the wake of a recent accident in South Africa when a truck carrying 28,000 litres of sulphuric acid overturned, depositing its load into the Nyl river and killing marine life.

AUSTRALIA

Cobre Montana pushing acid route to lithium

An Australian company called Cobre Montana is looking to commercialise a sulphuric acid-based lithium extraction process which the company says could less energy-intensive than the traditional ore roasting method, making it economically viable for recovering lithium from lower-grade ores, found in micas. Lithium is in increasing demand for batteries, but higher grade ores, mostly found in brine deposits in places such as Argentina, Bolivia and Chile, are in relatively short supply. Otherwise it is only economically viable to process ores such as spodumene or petalite, both lithium-aluminium silicates. Even at lithium oxide concentrations of 6%, however, production costs can be $3-5,000/t, and below 5% the roasting process becomes unattractive. Current global

SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

production is around 38,000 t/a of metal, with China the largest consumer.

Cobre Montana's process involves using micas with a lithium content of 2.0-4.5% which are ground and then leached in sulphuric acid at 90°C, and the lithium recovered from solution. The company claims operating costs of $1,800/t, lower even than the $2-2,500/t of brine extraction. Around one third of operating costs is the cost of sulphur for sulphuric acid production, according to Cobre, with some of that offset by production of potassium sulphate which can be sold on as a fertilizer. So far the process has only been tested at pilot plant level, and the company is now in discussion with European Metals Holdings to exploit mica reserves in the Czech Republic at the demonstration plant scale.

PERU

Tia Maria delayed but still continuing according to SCC

Grupo México and its subsidiary Southern Copper Corporation (SCC) have reiterated their commitment to Peru in general and the Tia Maria project in particular, which has become the focus of local opposition over fears of environmental damage. Protests and strikes have led to a state of emergency in Islay province and the death of one protestor. Over $1.4 billion will be invested in the Tia Maria Project, which will produce 120,000 t/a of copper using leaching, solvent extraction and electrowinning (SX/EW). SCC has amended its environmental impact assessment to use only seawater, transporting this more than 25 km (15.5 miles) across and 1km up, and constructing a desalination plant at an additional cost of $95 million to allay concerns about water pollution in the Tambo valley. The project has been 'paused' until July to allow time for the company to address local concerns, and SCC has indicated that this period could be extended further.

MADAGASCAR

More problems for Ambatovy

The Ambatovy nickel leaching operation in Madagascar, a joint venture between Sherritt International (40%), Sumitomo (27.5%), Korea Resources (27.5%) and SNC-Lavalin (5%), has suffered more issues which have prevented the site from reaching its target of 90% of nameplate capacity. According to site operator Sherritt, strikes at both the mine and plant, and a transformer failure leading to damage to the two ore thickeners have brought operating rates down. Sherritt said the operation's finished nickel output for May was 3,874 tonnes (as well as 257t of cobalt), or about 76% of capacity, up from May, where the plant ran at about 63% of capacity. Ore throughput in the HPAL circuit was 354,109 t, or about 71% of nameplate capacity. The company says that it expects that one ore thickener will return to service in July and the other in 3Q 2015. The project has also been plagued by low nickel prices, leading to a 12% reduction in staffing

CANADA

Arianne secures deal with First Nations

Mining company Arianne Phosphate has signed a cooperation agreement with local First Nations groups which pave the way for development at the company's Lac à Paul project, in Quebec's Saguenay-Lac-Saint-Jean region. The Innu clans of Pessamit, Essipit and Mashteuiatsh were signatories to the agreement, and Arianne says it is now looking at initiatives to optimise its mining plan and further reduce costs associated with the producing its high-purity phosphate concentrate.

Agrium considering selling phosphate business

Agrium's chief financial officer Stephen Douglas says that the company is considering selling its phosphate business in the next three to five years. Speaking at a BMO Capital Markets conference, CFO Steve Douglas said that the phosphates business was difficult and expensive, with potential for further industry consolidation. The company recently reported increased Q1 net earnings despite lower sales volumes for potash, phosphate and ammonia, mainly due to lower output from the company's potash operation while it works to bring its 1 million t/a expansion at its Vanscoy Saskatchewan mine to fruition.

Copper North revises Carnacks assessment

Copper North, which is developing a copper, gold and silver project at Carmacks in Canada's Yukon Territory, says that the company is continuing to restructure its finances and optimise project costs, with the aim of presenting a revised economic assessment with a new leach plan. The project is expected to produce some 15,000 t/a of LME Grade A copper cathode via SX/EW, as well as 17,300 ounces of gold and 165,000 ounces of silver. Copper North says that it has reduced capex, focusing on a metallurgical test work program that began last September, demonstrating that the oxide resource at Carmacks had favourable leach dynamics.

"The metallurgical test results have been very instructive; a finer crush on leach materials coupled with increased temperatures in the leach circuit, results in much improved leach kinetics. Leach times are very fast. The test work has yielded much improved leach efficiency and reduction of operational and environmental risks," said Copper North's president and CEO, Dr. Harlan Meade.

Copper North said it now expects initial capital costs of $150M for the project, about 30% less than the preliminary economic assessment.

SYRIA

Islamic State in control of phosphate mine

Following the widely publicised capture of the ancient city of Palmyra, Islamic State has consolidated control over eastern parts of Syria and has reportedly captured two phosphate mines at Khunayfis, 70km south of Palmyra. The mines are the second largest in the country, with the capacity to produce up to 800,000 t/a of phosphate rock, which has been one of the few remaining major raw material exports supporting the beleaguered government of president Bashar al-Assad.

Some 345,000 tonnes of phosphate were exported from Syria in 1Q 2015 alone, worth $35 million to the regime. IS had previously also captured the Akashat phosphate mine and Al-Qaim triple superphosphate plant in Iraq's western Anbar province, just across the border, although it is believed that the processing facilities there have been damaged by air strikes. In addition to its oil resources, Reuters has estimated that Islamic State already obtains up to 10% of its revenue from phosphate rock sales, although it is not clear how this is arranged or who is buying. In theory, according to the most recent US Geological Survey figures, capturing both Syrian and Iraqi phosphate resources puts IS as the world's third largest holder of phosphate reserves, after Morocco and China.

ZAMBIA

FQM says smelter production is ramping up

First Quantum Minerals Ltd. (FQM) says that since the start-up of its Kansanshi copper smelter in February 2015, operations are continuing to ramp up, with progress "well ahead of expectations." According to the company, the daily copper concentrate throughput currently averages 3,000 t/d, with periods in excess of the 3,500 t/d nameplate capacity. The feed to the smelter is currently comprised of a mixture of stockpiled and fresh concentrate from the Kansanshi mine (above) and fresh concentrate from the new Sentinel mine. Concentrate inventory at Kansanshi has been reduced from 59,900 tonnes to 29,600 tonnes (in terms of contained copper) at the end of 1Q 2015. The smelter has also produced over 180,000 tonnes of sulphuric acid, which have been used in the mine's oxide and mixed circuits.

Philip Pascall, First Quantum's chairman and CEO, said: "We are very pleased with the performance of the smelter. The achievement of over 100% of nameplate capacity in just three months from start-up is unprecedented. It is a credit to the design and project teams and illustrates the strong capabilities of the operations management and staff. The smelter's value to our Kansanshi mine in particular is already very evident. For the first time in several years, the mine is able to operate without the constraints of limited availability and widely-fluctuating sulphuric acid prices and the lack of smelter capacity in Zambia. At our new Sentinel mine, commercial production on the entire facility is expected in the third quarter 2015 following delivery of the full power requirement, which is on track for August. This, together with the smelter will complete a significant phase in the expansion of our production capacity."

REPUBLIC OF CONGO

Cominco optimistic about Hinda

Cominco Resources Ltd, which is developing the Hinda Phosphate Project in the coastal province of Kouilou, says that the definitive feasibility study indicates that the $600 million development cost could be paid back within 26 months. In a statement, Cominco said that the Hinda deposit is one of the world's largest and thickest undeveloped phosphate JORC-class ore reserves, with a low overburden to ore ratio and can be open pit mined with no requirement for blasting. The open pit mining operation will produce 20 million t/a of ore at capacity, with a beneficiation plant that will generate 4.1 million t/a of saleable rock concentrate at 32% P_2O_5 content. A slurry pipeline will transport the product 42km from the mine to the export facility at Pointe Indienne.

SULPHUR
ISSUE 359
JULY-AUGUST 2015
BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

Darren Bridges.

Blasch Precision Ceramics has announced the appointment of **Darren Bridges** of Specialized Engineering Services Pty Limited as their exclusive representative in Oceania, covering Australia, New Zealand, Papua New Guinea and New Caledonia.

Bridges is a chemical engineer who joined Specialized Engineering Services in 2004. Prior to that he was the sulphuric acid plant manager at the Kalgoorlie nickel smelter. He has experience in plant operation, troubleshooting and plant turnaround planning and execution, all with a strong emphasis on safety. In his new role, he will focus on providing Blasch's innovative solutions for refractory applications in the petrochemical and refining, mining and power generation markets within this territory.

Mosaic has named **James 'Joc' O'Rourke** as the phosphate fertilizer giant's new president and chief executive. O'Rourke, 54, joined Mosaic in 2009 and since 2012 has served as executive vice president of operations and chief operating officer. He will succeed the retiring James Prokopanko as president and CEO on Aug. 5, the company announced Thursday.

"The board has full confidence in Joc and the rest of Mosaic's talented management team," said Robert Lumpkins, chairman of the company's board. "Together, they will help Mosaic build on Jim's legacy of success for our employees, customers, investors, communities and other stakeholders."

Before joining Mosaic, O'Rourke was president of the Australia Pacific region for Barrick Gold Corp. and responsible for Barrick's 10 gold and copper mines in Australia and Papua New Guinea.

"Jim [Prokopanko's] leadership took Mosaic from its early days to a company that boasts the best combination of people, assets, innovation and global reach in the crop nutrition industry," O'Rourke said in a statement. "We will maintain our steadfast focus on our customers and other stakeholders, and we will use today's solid foundation as a platform for further growth."

Prokopanko said he is confident of O'Rourke's leadership and of the company. "It has been a great privilege to serve as CEO and help build the world's leading crop nutrition company alongside some of the most talented people I have ever known," he said. "I deeply appreciate the outpouring of support I received during my illness last year, and I am happy to be healthy today. I plan to enjoy my good health with my family." Prokopanko had taken leave last summer because of cancer treatments.

Calendar 2015/2016

JUNE

24
ASRL Chalk Talks,
CALGARY,
Alberta, Canada
Contact: Patricia Alegre,
Alberta Sulphur Research Ltd
Tel: +1 403 220 5346
Fax: +1 403 284 2054
E-mail: asrinfo@ucalgary.ca

SEPTEMBER

21-23
IFA Production and International Trade Conference, TAMPA, Florida, USA
Contact: IFA Conference Service,
28 rue Marbeuf, 75008 Paris, France
Tel: +33 1 53 93 05 00.
Email: ifa@fertilizer.org

OCTOBER

18-20
2nd Annual Middle East Sulphur Plant Operations Network (MESPON) Forum,
ABU DHABI, UAE
Contact: UniverSUL Consulting,
PO Box 109760, Abu Dhabi, UAE
Tel: +971 2 645 0141
Email: info@universulphur.com

NOVEMBER

9-12
Sulphur 2015, TORONTO, Canada
Contact: CRU Events, Tel: +44 20 7903 2167
Email: conferences@crugroup.com

17-19
European Refining Technology Conference,
ROME, Italy, Contact: Eliot Morton, GT Forum
Tel: +44 20 7316 9832
Email: eliot.morton@gtforum.com

JANUARY 2016

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

FEBRUARY

21-24
66th Laurance Reid Annual Gas Conditioning Conference, NORMAN, Oklahoma, USA
Contact: Betty Kettman,
University of Oklahoma
Tel: +1 403 325 3136
Email: bettyk@ou.edu

MARCH

13-15
Phosphates 2016,
PARIS, France
Contact: CRU Events
Tel: +44 20 7903 2167
Email: conferences@crugroup.com

20-22
AFPM Annual Meeting,
DALLAS,
Texas, USA
Contact: Yvette Brooks
Email: ybrooks@afpm.org
Web: www.afpm.org

20-24
SOGAT 2015,
ABU DHABI, UAE
Contact: Dr Nick Coles, Dome Exhibitions
Tel: +971 2 674 4040
Email: nick@domeexhibitions.com

APRIL

11-13
TSI World Sulphur Symposium,
VANCOUVER, Canada
Tel: +1 202 331 9660
Email: sulphur@sulphurinstitute.org
Web: www.tsi.org

CONTENTS

SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

Phosphate demand for sulphuric acid

Phosphate mining in Togo.

PHOTO: SSR

The processing of rock phosphates, especially for fertilizer use, continues to represent the largest slice of sulphuric acid demand, and major expansion programmes in Morocco, Saudi Arabia, China and Brazil will boost acid demand over the coming years.

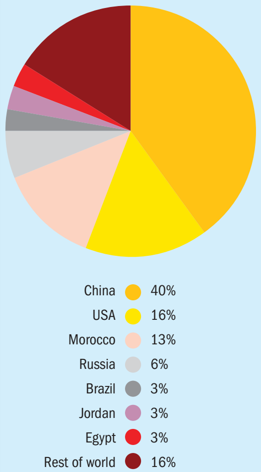
The segment of sulphuric acid demand represented by phosphates is around 55%, most of that – around 90% – for fertilizer use, the remainder for various industrial phosphate uses, mostly in the food and animal feed industries as well as detergents, cleaners, metal finishing, toothpaste and many others. As the largest segment of demand, sulphuric acid and by extension sulphur demand continue to be driven mainly by the phosphate fertilizer market.

Demand: global agriculture

Phosphate fertilizer demand is set by the pace of the global agricultural economy and world demand for food. This is an area that has seen consistent, steady growth over the past few decades and for the moment there seems no reason for it not to continue, as global population grows. Although the pace of population increase is slowing, especially in China where the effects of the 'one-child' policy have led to a major demographic shift, global population is continuing to increase. UN Food and Agriculture Organisation (FAO) statistics suggest that over the next 10 years to 2025, the world population will increase to 8.1 billion, 4.4 billion in Asia, mainly south and east Asia, 1.5 billion in Africa, 0.9 billion in the Americas, and 0.4 billion in Europe. The rate of increase is sharpest now in Africa, with a 26% increase, and India and south Asia are seeing an 11% rise over that period, just above the global average of 10%. China, conversely, will only see a 3% rise. Over and above that, as incomes increase, there is expected to be increased demand for animal protein, leading to a 17% increase in farmed animals, especially poultry. Overall these two trends are expected to lead to a 15% increase in demand for grain worldwide, with the areas with the greatest overall food demand increase likely to be Africa, South America, South and East Asia – also the areas which currently have the lowest calorific intake.

In the short term, this underpinning of demand has kept crop prices stable and in spite of record production in North and South America in 2014/15, the strong dollar and weaker economic outlooks in major consumers like Brazil and China, Russian export restrictions and concerns about drought in some regions have kept things on an even keel. There were fears that Indian consumption might be affected by delayed monsoon and late planting, but fortunately these seem not to have been borne out and although planting was delayed it was at an almost identical level to 2014. CRU expects phosphate fertilizer consumption globally to rise slightly to 43.0 million tonnes P_2O_5 in 2015, and overall phosphate demand will be 49.7 million tonnes P_2O_5 this year. Part of the non-fertilizer demand for phosphates is for animal feed and in human food production (e.g. phosphoric acid as a preservative) and as we have seen above, demand in these areas is also forecast to increase. IFA predicts world phosphate demand will grow at its average long term growth rate of 2% per year between 2014 and 2018, and anticipates that global phosphate demand to grow by 3.7 million t/a (P_2O_5) by 2018, with South and East Asia and Latin America representing about 75% of this demand increase.

Fig 1: **Phosphate rock production**, 2013



Total: 193 million t/a (tonnes product)

Source: IFA

Supply: phosphate rock

The raw material of phosphate fertilizer (indeed all phosphate production) is phosphate rock. Although phosphate production occurs in 34 different countries around the world, it is concentrated in just a handful, as Figure 1 shows. Although there have been many attempts in recent years to develop new phosphate mines in other locations, including offshore deposits off the coasts of Namibia and New Zealand, rock tonnages from many producers have remained remarkable consistent over the past decade. On the debit side, the main changes have been a run-down in production in North America (both the US and Canada) and South Africa, as well as the major disruptions to production from Tunisia and Syria – in the first case due to labour disputes following the 'Arab Spring', and in the second case due to the civil war there. While in terms of production increases, there have been significant additional tonnages from Brazil, Vietnam, Egypt, Morocco, the eye-catching new production at Ma'aden in Saudi Arabia, but – most impressively – the huge increase in phosphate rock production in China over the past decade, where output leapt from 41.5 million t/a (tonnes rock) in 2002 to 78 million t/a in 2012, according to IFA figures, dwarfing increases in production elsewhere. Indeed, taking the increases and decreases in production elsewhere, which roughly balance out, it is arguable that almost all incremental production over the past decade has been represented by China.

Another of the major trends over the past few decades has been towards greater downstream integration between phosphate rock production and phosphate processing. In 2013, internationally traded phosphate rock represented only 13% of the market, down from 20% a decade ago, with the rest consumed within the country of origin, integrated into downstream phosphate production. About one quarter of this global trade in phosphate rock was accounted for by India alone, which has a large downstream phosphate industry to feed but very little domestic rock production, and which instead imports rock from Jordan, Tunisia, Morocco and other Middle Eastern and North African countries via long-term joint ventures.

Again this increase in downstream integration has been in no small part due to China's massive investment in phosphoric acid and downstream mono- and di-ammonium phosphate (MAP/DAP) capacity, and the fact that a lot of new capacity, in e.g. Saudi Arabia, has been built integrated with downstream production, but in recent years Morocco too has begun a concerted effort to move down the value chain and capture more of the global DAP market via its Jorf Lasfar project, more on which below.

At the moment the number of new phosphate mining projects in the pipeline total as much as 95 million t/a of capacity for the period 2014-2019, which is far in advance of anticipated additional phosphate demand. Clearly not all of this capacity can proceed, and the best bet is generally for additional supply from established producers and market players where capacity expansion programmes are under way, especially when tied in to downstream developments. Taking this into account, extra rock supply from Saudi Arabia and Jordan could account for 9 million t/a to the end of the decade, China another 7 million t/a and Morocco has particularly ambitious plans to add 22 million t/a of mining capacity to 2025. Tunisia also has the potential for 4 million t/a of phosphate rock supply that is currently constrained by disputes there to return to production, provided that a resolution can be found.

In its most recent demand outlook (May 2015), IFA projected that global phosphate rock supply would grow 16% over the period 2014-2019, reaching a total of 255 million t/a, with Morocco, Saudi Arabia, Jordan and China accounting for 80% of the 35 million t/a increment.

Supply: phosphoric acid capacity

World phosphoric acid production in 2013 is shown in Table 1. This total has increased by about 30% over the past decade, but this figure obscures major regional changes in production. In particular, the slow run-down of capacity in North America, especially the US, and the huge increases in capacity in China, which has almost tripled in 10 years.

As noted above, phosphate rock capacity additions are most likely where they are integrated with downstream phosphate processing. These will therefore require additional volumes of sulphuric acid, almost all of it from sulphur burning acid capacity (China's industry also takes major volumes of acid from smelting, as detailed elsewhere in this issue). A total of 30 new phosphoric acid plants are scheduled to become operative between now and 2019, according to IFA. In particular, large additions to capacity are expected in Morocco, Saudi Arabia, China and Brazil. While much new phosphoric acid capacity in recent years has been in China, China represents only 25% of this new demand, with three quarters being developed elsewhere, much of it in Morocco.

Table 1: **World phosphoric acid production, 2013,** (million tonnes product)

China	31.7
USA	15.2
Morocco	8.3
Russia	4.7
India	2.6
EU	2.4
Brazil	2.3
Tunisia	1.9
Saudi Arabia	1.6
Israel	1.1
Others	7.0
Total	**78.8**

Source: IFA

SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

Morocco

At the 2015 Phosphate conference in Tampa in March, OCP reported on progress with the company's massive expansion of the Jorf Lasfar and Safi complexes on the northwestern coast of Morocco. OCP own an estimated 75% of the world's phosphate reserves and phosphates are the backbone of the Moroccan economy, and so the developments at Jorf Lasfar and other sites are part of a strategic vision for the country's future, with $16 billion of investment planned over the period 2008-2025. OCP plan to add 1.8 million t/a (P_2O_5 basis) of capacity to 2018, and another 4.2 million t/a to 2023. As well as 25 million t/a of mining capacity (product basis) at the existing mining sites near Khouribga and Gantour, and the opening up of a new mine at Meskala, there are also six new beneficiation plants under development; three at Kouribga, and one each at Gantour, Meskala and Laayoune, and two slurry pipelines to bring the concentrate to processing plants. The main gravity-driven slurry pipeline, which runs 187km from Khouibga to Jorf Lasfar, and which can carry 38 million t/a of concentrate, was completed last year. Another 10 million t/a pipeline is also planned from Gantour to Safi. Meskala, which is the largest new phosphate deposit to be developed since the 1970s, according to OCP, is also planned to have a pipeline connecting it the 95km to Safi in the longer term.

Downstream developments at the 'phosphate hubs' of Safi and Jorf Lasfar include four fertilizer plants at Jorf Lasfar, the first of which is now commissioning, and the other three of which are planned to be complete by the end of 2016. Another six will form Jorf Lasfar Phase II. Jorf Lasfar Phase I will add 2.25 million t/a of P205 capacity, and Phase II another 2.7 million t/a. The refit of Safi will add another 1.17 million t/a P_2O_5 by 2022. Overall Morocco's P_2O_5 production will reach 10.6 million t/a by 2022. Each of the MAP/DAP complexes at Jorf Lasfar also includes a sulphur-burning sulphuric acid plant which is expected to produce 1.5 million t/a of acid and consume 500,000 t/a of sulphur. By the end of Phase 2, these will have thus added 5 million t/a to Morocco's sulphur consumption for sulphuric acid production. Morocco's demand for sulphur for sulphuric acid production is expected to reach 6 million t/a by 2017, and 10 million t/a by 2022.

Saudi Arabia

Saudi Arabia's production capacity for phosphate fertilizer is expected to ramp up to 7.4 million t over the next two years. Ma'aden expects construction of a new 2.6 million t/a capacity DAP plant and a 0.76 million t/a NPK capacity plant at Ras Al Khair on the gulf coast to be completed by the end of next year. The $7 billion Umm Wa'al project in the northwest of the country will also have the capacity to produce 90,000 t/a sodium tripolyphosphate (STPP) and 250,000 t/a of monocalcium phosphate (MCP) and dicalcium phosphate (DCP) – and could enter production within two years. A $4.1 billion finance package for the project, a joint venture between Ma'aden, Mosaic and Saudi Basic Industries Corporation (SABIC), is expected to be agreed by the end of June.

Sulphuric acid production for the new phosphate production is expected to be 5 million t/a at full capacity, requiring an additional 1.5 million t/a of sulphur.

China

According to CRU figures, China produces around 14-14.5 million t/a (P_2O_5) of phosphoric acid and another 2-2.5 million t/a (P_2O_5) of single superphosphate (SSP) and magnesium phosphate. Most of the phosphoric acid goes into MAP/DAP production. Of China's 17 million t/a of phosphate production, just over 80% is consumed domestically, and the rest is exported, mostly as DAP. China's rapid ramp-up of phosphate production has led to overcapacity and exports of significant tonnages of phosphate fertilizers since 2007 in spite of the imposition of seasonal export taxes (these are now a flat rate of $16/t, rather than being concentrated in seasons of high domestic demand, which will at least even the exports out across the year). Exports of DAP reached a record 3.8 million t/a in 2013 (tonnes product) with MAP exports close to 0.7 million t/a, and it is expected that surpluses will remain in the region of 5-5.5 million t/a over the next few years.

> **China is aiming for zero growth in fertilizer consumption by 2020.**

Even so, there are plans for more DAP and MAP capacity in China, with seven new phosphate fertilizer plants expected to come on-stream in Sichuan, Hubei and Xinjiang provinces before 2018, which will add 0.9 million t to China's 9 million t/a DAP capacity and expand its existing 7.2 million t capacity for MAP by 0.2 million t. However, environmental regulations are beginning to tighten, and there seems to be a policy of moving towards full market pricing (via the addition of VAT, for example, from which phosphate fertilizers are currently exempt), and China is aiming for zero growth in fertilizer consumption by 2020, targeting rather more efficient application. All of these will crimp the rate at which domestic demand can increase. Conversely, there has been rapid expansion of the industrial phosphate sector, although this remains small compared to the fertilizer phosphate sector in China.

Brazil

Brazil has rapidly expanded its agricultural production in recent years, particularly via the opening up of the cerrado savannah region. The country now imports about half of its phosphate fertilizer requirements and as a consequence there have been significant developments to expand domestic phosphate capacity. State producer Fosfertil is in the process of expanding its phosphoric acid capacity from 1.0 to 1.5 million t/a (P_2O_5), and a number of projects slated for completion by 2018 could see Brazilian phosphate fertilizer capacity increase to 4.4 million t/a (P_2O_5), a 1.1 million tonnes increase on 2013 capacity. Vales Fertilizante's Patrocinio [Salitre] project and Anglo American's Catalao project combined are expected to add 680,000 t/a (product) to Brazilian MAP capacity and 260,000 t/a to TSP capacity. Canadian-owned MBAC also plans to boost single super phosphate (SSP) production at its central Brazil Itafos Arraias site from 375,000 t/a to 500,000 t/a over the next two years.

Elsewhere

There has been additional phosphoric acid capacity in Jordan, where the Jordan-India Fertilizer Company (Jifco) has added 475,000 t/a P_2O_5, and Petro Jordan Abadi in Indonesia another 200,000 t/a. VinaChem in Vietnam has also added 150,000 t/a P_2O_5 of phosphate processing capacity. There has also been some expansion in India, and PT Petrokimia Gresik in Indonesia is also building new phosphoric acid capacity for NPK production. These additions have been balanced by closures in the US; PCS idled capacity at its White Springs, Florida facility in July 2014, and Mississippi Phosphates closed its

Pascagoula plant later in the year. Between them these plants accounted for 800,000 t/a (P_2O_5) of phosphoric acid capacity. There will be some balancing increase by debottlenecking at Simplot's Rock Springs, Wyoming plant, but overall the steady decline in US phosphate processing continues.

SSP

While phosphoric acid production (as an intermediate) is the largest consumer of sulphuric acid, it is also possible to produce phosphate fertilizers directly from phosphate rock, by reacting the rock with sulphuric acid to produce what is known as single superphosphate (SSP). Each tonne of SSP produced requires 0.37 tonnes of sulphuric acid. As the simplest and cheapest phosphate fertilizer to produce, SSP once dominated the market, especially in China, but has declined with the rise of MAP and DAP and other higher analysis phosphate fertilizers. Nevertheless, in 2013 some 33 million tonnes (6.1 million t/a P_2O_5) of SSP were produced and consumed. SSP consumption has been dropping in China, which produced 45% of the world's SSP that year, but it has been rising in India and Brazil, which between them represent one third of production. The 500,000 t/a Itafos SSP plant in Brazil, which started production in 2014, was mentioned earlier, and another 1.9 million t/a of SSP capacity is also under discussion or development in Brazil. India likewise has seen a renewed interest in SSP, in part because of the cost of imported DAP under India's revised subsidy scheme. Domestic SSP production is set to rise 3 million t/a from 2015-2018. These new plants could increase sulphuric acid consumption by an additional 1 million t/a (approximately) in each country.

Table 2: **Phosphoric acid capacity increases, 2014-2019** (million t/a P_2O_5)

China	+2.2
Morocco	+3.6
USA	-0.8
Saudi Arabia	+1.5
Brazil	+1.1
India	0
Tunisia	+0.1
Jordan	+0.1
Indonesia	+0.2
World	**+7.8**

Impact on acid demand

Taking the phosphoric acid capacity increases and decreases above together, as Table 2 shows, capacity increases are set to add 7.8 million t/a of P_2O_5 in the five years to 2019. This represents the equivalent of 23.4 million t/a of additional sulphuric acid demand. Another 2 million t/a can be accounted for by single superphosphate production, for a total of just over 25 million t/a of acid demand.

It is likely that most of this (outside China) will be fulfilled by sulphur-burning acid capacity – the figures in Table 2 thus also to a large extent represent the equivalent tonnage of sulphur that will be required in each of the main regions. It seems clear that in spite of some headway being made with thermal phosphate processing in Florida, phosphate fertilizer and industrial phosphate production are unlikely to loosen their grip on the global sulphuric acid industry in the foreseeable future.

SULPHUR
ISSUE 359
JULY-AUGUST 2015

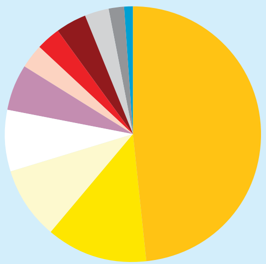
BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

Prospects for new smelter acid production

Left: The Kansanshi smelter, Zambia.

Fig 1: Global metallurgical acid production, 2014



Source: Integer

Base metal smelting and the sulphuric acid that comes with it continues to be a major slice of acid production. Although copper markets have been subdued of late, changing Asian markets and a push to remedy environmental emissions has continued to drive new smelter investment.

Out of total global sulphuric acid production of around 240 million t/a, the amount represented by metallurgical acid was 72 million t/a in 2014, or just over 30%. This acid is generally the product of smelting to recover ores of 'base metals' – a catch-all term for all non-precious metals, including iron, nickel, copper, zinc, lead and aluminium. Smelting of oxide ores like iron typically uses carbon as a reducing agent and generates carbon dioxide. Smelting of sulphide ores, however, is an oxidative process which generates sulphur dioxide. The most common metal processed as a sulphide ore is copper, and most (ca. 70%) metallurgical acid is the product of copper smelting, but zinc and lead are also most commonly found as sulphide ores and their processing also generates significant volumes of acid. Nickel is more commonly found as lower grade oxide-type ores (laterites) but its recovery has traditionally relied instead upon higher grade sulphide ores, which are again generally smelted.

The smelting process

Pyrometallurgical techniques use heat to separate copper from copper sulphide ore concentrates. Mining usually produces ores with less than 1% copper, and these must be concentrated prior to smelting, generally at mine sites, by crushing, grinding, and a process called flotation, which separates the ores to produce a concentrate with somewhere from 15-35% copper content, as well as around 25% sulphur. The concentrate is then usually roasted at around 650°C to reduce impurities and produce calcine, which is then fed to the smelter. Some (from 20-50%) of the sulphur is driven off as sulphur dioxide at the roasting stage, which produces matte, a molten mixture of copper and iron sulphides and some heavy metals, containing 35-65% copper. Converting the matte via smelting then yields a high-grade "blister" copper, with 98.5–99.5% Cu, which is typically further refined in an anode furnace, cast into "anodes", and sent to an electrolytic refinery for final impurity elimination. The smelting process can include reverbatory, electric arc or flash furnaces or the Noranda process, which combines roasting, smelting and converting in one operation. In all cases, however, almost all of the remaining sulphur is generally driven off as sulphur dioxide. This scheme is followed in its broad outline for smelting of all sulphide type ores; zinc, lead and nickel.

The gaseous effluent from base metal smelting was originally often simply emitted from a chimney, allowing the sulphur dioxide to disperse to atmosphere. However, this not only wasted a potentially valuable resource but also gave rise to acidic emissions leading to respiratory problems in local areas and acid raid further afield. The off-gas also often contained elevated levels of copper and selenium, and particulate matter containing arsenic, cadmium and mercury, all of which can contaminate soils and lead to various diseases in humans and animals. From the 1970s onwards permitted emission levels of all of these pollutants have steadily tightened, and higher and higher levels of SO_2 are now recovered and converted into sulphuric acid from smelters.

Furthermore, the use of the older, reverbatory-style furnaces has gradually dropped away over the years, while electric arc furnaces remain a relatively niche use, and flash furnaces have steadily gained predominance. Flash furnaces produce a more concentrated SO_2 waste stream than other types, lending them more readily to downstream acid production.

Table 1: China's sulphuric acid balance, million tonnes/year

Year	Consumption	Production				Net import
		Sulphur burning	Smelter acid	Pyrites	Total	
2006	51.5	21.5	11.4	15.9	49.3	2.1
2007	59.0	26.2	13.2	17.1	57.0	2.0
2008	55.0	20.8	15.4	16.9	53.8	1.2
2009	62.5	28.0	17.8	13.8	59.7	2.8
2010	71.7	33.0	19.3	17.8	70.3	1.4
2011	80.4	38.4	21.3	19.7	79.7	0.7
2012	85.0	39.0	23.9	20.6	84.0	0.3
2013	87.6	41.7	24.8	20.0	86.5	1.1
2014	89.1	42.4	25.4	20.0	87.8	1.4

Source: China Sulphuric Acid Industries Association, AciDS Co Ltd., CRU

Acid production

Since smelter acid is involuntary production, with its economics driven primarily by metal markets, it tends to be relatively insensitive to sulphuric acid prices. Copper prices have averaged around $6,000/t in recent years, for example, whereas sulphuric acid prices are below $100/t. Metallurgical acid production has therefore moved with the base metal industry, whose consumption and production has drifted with the global industrial centre of gravity from traditional producers in North America, Europe and Japan/Korea towards newer industrialising countries, especially China. Figure 1 shows the global breakdown of metallurgical acid production in 2014, dominated now by East Asia in general and China in particular.

Copper is used in a diverse range of industries, from wiring and electrical goods to auto manufacture and industrial uses, and copper prices have fallen sharply this year as China's economy slows. Prices are back to levels in the slump that followed the crash of 2008, and major miners like Freeport McMoRan have cut dividend forecasts in spite of floods in Chile which impacted upon supply earlier in the year. Fears that the slump in the Chinese stock market may reflect a deeper malaise in the economy have increased jitters about demand for base metals and made financing for new copper mining and smelting projects harder to come by. However, in spite of some forecast closures, there is still a tail of new projects, especially in Africa and Southeast Asia, which are likely to boost smelter acid supply in the medium term future.

East Asia

Japan and South Korea have traditionally been the two largest exporters of sulphuric acid, as they run several large smelters with a significant surplus over domestic acid demand. There are seven major copper smelters in Japan, at Tamano, Sanagoseki, Naoshima, Hitachi, Onohama, Kosaka and the Sumitomo Toyo copper smelter. Pan Pacific Copper at Sanganoseki, Sumitomo Toyo can both generate up to 1.5 million t/a of acid, Tamano nearly 900,000 and Onahama 600,000 t/a. The Sumitomo/Dowa Akita zinc smelter produces another 300,000 t/a of acid. Japanese smelter acid production dipped in 2011 due to the after-efects of the earthquake and tsunami but recovered to 5.2 million t/a in 2012. Total acid output is generally pretty steady at around 6.5-7.0 million t/a, with consumption around 4 million t/a, leading to exports of 2.5–3.0 million t/a. In 2014 this figure was around 2.8 million t/a, with Sumitomo exporting large volumes (up to 1.3 million t/a) to its nickel leaching operations in the Philippines.

South Korea has a smaller acid output than Japan, at around 4.5-5.0 million t/a, of which about 3 million t/a is represented by smelter acid, mainly (1.4 million t/a) from the LS Nikko copper smelter and Korea Zinc (1.1 million t/a) at Onsan. Acid demand is also proportionately lower, and hence Korea also tends to export around 2.5 million t/a of acid, although in 2014 this increased to 2.9 million t/a, overtaking Japan as the largest exporter.

CONTENTS
What's in issue 359
COVER FEATURE 1
Phosphate demand for acid
COVER FEATURE 2
America's refining renaissance
COVER FEATURE 3
Acid process simulation
COVER FEATURE 4
Reaction furnace linings

SULPHUR
ISSUE 359
JULY-AUGUST 2015
BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

China's industrialisation has seen sulphuric acid production and consumption both grow rapidly, as shown in Table 1. Sulphur-burning acid capacity has doubled in a decade as China has moved from importing large volumes of di-ammonium phosphate (DAP) to producing it domestically, overcapacity turning the country into a net exporter in recent years. But as the table also shows, smelter acid capacity has more than doubled during the same period, coming to occupy an ever-greater share of China's acid production. China's insatiable demand for copper for a variety of industrial uses has been the source of about 75% of this smelter capacity, and the acid has often gone into a myriad of other industrial processes (such as caprolactam manufacture for fibres) as well as fertilizer.

One notable feature however is that over the last couple of years the rate of increase has begun to slow as China's rapid growth has begun to ease back. During 2013-14, high global sulphur prices and low international acid prices also encouraged a degree of substitution by producers who tended to operate or buy acid from sulphur burning plants as smelter acid became advantaged and operated at close to capacity in 2014. This price differential may also have accounted for the increased volumes of acid imports seen in 2013 and 2014. However, it has now eroded and imports are forecast by CRU to reduce to 1.0 million t/a for 2015.

Smelter acid production does continue to increase in China, and there is around 4.8 million t/a of extra smelter acid production forecast to come on-stream between 2014 and 2019, and there has been some talk of China turning into a net exporter of acid as a result, but at the moment the main exporter is Two Lions, which runs a sulphur-based plant, and which had been acting as swing capacity.

South America

Chile is the world's largest copper producer, with 28% of the world's known copper reserves, according to the Chilean Copper Commission (Cochilco), and 31.5% of copper production. Although Chile is a large scale producer of hydrometallurgical copper from sulphuric acid leaching, there is also a large pyrometallurgical industry, and smelter acid represents over 5 million t/a of Chilean acid production, although demand, mostly for copper leaching, has tended to run considerably in excess of this. Chile's large smelters include Xstrata's Altonorte custom copper smelting operation located near Antofagasta in northern Chile and Codelco Norte, with up to 2 million t/a of acid capacity. State copper giant Corporacian Nacional del Cobre (Codelco) has other smelters at Potrerillos and Ventanas which can each produce 500,000 t/a of acid and El Teniente another million.

In spite of its leading position in copper, Chile is facing a hard time in maintaining that because of ageing mine assets and falling ore grades (from an average of 1% to 0.7% Cu) and Codelco is currently engaged in a $25 billion investment programme to 2020 to try and maintain production at the country's copper mines. However, while this may halt declining production, there is no net increase expected over the next few years. However, on the smelting side, at the same time, Chile is tightening environmental regulations, prompting investment in upgrading the country's existing smelter capacity. In December 2014, Outotec reported that it had been retained to revamp and upgrade the Potrerillos copper smelter and sulphuric acid plant at Codelco's Salvador Division in northern Chile. CRU estimates that in the 2014-2019 period, upgrades to Chilean smelters could add approximately 750,000 t/a of sulphuric acid production.

Just to the north, Peru is the world's third largest copper producer, and runs a major smelter at Ilo, with 1.7 million t/a of acid capacity. Ilo has faced persistent battles with the government over emissions, and operator SCC threatened closure in 2013 over a proposed reduction in SO_2 emissions to 20µg/m³, from the current 80µg/m³. A deal now seems to have been struck which will see the limit change held in abeyance in return for $350 million of environmental improvements over the next five years. Likewise the polymetallic smelter at La Oroya has faced environmental issues, as well as financial trouble, and the plant closed in 2008 and went bankrupt in 2009. A partial restart in 2012 of the zinc and lead circuits ended in 2014, and now the ageing smelter is up for sale to recover money for creditors. As far as new investment goes, Anglo-American continues to insist that it is "committed" to its $6 billion Quellaveco copper-molybdenum project in the south of the country, which has seen its scope expanded from 225,000 t Cu/a to 270,000 t/a, but there is not as yet a firm start-up date.

North America

North American smelting operations are concentrated in eastern Canada and the copper belt of the southwestern US. There were a spate of closures a few years ago, leaving only 11 smelters still operational in North America, with nine closed. US smelter acid production averages around 2.5 million t/a and Canadian production 2.0 million t/a. In Canada, Vale Inco is continuing with its plans to capture more SO_2 from the Sudbury smelter and the construction of a new nickel plant via its Clean AER project, although the closure of one of the furnaces at Copper Cliff will nevertheless result in lower acid output overall. The merger of Glencore and Xstrata is also likely to lead to some rationalisation of capacity in Canada according to industry analysts. On the other hand, environmental upgrades at US smelters may see capacity rise by a modest amount. For example, ASARCO Grupo Mexico is facing tighter emissions legislation at the Hayden smelter in New Mexico and is aiming to up SO_2 capture to 99.7% from about 97% at present.

India

India is actually one of the five largest operators of smelter capacity in the world. There are 10 smelters in India, dominated by two large copper smelters, at Hindalco's Birla Copper in Dahej and Vedanta at Tuticorin, with a total capacity of about 2.8 million t/a of sulphuric acid between them. Hindustan Zinc has a further 1.7 million t/a of acid capacity at three sites, and Hindustan Copper 230,000 t/a at two sites. Tuticorin has had a troubled history, being closed several times, most recently for several months during 2013, due to exceeding emission limits, but its license to operate was renewed in 2014 and operator Vedanta says that it produced 1.3 million t/a of sulphuric acid last year.

Europe and Eurasia

Europe has traditionally been a major region for metal smelting, with capacity of about 9.5 million t/a. Major producers include Atlantic Copper at Huelva in Spain with 1.0 million t/a and Asturianas Zinc with 800,000 t/a of acid capacity, and Aurubis in Bulgaria with 1.25 million t/a. Production has run at about 7.5 million t/a in recent years (the European Sulphuric Acid Association – ESA – reported 7.5 million t/a of output for 2013), and Europe's exports of around 3 million t/a of acid tend to come from smelters. RTB Bor in Serbia recently completed a modernisation of its copper smelter which doubled capacity, and installed a new sulphuric acid plant with 600,000 t/a of capacity, although the company says that acid output for 2015 is likely to be about 300,000 t/a as it ramps up its new flash smelters.

The FSU has also been a major producer of smelter acid. Indeed, globally it ranks fourth in terms of copper smelter output, with a large facility at Norilsk which also processes nickel. Russian smelter acid production is around 3 million t/a, and there is additional capacity in Kazakhstan and Uzbekistan, but this total is expected to increase by about 1 million t/a over the next few years, as older smelters with poor environmental performance are brought up to international norms. Ural Mining's Svyatogor smelter in Russia signed a contract earlier this year with Outotec for a major upgrade, and Kazakhstan is looking at increasing smelter output with more domestic copper concentrate processing. One anomaly has been Norilsk Nickel, which has plans to take SO_2-containing smelter off-gas and react it instead with hydrogen sulphide to produce 1 million t/a of sulphur.

Africa

Southern Africa's 'copper belt' has seen a number of new investments over the past few years in new smelter acid capacity, including at the Chambishi copper smelter in Zambia, and last year at Mopani Copper Mines (MCM), where the $460 million Mufulira smelter upgrade project has lifted concentrate processing by 200,000 t/a and has improved SO_2 capture from 50% to 97%. The $500 million expansion of the First Quantum Minerals (FQM) smelter at Kansanshi mine in Solwezi began operations in February 2015, according to FQM, and production is now ramping up, with 180,000 tonnes of acid already produced this year. The new smelter will have the capacity to process 1.2 million t/a of concentrates from the new copper oxide circuit (already complete) to produce more than 300,000 t/a of copper. The smelter will also produce more than 3,000 t/d of sulphuric acid.

Again much of the push for new acid capacity is to ameliorate SO_2 emissions. This has been the impetus for the new acid plant at Dundee Precious Metals (DPM), which says that its new $280 million sulphuric acid plant at Tsumeb is now complete. The plant will have a capacity of 300,000 t/a of sulphuric acid, 90%of which will be sold to Rossing Uranium for leaching operations. However, at the moment Rossing is looking at taking the acid 535km by road, as there are issues with local rail capacity. Further south, BCL in Botswana is also looking at sulphuric acid production from its Slebi-Phikwe smelter, which currently releases 530,000 t/a of SO_2.

Southeast Asia

There are some large smelters in the region, such as Philippine Associated Smelting And Refining (PASAR) in the Philippines and Gresik in Indonesia, but overall the region tends to be an exporter of copper concentrate and other base metal ores to smelters elsewhere in Asia, mainly China. However, Indonesia's government wishes to capture more of the value chain and so has toyed with the idea of restricting the export of copper concentrates and other unprocessed or semi-processed raw materials, trying to force operators into building metal refineries and smelters in the country. At the moment the export ban is slated for 2017, although the government has hinted it may relax this if companies have not yet been able to develop downstream capacity. Last year, US mine operators Freeport and Newmont, which produce 97% of Indonesia's copper, faced lengthy export stoppages related to the rules. Both companies eventually cut a deal with government to resume exports, but they had to present their plans for full domestic processing of their mining output by 2017. Indonesia has now rowed back on its demand for Freeport to build a $1.5 billion copper smelter in Papua province, saying a regionally owned enterprise would take on the project instead, but Freeport's planned expansion of Indonesia's sole copper smelter at Gresik, part owned by Mitsubishi Materials Corp , could be completed by 2017. Indonesia has 25 proposals for smelters of various kinds, including 14 nickel and 3 copper. Privately owned PT Indovasi Mineral Indonesia, PT Nusantara Smelting and PT Indosmelt are developing copper smelters – Indosmelt at Sulawesi, where construction is due to begin this year, but no new capacity is expected to come on-stream before 2017-18. In the Philippines, PASAR, now owned by Glencore, suffered damage from a typhoon in 2013 but says that its $600 million expansion programme is still continuing.

> **Investment is relatively insensitive to the current slump in base metal markets.**

Elsewhere

In Australia, GlencoreXstrata owns the Mount Isa copper smelter that is feeding smelter gas to Incitec Pivot's Phosphate Hill operation to supply around 700,000 t/a of sulphuric acid to the phosphates project there. Following Glencore's acquisition of Xstrata, there smelter, which was originally set to shut in 2016 when under Xstrata ownership, now looks set to close in 2017. However, the Nyrstar lead smelter at Port Pirie is undergoing an upgrade including a new sulphuric acid plant which is due to be completed in 2016.

Iran is also expanding production at its Sarcheshmeh copper facility which will add more acid production over the next few years.

New smelter production

Aside from China, then, where around 4.8 million t/a of new smelting capacity to 2019 is part of the tail end of the massive investment in copper extraction and processing that has occurred in the country, and Indonesia, where the new smelters are an attempt to capture more value from the copper production chain, much of the new smelter acid production under development around the world is the result of currently operating smelters being forced to install SO_2 capture and downstream acid production as a result of environmental regulation. This being the case, the investment is relatively insensitive to the current slump in base metal markets, as it is a condition of continued operation for the smelter. And with the exception of Norilsk Nickel, which is aiming to produce sulphur instead of sulphuric acid, all of this new investment will lead to more acid production – about 5-6 million t/a outside China, for a total of around 10 million t/a of extra smelter acid production to 2019. China, Africa, Russia and Southeast Asia are the main locations for new capacity, with smaller additions in North and South America and Eastern Europe, while some capacity is due to close in Australia and Canada.

SULPHUR
ISSUE 359
JULY-AUGUST 2015

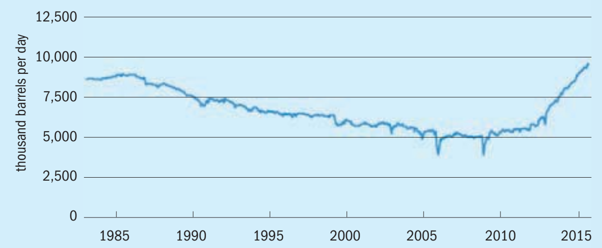
BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

America's refining renaissance

ExxonMobil's refinery complex at Baton Rouge, Louisiana.

The US tight oil boom has put a spring in the step of the country's refiners, and expanded processing of higher sulphur feeds is also generating additional sulphur production.

Fig 1: US production of crude oil



Source: US Energy Information Administration

US oil production at the end of June 2016 was reported to be running at levels close to a 40-year high. Figure 1 shows US oil production since 1985, and you need to go back to before the oil crisis of the 1970s to reach the kind of figures now being seen. Daily production has topped 9.7 million barrels/day (bbl/d) at times this year and is expected to average 9.5 million bbl/d. At this rate, the US is set to surpass Saudi Arabia and become the world's largest oil producer once again some time in the next couple of years. Some argue that it has already happened – if you take into account natural gas liquids, US 'oil' production was put at 11.6 million bbl/d in 2014 by BP – just ahead of Saudi Arabia's 11.5 million bbl/d.

The reason for America's surge in production is almost entirely down to increased production of oil and condensates from hydraulic fracturing of shales – shale gas and 'tight oil' production, and the expansion has been dramatic, with oil production almost doubling over the past seven years. The boom began with natural gas fracking, but its move into oil production has been if anything even more remarkable. On the gas side, in spite of persistent calls that domestic natural gas prices are "too low" to support production, and that producers were losing money, the run of low pricing has continued. Indeed, one of the most striking things about US gas production is that it does not even appear to have been affected by the fall in oil prices during 2014 as many thought it might. The theory was that 'wet' shale plays, which had depended on production and sale of natural gas liquids (NGLs) like ethane, propane and butane, whose prices were determined by the buoyant oil market, had subsidised shale gas production, and with their prices lower we would see margins squeezed and wells shut in. However, this has not happened, at least not yet. The reason is that gas production in the US seems to continue to become more and more efficient. In the northern Marcellus Basin, for example, the rig count has dropped by 50% since 2012 at the same time that production has almost tripled. Producing six times as much gas per rig has meant that the economics continue to remain favourable in spite of the oil price environment. And technology continues to improve, with 'smart' drill bits now able to adapt to rock conditions almost instantaneously.

As with gas, so with oil, with oil production rising even as the rig count falls – from 1,870 in July 2014 to just 628 in June 2015 (although this has since risen to 640 according to Baker Hughes), while oil production has risen at the same time from 8.6 million bbl/d to an astonishing 9.7 million bbl/d. If OPEC's decision not to support falling oil prices during 2014 was designed to put North American tight oil producers out of business, then it seems to have failed quite comprehensively, and indeed may have backfired, in that it seems to have encouraged even greater efficiency in US production while hurting OPEC members who rely upon oil revenues to balance their budgets. It is reckoned that Saudi Arabia requires an oil price of $105/bbl to make a budget surplus, Kuwait, the lowest cost producer about $55/bbl, and Libya, the highest, $185/bbl. By contrast, US oil prices have fallen as low as $50/bbl on heavy discounting by US oil rig operators. Consultancy IHS says that this has led to a fall in the average US break even cost necessary to sustain domestic oil production to around $32/bbl – way below anything OPEC can sustain, while the US fully burdened exploration and production breakeven cost is now put at $51/bbl by IHS CERA, and falling fast. In the meantime, OPEC's exports of Middle East light sweet crude to US refineries on the Gulf Coast have decreased by 45%.

Cheaper prices at the gasoline pump have also spurred domestic US demand. America is expected to consume more than 9 million bbl/d of gasoline this year, the highest level in eight years, with the recovering economy and higher employment levels also helping to boost demand. The average US retail price for gasoline was $2.80/gallon in June, nearly $0.90 cheaper than at the same time in 2014, and the US Energy Information Administration (EIA) expects prices to reach an average of $2.50/gallon in the second half of 2015.

Finally, cheap natural gas (currently below $3.00/MMBtu) has also helped refiners with the supply of energy to run their refineries and the supply of hydrogen for hydrotreating sour feeds.

Trade restrictions

Complicating matters for the US oil industry – although a boon for America's refiners – are restrictions on the sale and trade of oil. The federal ban on exports of US crude, itself a product of the oil crisis of the 1970s, is a problem for US oil producers because tight oil and shale gas production results in a lot of light fractions which cannot be sold abroad. There is more light crude than the US refining sector can use, meaning that American crude sells at prices below those of comparable international grades – West Texas Intermediate trades at a discount of several dollars per barrel to the international Brent crude price, in spite of being premium in the sense of being much sweeter than average global crudes. The discount is a clear advantage to those refiners who are configured to handle lighter crude. Additionally, one of the ways around the oil export ban is to export refined products instead, and this has become another positive for US refiners – and another reason why they are keen to keep the crude export ban in place!

Likewise the Jones Act which requires shipping of cargo between US ports to be carried on US built and flagged vessels, restricts the way that foreign oil can be moved around the country, and tends to support imports of crude over land, from Mexico and Canada, both of which export comparatively heavy, sour crudes, which helps in balancing the much lighter, sweeter crude being produced domestically.

Since the US was set up to process imported crudes, many of the refineries are on the east, west and southern coasts, whereas new sources of crude have come primarily from the Mid-West (especially the Bakken shale) and from Canadian syncrude. Although there has been much investment in new pipeline capacity to carry these new supplies (including natural gas liquids pipelines from the shale gas regions), pipeline capacity has lagged behind increased supply. This has especially been true of Canadian oil sands crude, where the main trans-border pipeline – Keystone XL – has been held up for years by legal wrangles. As a result, one of the major phenomena of the past few years has been so-called 'CBR' – Crude By Rail. CBR has increased from just a couple of hundred thousand barrels per day in 2011 to over 2 million bbl/d in 2014, and the figure for 2015 is expected to be around 2.4 million bbl/d.

SULPHUR
ISSUE 359
JULY-AUGUST 2015
BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

Changing crude slates

What the impact of the past few years of change in the US oil industry have been therefore is to significantly change the crude slate which US refiners must face. In the 2000s, in anticipation of the world moving towards heavier, sourer crudes, there was a spate of investment in handling heavy, sour imported crudes. Now, of course, refiners must instead face a glut of light, sweet crude and natural gas liquids from oil and gas fracking.

Since the Second World War, when gasoline was rationed, US gasoline production and sales and refinery capacity have been aggregated via five so-called Petroleum Administration for Defence Districts (PADDs). Broadly speaking, PADD 1 covers the East Coast states, PADD 2 the Mid-West, PADD 3 the US Gulf Coast (USGC) states, PADD 4 the Rocky Mountain states, and PADD 5 the East Coast. Table 1 shows the number of refineries and their coking capacity – in effect their ability to handle heavier, sourer crudes. As can be seen, about 50% of US refining capacity, including most of the country's capacity to process heavy, sour crude, is along the Gulf of Mexico coast in Texas and Louisiana – PADD District 3.

More than 70% of the capacity for PADD 1, which processed 1.1 million bbl/d in 2014, is at refineries that do not have coking unit, and so historically most crude supply to the region has been light sweet crude imported from overseas. This has left the region without pipeline connections to domestic production regions. However, since 2010, rising light tight crude oil production in the Bakken formation in North Dakota has been transported by rail into PADD 1.

PADD 2 has more capacity and a much higher proportion of coking capacity. Since 2010, several Midwest refiners have reconfigured their facilities to process more heavy crude, adding a total of 157,000 bbl/d of coking capacity. PADD 2 imports crude across the border from Canada, including bituminous syncrude, and this has increased in recent years, reducing the region's dependence on domestic and imported crude moved by pipeline from the Gulf Coast.

PADD 4 is the smallest by refining capacity. Since the hugely productive Bakken shale is within this region, it has seen oil production in the region increase by more than 60% over the past four years, and is now the only net exporting region. PADD 5 processes Californian heavy crudes, Alaskan North Slope and light crudes from the Bakken formation, as well as imported oil from Mexico and overseas. Declining Alaskan production has been offset by increased Bakken crude.

Changes to crude oil supply pat terns are most pronounced in the US Gulf Coast. Net imports into the region have fallen by 2.3 million bbl/d, and light sweet crude imports have been largely replaced by domestic production from West Texas (Eagle Ford shale). In addition, from 2010 to 2014, the average API gravity of crude inputs rose by 1 degree, indicating that average crude slates are becoming lighter. Crude oil production in PADD 3 has increased by 1.9 million bbl/d since 2010 and receipts of crude oil from PADD 2, including both US and Canadian production, have increased as well.

Table 1: Breakdown of US refining capacity

District	No. refineries	Coking capacity (million bbl/d)	Non-coking capacity (million bbl/d)
PADD 1	9	0.4	1.0
PADD 2	26	2.9	1.2
PADD 3	51	7.8	1.9
PADD 4	17	0.4	0.3
PADD 5	30	2.0	1.0
Total	**133**	**13.5**	**5.4**

Source: EIA

Investment

The main question at the moment for refiners is how much extra light sweet crude they can handle, and refinery operators have been looking at modifications to deal with the changed feed slate. Fortunately, it's a much easier – and hence cheaper – prospect than building new hydrodesulphurisation capacity to handle heavy, sour feeds. Building new refineries in the US is a long and complex process with permitting and construction costs an issue, so the most likely scenario is a progressive sequence of tweaks to existing refineries, especially in the US Gulf Coast. For example Valero, the largest US refiner, says that it plans to add crude units in Houston and Corpus Christi, Texas designed to process oil from the nearby Eagle Ford shale.

One boost has come from the recent decision to relax the oil export ban for condensate, which may prompt more refiners to attempt to switch their output in this direction. But looming over all such investment decisions is the prospect of unrestricted exports of US crude, which could change the whole US oil market once again, removing the price disparity for light sweet tight crude.

Sulphur output

At first sight, the injection of several million barrels per day of light sweet crude into the US refining industry would seem to indicate that sulphur output from US refining would drop. However, so far this has mainly displaced imported light sweet crudes, and in fact processing of higher sulphur feeds has increased to try and balance the light sweet supply. PADD 3 refineries are still set up to process Canadian oil sands bitumen and Mexican Maya oil, both very heavy and sour, and the investments in desulphurisation capacity are largely already made, in order to comply with the Environmental Protection Agency's (EPA) Tier 2 gasoline sulphur programme (which reduced permissible sulphur content of fuels from 120ppm to 30ppm) and the forthcoming Tier 3 sulphur regulations, which will reduce the permitted sulphur content of gasoline still further to 10ppm by 2017. Refiners must also cope with new International Maritime Organisation rules on sulphur content of ships' fuel. From 1 January, vessels travelling within the US Emissions Control Area (ECA) have been required to use fuels with less than 0.1% sulphur from the previous permitted 1%.

The US Geological Survey says that US sulphur production has risen from 9.17 million t/a in 2010 to 9.76 million t/a in 2014, and all of this increase has come from additional processing of sour crudes at US refineries, and at the moment there seems to reason to believe that the trend will not continue. ■

SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

PHOTO: PRESSDIGITAL / ISTOCKPHOTO.COM

Interactive discussions in Vienna

Now in its third year, the European Brimstone Sulfur Recovery Symposium reconvened in Vienna from May 18-12 2015.

The 2015 Vienna Brimstone Sulfur Recovery Symposium will be remembered by many for the full participation and detailed open floor discussions and round table sessions when attendees, including many sulphur industry experts, shared information and industry experiences in the quest to improve the efficiency and safety of sulphur industry operations and to find solutions to various operating problems and anomalies.

The programme for this year's symposium followed the usual format combining a selection of presentations on a wide variety of topics interspersed with open Q&A, workshop and round table sessions.

Catalyst bed design

The first presentation was by Brian Visoli of Porocel Industries who reviewed and analysed several common design and operational rules of thumb pertaining to Claus catalyst beds, taking into account modern catalyst and plant performance testing data, laboratory study results and general operational experience. Care must be taken when applying rules of thumb to understand the assumptions and conditions behind the establishment of the guideline and how the situation in question may differ. It has been shown that the type of catalyst installed in the Claus converters may have a dramatic effect on the size and dimension of the catalyst bed(s) as well as the optimal operating conditions.

Reaction furnace temperature

The difficult task of determining the true temperature in the Claus thermal reaction furnace was the topic by Steve Croom of Delta Controls Corporation. In monitoring the temperature of Claus thermal reaction furnace refractory it is common practice to employ both thermocouples and infrared pyrometers on the same furnace.

This practice is advisable as it provides redundancy and eliminates common-cause failures. However it has been observed that in some installations, there is a discrepancy between the temperatures reported by the thermocouple versus the temperature reported by the pyrometer, particularly when the devices are mounted in the same area of the furnace. Usually trend data provides more useful data than mere instantaneous comparisons. If the deviation between a thermocouple and an adjacent pyrometer indicate that the pyrometer is slowly reading lower and lower relative to the thermocouple over time, the likely problem is occlusion of the IR sight path. If the thermocouple is reading lower and lower over time relative to the pyrometer (and to expectations), it may indicate a failure of the thermocouple purge permitting gradual corrosion of the elements.

SO_2 emissions reduction

Alessandro Buonomini of KT Kinetics Technology described a new SO_2 emission reduction unit (SER™) developed by KT to meet new gas flaring and venting regulations for a client in the Middle East. The challenge was to minimise acid gas flaring in all possible operating scenarios, including start-up, shutdown and bypass operation, such that the hourly average SO_2 emissions through the stack of the new does not exceed 250 mg/Nm³. The new SER™ unit is fully integrated into the existing sulphur recovery facilities and comprises an improved thermal incinerator system equipped with a special burner system and proprietary devices to enhance conversion of H_2S to SO_2 and a SO_2 scrubbing system. For the SO_2 scrubbing system, KT selected MECS' DynaWave technology from Dupont. The new SER™ system is capable of mitigating feedstock disturbance in all operating conditions in terms of rapid variation of flow rate and composition from upstream units to meet the new more stringent regulations.

Molten sulphur fire sealing steam requirements

The National Fire Protection Association standard for prevention of sulphur fires and explosions NFPA 655 is currently being updated and will be reissued in 2017. Sean McGuffie of Porter McGuffie reported on recommendations for proposed modifications to NFPA 655 focusing on the potential problems caused by the current NFPA 655 snuffing steam rate, which specifies a steam extinguishing system capable of delivering a minimum of 2.5 lb/min of steam per 100 ft³ (1.13 kg/min of steam per 2.83 m³) for the protection of covered liquid sulphur storage tanks, pits and trenches.

The air intake and exhaust systems of the air sweep systems for sulphur tanks and sulphur pits are typically designed with very low pressure drops for normal operation. If snuffing steam is fed to sulphur tanks and sulphur pits at the rate specified in NFPA 655, the built-up back pressure typically far exceeds the design pressure of the enclosure.

The presentation also included an analysis of actual field data for fires in sulphur tanks and pits and a recommendation for the NFPA 655 committee to consider regarding a steam rate to seal the enclosure and extinguish the fire in a sulphur tank and sulphur pit. Comments were also made on good engineering practice resulting from calculations and CFD analyses that have been completed.

Effect of MMEA

Methlymonoethanolamine (MMEA) is one of the secondary amines produced by the degradation of N-methyldiethanolamine (MDEA). It is frequently present in the MDEA solvents used in TGTUs and is also a contaminant in acid gas enrichment (AGE). The presence of MMEA seems to be associated with SO_2 breakthrough events from the sulphur plant into the TGTU amine system. MMEA is a highly reactive amine with fast kinetics, and its presence even in relatively small concentrations (typically less than 1% by weight) is shown to cause tremendous loss of selectivity by increasing the absorption rate of carbon dioxide. Ralph Weiland of Optimized Gas Treating presented two case studies that establish MMEA as a cause for much lower-than-expected selectivity in a TGTU and loss of sulphur plant feed gas quality in two AGE applications.

10 commandments of sulphur recovery

As a licensor of SRU technologies, Jacobs is frequently contacted by clients for support and advice when the SRU is not running properly. Mike Smeltink of Jacobs Comprimo® Sulfur Solutions presented practical experience from sites all over the world in the form of ten commandments, providing guidelines for design, construction, choice of equipment, commissioning and day to day operation.

Common problems related to refractory, burners, reactors, catalysts, condensers and process control. Some problems are related to design features but many others are due to improper installation of equipment. Most importantly, attention has to be given to day to day operation and handling of conditions that are outside of the normal design parameters.

New sulphur degassing technology

The sulphur industry employs several effective sulphur degassing technologies and the most common perform degassing outside the unit by some combination of air sparging and pressure. These technologies typically feature substantial air consumption, elevated pressures, a waste stream which must be treated, and a number of rotating equipment components. In his presentation, Jim Hartman of Controls Southeast introduced a new in-situ degassing technology which operates within the unit, upstream of the sulphur pit and without the need for additional air, pressure, ejector or rotating equipment. Furthermore, no waste stream is produced.

Utility considerations for SRUs

The final presentation by Elmo Nasato of Nasato Consulting identified the key design and operating considerations for the utility side of an SRU to raise awareness of its importance. The steam produced in an SRU is a critical utility for export and often has more value than the sulphur. Despite this, in comparison to the process side of sulphur recovery units, the utility side of the SRU is frequently neglected in both the fine details of conceptual design and in the normal day-to-day operation. Yet there are many examples where the utility side provides harsh reminders of the importance of keen attention in order to ensure reliable, safe and high on-line operation of the SRU. The industry is plagued with a shortage of personnel and the result has been limited mentoring and significant loss of design and operating experience. This problem has been magnified in the peripheral refinery cost centres such as the sulphur units and utility units. ■

CONTENTS

SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

Benefits of heat stable salts in tail gas treaters

Adding phosphoric acid to MDEA solutions in tail gas treating units (TGTUs) enables significantly deeper stripping of hydrogen sulphide (H_2S) in the regenerator and permits tail gas to be treated to as low as 10 ppmv H_2S. Most heat stable salts are the organic acid equivalents to phosphoric acid, and they function in exactly the same way. **C.E. Jones, R. Scott Alvis** and **R.H. Weiland** of Optimized Gas Treating, Inc. explain the mechanism through which stripping promoters act, showing that removing HSSs to very low levels can be detrimental to the operation of TGTUs, and provide guidelines on determining when and how much HSSs should be left in the treating solvent.

In commercial gas plants, amine treating solvents are invariably contaminated to some degree with a variety of materials, including:

- surface active agents
- products formed by the oxidation and thermal degradation of the amines themselves
- solids including products of reaction of the acid gases with vessel walls and piping
- contaminants present in or generated by the gas being treated.

This article focuses on the effect of contaminants in the last category that either enter the amine system with the gas itself, or are formed by reaction of certain gas components with the solvent. Contaminants in this fourth group are the heat stable salts (HSSs). As a class, they are especially troublesome in refineries because their precursors such as hydrogen cyanide and ammonia are unavoidably produced in a variety of operations so they are almost always present. The precursors of other HSSs, for example SO_2, are present in the tail gas from sulphur plants. Other HSSs can enter the amine system with the water used to replenish evaporation or other losses.

Heat stable salts are generally the anions of organic and inorganic acids, including formate, acetate, propionate, glycolate, thiocyanate, thiosulphate, oxalate, sulphite, sulphate, and chloride. Common cations are sodium and potassium. Because they are ions they exert no vapour pressure and so are completely nonvolatile. These ionic species remain in solution and cannot be steam or heat stripped; hence, the terms 'heat stable' and 'salt'. Sodium and potassium ions are not sourced in the gas; rather, they usually enter the amine system with poor quality water used to replenish losses from the treating plant. Hydrogen from gasoline reformers can contain hydrogen chloride which will absorb and react directly in acid-base neutralisation with the amine. Phosphate ion is another HSS, but it is one that is purposefully added to the solvent as phosphoric acid. The purpose of adding phosphoric acid is to enhance solvent regeneration by allowing lower solvent lean loadings to be reached with the same regeneration energy. Phosphoric acid is a stripping promoter. This suggests that HSS anions might also act as stripping promoters, something that is borne out in what follows.

It is instructive to trace the formation of HSS anions from their precursors. The most common precursors are hydrogen cyanide which enters with the refinery gas, ammonia which may be in the refinery gas or may be a reaction product of HCN hydrolysis, and sulphur dioxide which enters with sulphur plant tail gas. Oxygen is also required for the formation of certain HSSs. Formate and thiocyanate are products of the reaction of absorbed hydrogen cyanide. Formate forms by the hydrolysis of cyanide ion to ammonium formate (Reaction 1a); thiocyanate forms by the reaction of dissolved oxygen with H_2S followed by reaction of the oxysulphur anion with cyanide ion (Reaction 1c). Higher molecular weight organic acid anions are generated by the hydrolysis of higher molecular weight nitrile compounds (Reaction 1a). Ammonium ion from nitrile hydrolysis will give up an H^+ to the amine (Reaction 1b) and the resulting ammonia is then stripped by steam in the regenerator where it accumulates in the overhead condensing system. This leaves the protonated amine/HSS anion pair in the amine solution. Thiosulphate generally results from the reaction of dissolved oxygen with H_2S (Reaction 1d) or from SO_2 reaction with H_2S (Reaction 1e) in tail gas treaters when no HCN is present. Sulphite can form from absorption of sulphur dioxide, and sulphate can form either from oxidation of sulphite, or from the further oxidation of thiosulphate (Reaction 1f) (See Table 1).

Table 1: Formation of HSS anions

$$RCN + 2H_2O \rightarrow NH_4^+ + RCOO^- \quad \text{(R=H or alkyl group)} \quad (1a)$$

$$NH^{4+} + R_1R_2R_3N \rightleftharpoons R_1R_2R_3NH^+ + NH_3 \quad (1b)$$

$$2HCN + O_2 + 2H_2S + 2R_1R_2R_3N \rightarrow 2R_1R_2R_3NH^+ + 2SCN^- + 2H_2O \quad (1c)$$

$$2H_2S + 2O_2 + 2R_1R_2R_3N \rightarrow 2R_1R_2R_3NH^+ + S_2O_3^{2-} + H_2O \quad (1d)$$

$$2H_2S + 4SO_2 + H_2O + 6R_1R_2R_3N \rightarrow 6R_1R_2R_3NH^+ + 3S_2O_3^{2-} \quad (1e)$$

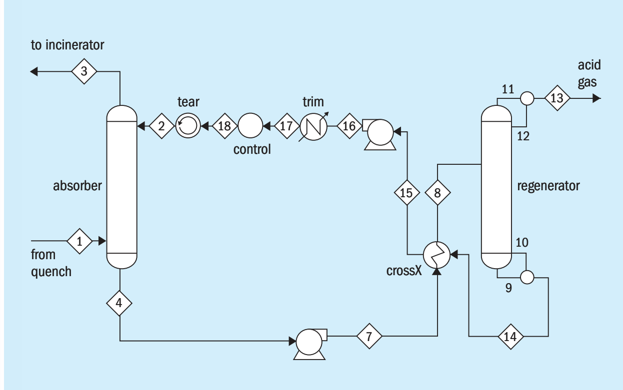
$$S_2O_3^{2-} + {}^5/_2\,O_2 \rightarrow 2SO_4^{2-} \quad (1f)$$

For a strong acid H_nX where X is an n-valent anion (Cl^-, SO_4^{2-}, etc.), the reaction with amine is:

$$H_nX + nR_1R_2R_3N \rightarrow nR_1R_2R_3NH^+ + X^{-n} \quad (2)$$

Unlike the acid gas-amine reactions, none of these reactions are thermally reversible. HSSs permanently tie up part of the amine as $R_1R_2R_3NH^+$ ion and the amine becomes partially protonated, i.e., neutralised. [Note: The ionic pseudo-compound $R_1R_2R_3NHX$ is called a heat stable amine salt (HSAS) even though it exists only in the fully dissociated form, $R_1R_2R_3NH^+ + X^-$, in aqueous solution.] The amine is gradually converted to HSAS so it becomes inactivated. Heat stable salt anions are also known to complex iron which accelerates corrosion in the hot, lean section of the amine unit. Contact between complexed iron and higher concentrations of H_2S in the absorber generates iron sulphide particles which can foul equipment, lead to loss of treating capacity and further exacerbate corrosion by eroding the protective iron sulphide film on carbon steel piping and equipment surfaces. Although the foregoing description paints a bleak picture of HSSs, they may not always be bad. How and by what mechanism they influence the amine treating process are questions that are addressed quantitatively through a case study, and the results are explained through chemistry.

Fig 1: **Process flow diagram of the TGTU in the case study**



Case study

The case study is of the refinery tail gas treating unit (TGTU) shown in Fig. 1. This is a conventional system using 33.37 wt-% MDEA contaminated with 0.33 wt-% DEA to treat tail gas from an SRU. The tail gas has been water quenched so it is saturated with water. Acid gases are 1.7% H_2S and 3.4% CO_2. The contactor contains 6.1 m of FLEXIPAK® 2Y structured packing to minimise pressure drop and maximise tower capacity. The regenerator has 20 valve trays with rich amine feed to the third tray from the top.

TGTUs are typically run on a separate solvent circuit; however, this one was being run as part of the refinery MDEA system. An analysis performed by the solvent vendor showed that in addition to being contaminated with DEA, the solvent contained several heat stable salts (HSSs) present at the following concentrations: thiosulphate, 5930 ppmw; oxalate, 220 ppmw; acetate, 1150 ppmw; formate, 815 ppmw. The total HSSs level was 0.8115 wt-% (8,115 ppmw). Perhaps surprisingly, the unit nevertheless was producing a vent gas with only a few ppmv H_2S, a very low concentration for a TGTU where 100 ppmv is much more the norm. The solvent is obviously quite contaminated and operations were considering reclaiming. The question was asked: If we reclaim the solvent by removing all the HSSs, will treating performance be affected, and if so, by how much? The right place to start answering this kind of question is a good, reliable simulation capable of modeling the real equipment performance when using the as-analysed, contaminated solvent.

ProTreat® is a completely predictive mass transfer rate based amine treating simulator and was used to model the complete plant, including the details of the actual internals of both the absorber and the regenerator columns. The software accounts for the detailed solution analysis (HSS profile), and uses measured reboiler duty. The predicted hydrogen sulphide treating achieved using the contaminated as-analysed solvent is 6.7 ppmv H_2S, with a CO_2 slip of 77%.

If a model that did not account for HSSs had been used, the predicted H_2S treating would have been more than 100 ppmv, well over 10 times the observed value. Table 2 shows the simulated effect of various levels of HSS removal (degrees of reclaiming) on lean solution quality and H_2S treat. The H_2S leak is plotted as a function of HSS removal in Fig. 2. The results suggest that an additional contribution to the refinery's allowable sulphur emissions would almost

Table 2: Effect of HSS level on TGTU performance

Total HSSs as %age of analysed level	Lean CO_2 load (mol/mol)	Lean H_2S load (mol/mol)	H_2S leak (ppmv)	CO_2 slip (%)
0	0.000253	0.0109	100	76.1
10	0.000383	0.00852	94	76.1
25	0.000268	0.00577	89	76.2
50	0.000153	0.00249	51	76.6
75	0.0000920	0.000789	21	77.0
100	0.0000578	0.000194	6.7	77.2
125	0.0000384	0.000045	1.9	77.6

SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

certainly result from reclaiming, even if carried out only moderately. Apart from benchmarking the reliability of the simulator, the first lesson is that at least in a TGTU, a clean solvent may not treat to nearly as low a residual H_2S level as a contaminated one. An acceptable level of contamination is determined by the competing factors of very efficient treating and the need to keep corrosion rates within tolerable limits.

CO_2 slip is hardly affected by reclaiming, but reclaiming has a tremendous effect on the unit's H_2S leak. Notice also that when the solvent contains its full complement of HSSs, lean loadings are reduced by a factor of six for CO_2 and a factor of 250 for H_2S compared with the clean solvent. The second lesson is: the processing effect of HSSs really makes itself known in the regenerator where much lower loadings can be achieved when the solvent contains HSSs. Perhaps this should not be so surprising. After all, it is well known that the addition of small amounts of phosphoric acid gives superior tail gas treating—this is the basis for several specialty solvents offered by vendors. They go by various names such as protonated amines, partially-neutralised amines, and acidified amines. The effect of phosphoric acid in this case study is examined later.

Conclusion 1: A clean solvent may not treat to nearly as low a residual H_2S level as a contaminated one.

Conclusion 2: Heat stable salts removal has very little effect on the CO_2 slipped in MDEA treating.

Conclusion 3: The presence of a substantial concentration of HSSs allows the regenerator to produce a much more cleanly stripped solvent, at least using MDEA.

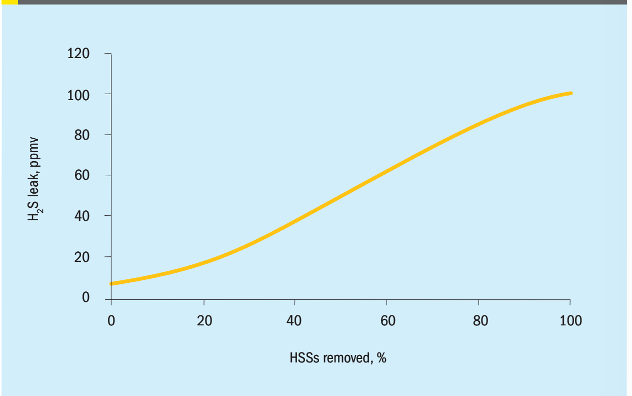
Mechanism

Acid anions in MDEA treating solutions promote solvent regeneration by shifting the equilibrium of the acid gas-amine reactions. For example, when H_2S is present in MDEA solvent, very little of it actually exists as the molecule H_2S because when hydrogen sulphide chemically (and instantaneously) dissociates in the solution, the hydrogen ion it produces is immediately neutralised by the amine:

$$H_2S \rightleftharpoons H^+ + HS^- \quad (3)$$

$$R_1R_2R_3N + H^+ \rightleftharpoons R_1R_2R_3NH^+ \quad (4)$$

Fig 2: **Effect of heat stable salt removal on H_2S leak from absorber**



The overall reaction is

$$H_2S + R_1R_2R_3N \rightleftharpoons R_1R_2R_3NH^+ + HS^- \quad (5)$$

Here R_1 is the methyl group and R_2 and R_3 are the ethanol groups that make up *N*-methyldiethanolamine (MDEA). When part of the amine is neutralised by a small amount of an acid cation, the concentration of the protonated form of the amine is higher than it normally would be. This tends to push the reaction equilibrium to the left, towards free dissolved hydrogen sulphide. In a regenerator, therefore, stripping is favoured.

At high acid gas loadings the impact of a small amount of additional protonation is completely negligible because the protonated amine concentration is already very high: in other words, there is only a very small change to an already high concentration. But in the reboiler, for example, the H_2S loading will already be very small (if low H_2S leak is to be achieved from the TGTU), so even a small amount of additional protonation is highly significant relative to the very low concentration of protonated amine normally present there.

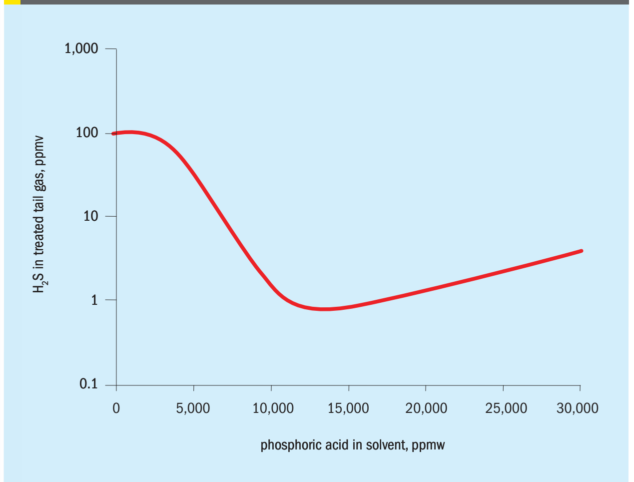
In fact, the additional protonation can be 10 to 100 times higher than what would normally be found in well-regenerated, clean, generic MDEA. The additional amine protonation displaces Reaction (5) strongly to the left, towards the formation of free, molecular H_2S capable of desorbing from the solution. Greater non-acid gas generated protonation enhances solvent regeneration. However, the effect of additional protonation on absorber performance somewhat counteracts its effect on stripping and, depending on circumstances, it may overwhelm the stripping benefit altogether.

The higher H_2S back-pressure caused by the increased protonation arising from HSSs negatively affects absorption. However, it turns out that in TGTUs, its beneficial effect on reducing the lean loading in the regenerator far outweighs its negative effect on back-pressures in the absorber. As shown in the Case Study, the result can easily be a factor of 10 or 20 times lower H_2S leak when HSSs are present in small amounts. Of course, caution is needed not to let HSSs build up too high because they are corrosive.

But caution is also needed not to reclaim too aggressively or what once was superb treating may become very poor treating, unfortunately discovered only post-cleaning. Accurate simulation makes it very easy to predetermine the desired HSS removal level (from a process standpoint) prior to solvent cleaning. Even if the corrosion resulting from high HSS concentrations is unacceptable and the HSSs must be removed, their beneficial effect can still be had by replacing them with a small amount phosphoric acid which supplies the very effective trivalent phosphate cation.

Conclusion 4: Heat stable salts have a highly significant effect on hydrogen sulphide removal in TGTUs and solvent cleaning must be carried out judiciously to avoid nasty surprises. Accurate process simulation is the most effective way to ensure a prudent decision.

Fig 3: **Effect of phosphoric acid conc. on the H_2S leak from the TGTU absorber**



Case study continued – Phosphoric acid

Phosphoric acid is a well-establish stripping promoter frequently used in TGTUs. If the MDEA used in a refinery tail gas treating system easily becomes contaminated with HSSs, there seems little point in adding phosphoric acid to the mix because reclaiming will be all too frequent, and whenever the solvent is reclaimed phosphoric acid will also be removed. However, in gas plants HSSs are not usually a problem so the use of phosphoric acid is generally found to be beneficial in gas plant TGTUs.

The details of the case study remain the same but the mixture of HSS contaminants is replaced with various levels of phosphoric acid. Included is one-for-one replacement of the total HSS level with an equal mass concentration of phosphoric acid to get a direct comparison between a mixture of various HSS components and phosphoric acid. Fig. 3 shows the effect of phosphoric acid concentration on the H_2S leak from the TGTU.

In this case, there is an optimal concentration of between 1.3 and 1.4 wt-% at which the most benefit is realised. A minimum (or maximum) can always be explained by the presence of two competing effects.

On the low concentration side of the optimum, increasing phosphoric acid concentrations drives the equilibrium Reaction (5) to the left. And even as the concentration increases well beyond the optimum level, the loading of both acid gases in the solvent continues to drop. Counteracting this is the increased equilibrium partial pressure of hydrogen sulphide at the top of the absorber which is caused by the higher salt (phosphate ion) concentration, despite the lower H_2S loading of the solvent. Higher backpressure limits the achievable hydrogen sulphide leak.

The optimal concentration is not a uniformly fixed value. Commonly, about 5,000 ppmw is recommended and this usually provides excellent treating down to some 10 ppmv H_2S leak. However, the true optimal concentration depends on the unit and its operating conditions. Note however, that phosphoric acid is a good cleaning agent and, if used in excess, it could possibly remove iron sulphide protective films.

Conclusion 5: Just like HSSs, phosphoric acid can be an effective stripping promoter in TGTUs. But there is an optimal level for maximum effectiveness and just what that optimal concentration is depends on the particulars of the operation. One concentration does not 'fit all'.

Conclusion 6: High HSS levels are known to be corrosive and this may be the deciding factor dictating when reclaiming should be done. In the same way, phosphoric acid is also corrosive in the sense that it can solubilise iron sulphide protective films. Concentrations greatly in excess of what is necessary to achieve the desired level of treating should not be used. If reclaiming is to be done without benefit of simulation, it might be prudent to set aside a quantity of contaminated solvent to be added back in case the TGTU fails to treat adequately using the cleaned solvent.

Conditions for beneficial retention of HSSs

The important unaddressed questions are: what are the conditions necessary for HSSs and phosphoric acid to be beneficial, and when will they negatively affect treating? There are two necessary, although not sufficient, conditions for acid anions to be beneficial:

- The main amine constituent in the solvent must not be a carbamate former, although small amounts of amines reactive with carbon dioxide and small amounts of CO_2 are permitted.
- Operationally, the absorber must be lean-end pinched.

If the amine forms a carbamate as in Reaction (7), then not only will the hydrogen ion produced by H_2S dissociation neutralise part of the amine according to Reaction (6), but there will also be a substantial amount of protonated amine coproduced with carbamate formation. Carbamate formation is not nearly as easy to thermally reverse as hydrogen sulphide absorption so there will almost invariably be a substantial concentration of protonated amine. Therefore, adding even a few weight percent HSSs will not increase the protonated amine concentration enough to shift materially the equilibrium of Reaction (6) towards the formation of free, dissolved, volatile hydrogen sulphide.

$$H_2S + R_1R_2R_3NH \rightleftharpoons R_1R_2R_3NH_2^+ + HS^- \quad (6)$$

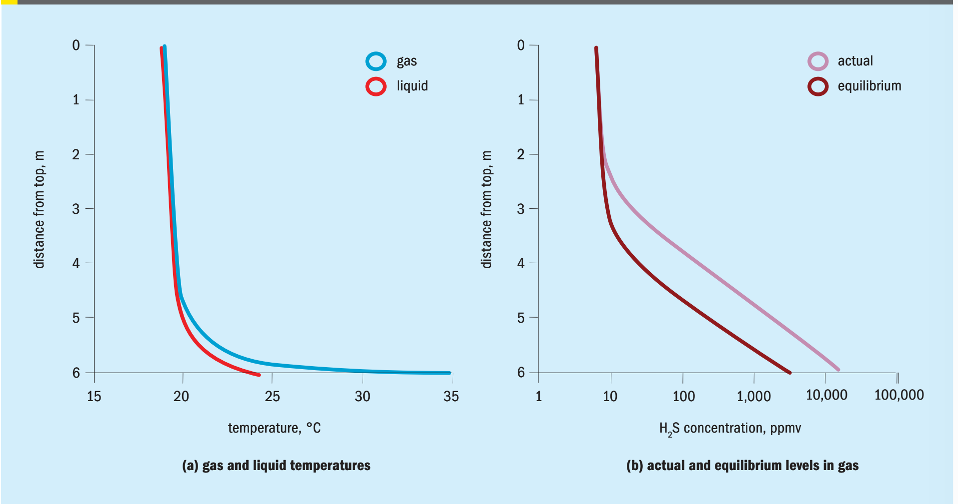
$$R_1R_2R_3NH + CO_2 \rightleftharpoons R_1R_2R_3NH_2^+ + R_1R_2NCOO^- \quad (7)$$

The significance of the first condition then is that MDEA and TEA, being tertiary amines, are certainly not carbamate formers, so acid anions may possibly allow stripping of acid gases from these solvents to unprecedented levels. The same is true of hindered secondary amines. Despite not being tertiary, carbamate formation is blocked by stearic hindering so amines in

SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

Fig 4: **Temperature and CO_2 composition profiles in the TGTU absorber**



this class may also respond well to HSSs and the purposeful addition of other acid anions. The solvent must be one that is well suited for slipping carbon dioxide. On the other hand, no amine that reacts with carbon dioxide, releasing hydrogen ion, stands any chance whatever of benefiting from leaving HSSs in the solvent, or from adding a stripping promoter.

The second factor is that the absorber must operate lean-end pinched. In practical terms this means the hydrogen sulphide in the treated gas must be determined directly by lean solvent H_2S loading. But how does one know if an absorber is lean-end pinched? This is another area where a high quality simulation can provide valuable insights. The TGTU absorber gas and liquid temperature profiles, and the profiles of the actual CO_2 concentration in the gas together with the CO_2 concentrations that would be in local equilibrium are shown in Figs 4(a) and (b).

The temperature profiles in Fig. 4(a) are not constant across any section of the absorber at all, so one might be hesitant to call the operation lean-end pinched. However, temperatures continue to change very slowly even across the upper section of the packing because carbon dioxide is absorbed throughout the entire packed bed. However, as Fig. 4(b) shows, the hydrogen sulphide concentration in the gas is in almost perfect equilibrium with the liquid over the top 1-1½ m of packing, i.e., at the lean end of the tower. A column's operation is called pinched when there is no driving force for absorption in some region of the column. Sometimes an absorber is rich-end pinched (typically carbon capture by amine solvents)[1], and in other cases it is bulge pinched[2]. In the present case, the absorber is certainly operating with a lean-end pinch.

The hydrogen sulphide leak from this TGTU is determined solely by the lean solvent loading, and the temperature and pressure at the top of the contactor. If the simulated, actual and equilibrium H_2S concentrations did not coincide anywhere in the absorber, it would not be in a pinched state.

Conclusion 7: HSSs and stripping promoters only work in amine solvents that do not react and form carbamates with CO_2. If carbamates are formed, carbon dioxide is next to impossible to reduce to very low levels using heat, a significant protonated amine concentration always remains, and having a few thousands of ppmw HSS or phosphoric acid does not materially shift the equilibrium of H_2S dissociation.

Conclusion 8: Any potential benefit from the presence of HSSs or the use of stripping promoters is limited to absorbers that are operating in a lean-end pinch state.

Concluding remarks

Reclaiming decisions should start with a good set of simulations generated using a process simulator that has high accuracy and reliability. Only mass and heat transfer rate based simulations meet this criterion. The simulator must also be able to model the actual system under study, especially the detailed solution chemistry and the mass transfer behaviour of the real column internals being used. Accurate regenerator modeling is just as important as simulating the absorber simply because the regenerator sets the acid gas lean loadings and regeneration is where HSSs and stripping promoters exert their primary effect, generating a super lean solvent.

References

1. Weiland R.H., Hatcher N.A. and Alvis R.S.: "Rich-end, Lean-end, and Bulge Pinches in Amine Treating", paper presented at GPA Europe Annual Conference, Madrid, Spain (Sep 2014).
2. Weiland, Ralph H., Hatcher, Nathan A., Alvis, R. Scott: "Bulge Pinched CO_2 Absorber in an LNG Plant", *LNG Industry* (Jan 2015).

Acknowledgement

This article was presented at the Sulphur 2014 Conference in Paris, France, 3-6 November 2014.

SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

Sulphuric acid process simulation and modelling

Numerical simulation and modelling are strong tools for analysis, design, development, and optimisation of equipment and processes, as well as operator training. While fast computers allow for more realistic models, dynamics simulations and CFD calculations in complex geometries, the key to accurate model predictions remains the incorporation of experience from lab, pilot and industrial data analysis into the models.

Modelling is an invaluable tool for plant design (Fig. 1). It would not be possible to build todays large scale facilities without the confidence that modelling provides in the ability to design a plant that will work acceptably and safely from the very first start-up.

Typically, physical properties of the components, reaction data, material and energy inputs/output, equipment models and economic information are input into the model and a set of predictions about the temperatures, pressures, compositions, costs, etc. are the results. The plant designer can then modify elements of the design to optimise the plant to achieve the client's objectives.

Process simulation is a powerful tool that enables engineers to complete sophisticated design, development, analysis, and optimisation of plant designs before significant resources are committed for detailed engineering.

While there are enormous benefits to modelling in the design and operation of a chemical plant, like all powerful tools, great care must be taken in their use. The modelling tools will provide a result even if incorrect data is used, and even the mathematical structure of the model needs to be picked properly to be reliable. Experience and a history of validating models are required to interpret the results and to have the confidence to make major investment decisions based on them.

A typical application for simulation tools is the optimisation of gas mixing. The mixing of hot and cold gases is a typical operation in plants to e.g. control inlet temperatures to the catalytic beds. In order achieve the best performance of the catalyst in terms of conversion per catalyst volume a prerequisite is uniform gas distribution regarding flow, composition and temperature at the inlet of each catalyst bed.

Fig 1: **Sulphuric acid plant with process design optimised using modelling**

PHOTO: CHEMETICS

In the example shown in (Fig. 2), the mixing of three gas streams upstream of a gas-gas heat exchanger was simulated and the mixing path optimised. Thanks to the use of a computational fluid dynamics tools in this case, the temperature variation could be minimised from over 100°C to less than 10°C.

Sulphuric acid plant modelling

A sulphuric acid plant computer model allows users to manipulate process inputs such as gas flows or gas strengths and observe the subsequent changes in the process conditions and performance of the acid plant equipment. These simulations can be accomplished using a variety of tools including commercial simulators, dedicated third party software, or user-created models.

Acid plant simulations can be very useful for operators and equipment vendors alike as it allows the user to obtain stream data from the plant for current and future conditions. For equipment replacement projects it allows the user to provide stream data conditions required by equipment vendors. Comparing a plant's current operating data with an accurate simulation may reveal areas of poor equipment performance such as fouling and poor catalyst activity. The simulation will also allow the user to determine bottlenecks within the plant, blower power requirements, and energy production for varying rates or conditions. Sensitivities to changing process conditions can also be investigated and used to improve process control strategies, provide insight into dynamic operation, plant start-up, and methods of improving plant reliability.

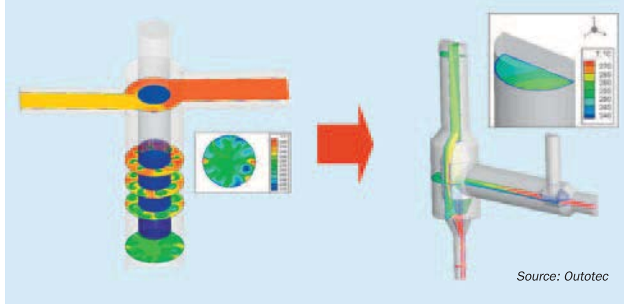
All of these benefits are extremely useful, but achieving them with an accurate simulation requires a great deal of knowledge and work. First, a commercial or third party program may be leased which may have a high cost. Alternatively a simulation can be created in a spreadsheet which requires significant time and considerable know-how of sulphuric acid plants, operation, chemistry and engineering. Additionally a property package that works for sulphur-sulphuric acid-SO_2 systems must be selected or developed. Finally detailed information for the plant equipment including gas exchangers, blowers, catalyst conversion and other components must be entered.

Troubleshooting and debottlenecking

A valuable but less appreciated use for modelling is as a tool for troubleshooting and debottlenecking for existing plants.

Troubleshooting is generally done when actual plant performance is different to past operational experience or the original flowsheet design. It is used to diagnose what is causing the deficiency in the operating results and provide guidance to corrective adjustments or modifications. By developing models that simulate the effects of various malfunctions and trying to match the observed plant operating conditions, a "virtual plant inspection" can be conducted. This allows the possible causes to be narrowed down to minimise the amount of maintenance downtime required to repair by being prepared for the issue before the plant is stopped.

Fig 2: **Simulation for the optimisation of gas mixing**



Source: Outotec

Debottlenecking is generally done when the plant is required to operate in a different mode than initially designed or the plant is required to have an increased capacity. The result of a debottlenecking effort is typically suggested changes to operating conditions and can also include suggested changes to plant equipment along with a prediction of what the plant performance will be when the changes are implemented.

These applications take advantage of the fact that there is real world data to feed back into the model that provide a real comparison point; however there are additional challenges to overcome. The plant data that is collected is typically incomplete and sometimes inconsistent due to changes in operating conditions during data collection; the equipment may not be performing as originally designed due to wear, fouling or even premature failure, and there are many constraints that can't be input directly into the model. Some of the extra constraints are physical restrictions at the site, cost differences depending on existing equipment and its condition, and time to implement changes.

Acid plant simulation tools

In the early days between 1960 and 1980 in-house process simulators were developed by company engineers and ran on computer mainframes. The 1980s and '90s gave rise to more sophisticated PC based simulation programs, one of the most widely used and recognisable being Hyprotech's Hysim later known as Hysys. This program introduced in the '90s for Windows allowed for an interactive, backward calculation capable simulation environment with greatly increased flexibility. Honeywell purchased the code for Hysys in 2004 which is marketed under the name Unisim and offers a suite of packages. Aspen Technologies' Aspen Plus simulator was created in 1981, Aspen now offers Aspen Plus and Hysys along with a suite of packages for steady state, dynamic modelling, special physical property packages, heat exchangers, cost estimation, etc.

These commercial simulators offer significant flexibility in design however the lease costs can be high and there is a still a need to develop equipment models and proprietary physical property packages to handle the sulphur and acid streams.

The third tool available for process simulation is a user-created model. With this the user can create a model of an individual piece of equipment or an entire acid plant. This tool provides the user with total control of the programs inputs and outputs, however it also requires a good understanding of the unit operations of the acid plant as well as the development of good physical property data correlations.

Limitations of models

Models have a critical limitation; they are representations of real systems, but they are not real systems. While this may seem to be a trivial statement, often problems are encountered when professionals trust the results of a model without validating it.

Fundamentally the results are based on a computer executing the input calculations. The computer will execute whatever it is told to, exactly as it is told to even if that makes no sense in the real world system that is being modelled. Examples where this can occur are errors in the connections in the models, errors entering the data, incorrect reactions, and using the wrong

SULPHUR
ISSUE 359
JULY-AUGUST 2015

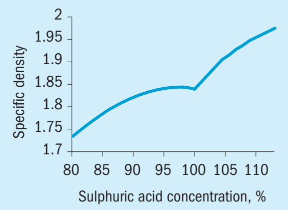
BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

PHOTO: CHEMETICS

Fig 3: **Design models for these acid towers were confirmed using plant data**

Fig 4: **Changes in specific density of sulphuric acid/oleum relative to acid concentration**



Source: Chemetics

calculation methods. With some of these errors it is possible to get apparent mass being created or destroyed, negative values, heat transfer the wrong direction, etc. More sophisticated modelling software will provide some error checking for the most obvious errors, however smaller errors that provide results within these crude bounds can be accepted without warning.

A significant source of error is from the property estimation methods typically included in the modelling software. Reliable physical property data typically only exists for pure components, and selected common mixtures that exhibit close to ideal behaviour. Models are used to estimate the physical properties of mixtures and components that are not directly supplied in a database. These models suffer all of the difficulties that the higher level models also do, but are also more difficult to validate due to the lack of laboratory data. In addition, there are many mathematical forms that these property models can take and many of these can be selected within the same software package, giving significantly different results. It is important to note that strong sulphuric acid in the 80-100% weight range is non-aqueous and is not easily modelled using conventional property estimation methods. This is described in detail in the next section below.

The key to reliably using models is to validate results with real world data (Fig. 3). Bench scale testing, Pilot plants, and trials at existing facilities can be helpful in providing comparison data. The model should be configured to match the real world data as close as possible, while using the same property configurations and assumptions as would be used for the full scale project.

Chemetics customisation of physical properties

Standard "off the shelf" property calculation methods use formulas derived from theoretical assumptions about how properties vary with a small number of parameters to represent the properties of a mixture. Different methods use different formulas; however all have a limited number of parameters and don't accommodate complex concentration to property relationships well.

Sulphuric acid and oleum have properties that are highly non-linear with concentration, as an example the density increases with increasing concentration, but essentially levels off above ~93%, and then actually decreases slightly by 100%. In the oleum range the density increases again, with a much steeper slope than in the acid range. This effect is summarised in Fig. 4. Changes in direction or discontinuities in slope of the property values cause errors when using standard property packages.

Chemetics uses several different customised property sets for sulphuric acid depending on the concentration due to the drastically different shapes of the concentration to physical property relationships. Chemetics has done extensive customisation of physical properties specific to the sulphuric acid industry to address these issues.

Two examples of models used for troubleshooting and for debottlenecking are given below:

- troubleshooting in a regeneration sulphuric acid plant
- debottlenecking a metallurgical gas sulphuric acid plant.

Example of troubleshooting

A regeneration sulphuric acid plant found that they were having slowly worsening SO_2 emissions. Repairs had already been attempted on the hot heat exchanger; however the emissions were still worsening to the point of forcing production rate reductions.

The site was limited in access to some sampling locations and to the accuracy of the measured temperatures, concentrations and flows due to the age of the instruments. The site data did not have a clear cause of the performance issues so a modelling study was initiated to help determine the cause of the performance issue.

To execute the modelling study models were prepared with different plausible failures. Examples of these models are leaks in each gas exchanger or degraded catalyst in certain beds. The models were adjusted to match the observed plant data as closely as possible. Each model was then compared with the whole set of plant data, gas sampling results, and other observations to determine which failure scenarios could account for the specific differences seen in the plant vs the baseline flow sheet performance.

The results indicated a major leak on the cold reheat gas exchanger and a minor leak in the cold exchanger (Table 1). The plant can then use this to prepare repair and replacement plans prior to the next turnaround and avoid costly additional downtime. An additional result of the model was an analysis of what operating parameters to focus on optimising to maintain acceptable emissions while the long term repair plans are being prepared and executed.

Table 1: **Summary of scenarios**

Key observation accounted for?	Scenario					
	Bed 4 catalyst	CHX leak	CRHX leak	HHX	IRHX	CHX + CRHX
Emissions	yes	yes	yes	no	yes	**yes**
ΔSO_2 across CHX	no	yes	no	no	no	**yes**
SO_3 after CRHX	no	no	yes	no	no	**yes**
SO_3 after IRHX	no	no	yes	no	yes	**yes**
Likelihood (based on condition)	low (mostly new)	high	high	certain	unknown (not inspected)	**high**

Fig 5: **Chemetics radial flow cold heat exchanger ready for shipment**

PHOTO: CHEMETICS

Example of debottlenecking

A metallurgical plant was running the preheater over 80% of the time in order to maintain acceptable bed inlet temperatures, which was a major extra cost for the site. The inlet gases for the plant had changed over time such that the original flow sheet data and design basis was essentially meaningless to the real operation of the plant.

When the cold gas exchanger reached the end of its life, a debottlenecking study was conducted to determine a new design basis for the cold exchanger.

The study identified that the required autothermal scenario had changed to require an increased capacity on the cold exchanger. In addition the study identified that the observed temperature data represented significantly less heat being retained than the theoretical models calculated should be available. The site confirmed major insulation degradation issues, but had not prioritised their repairs. The study result provided the justification to conduct an insulation improvement campaign.

The improvements to the insulation combined with the new cold gas exchanger (Fig. 5) have resulted in an over 90% reduction in preheater usage.

The lesson to draw from this example is how a good modelling process can help quantify the losses due to chronic issues that may otherwise go uncorrected.

NORAM Engineering acid plant simulation

NORAM Engineering specialises in the design and debottlenecking of sulphuric acid plants and equipment and uses sulphuric acid plant simulation to investigate, diagnose and optimise the sulphuric acid plant.

Inputs

A sulphuric acid plant simulation is only as good as the information that is put into it. The more information the user has on the plant operations and equipment, the more detailed and accurate the simulation will be. However caution must be taken with any plant operating data as some process readings can be unreliable due to instrumentation errors. With these cases, a more experienced simulation engineer is a valuable asset in determining reasonable operating input data. The following is a list of necessary acid plant information to get a simulation started:

- plant process flow diagrams (PFDs) and piping and instrumentation diagrams (PIDs)
- gas-to-gas heat exchanger drawings or rating sheets
- acid cooler drawings or rating sheets
- pressure profile and gas flow rates of the entire plant for a model starting point
- temperature profiles
- acid concentrations and flow rates
- catalyst type and masses
- blower performance curves.

Additional information such as SO_2 concentrations, steam flow rates, etc. are also useful in producing an accurate model.

Physical property prediction

Accuracy of physical properties is very important. This information will dictate how all the components in the system react, and therefore how accurate the simulation will truly be. In simple terms these property predictions or equations of state are equations and coefficients used to predict component and stream physical properties for various conditions. These physical properties include:

- heat capacity
- density
- volume
- viscosity
- conductivity
- enthalpy
- solubility
- vapour pressure
- equation of state parameters
- acid dewpoint.

These are some of the physical properties required for an acid plant simulation. The gas, steam and acid systems generally use different equations of state and must therefore be modelled separately. For the gas side, simulation using some of the equations of state that provide accurate models include: Peng-Robinson, Reidlich-Kwong, RK-Soave. For the sulphuric acid side, complications arise, as sulphuric acid is a non-ideal electrolyte solution a proprietary property set must be established based on reliable operating data. When using a user-created model, gas stream heat capacities and acid stream enthalpy predictions can be based on physical property data and correlations available in the public domain.

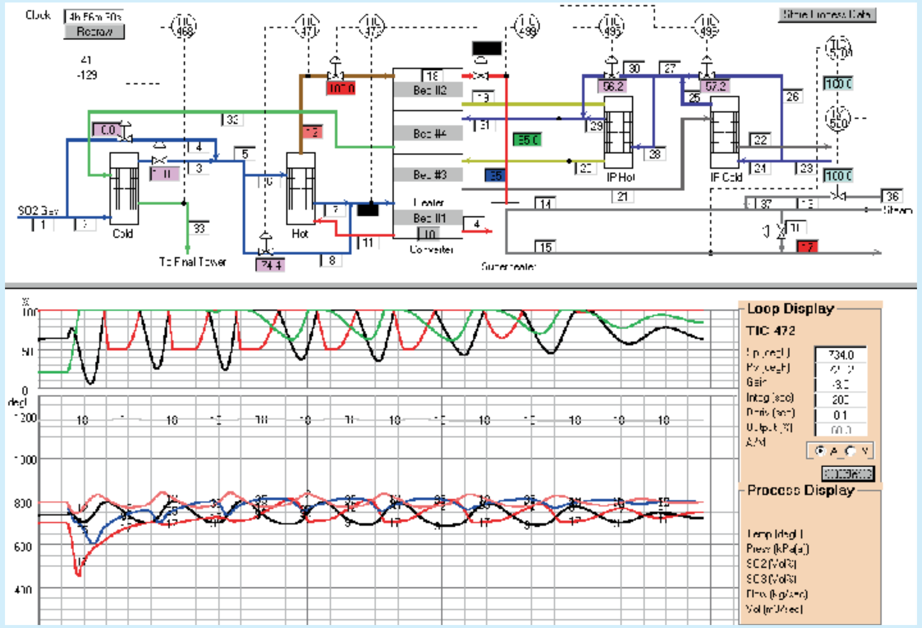
Unit operations

Once all of the plant inputs have been gathered and the physical property predictions have been set the final step is to define the unit operations within the plant. For the sulphur furnace a conversion or Gibbs reactor may be used. Ensure the furnace outlet temperatures are accurate as some property packages are inaccurate for sulphur combustion. A compressor model is used for the blower with the efficiencies input from the manufacturer's blower curve. An even better model for the blower is to curve-fit the blower curve as a function of energy/mass (kJ/kg) versus flow. A splitter module, or a tower block can be used for the acid towers. Here you can assume that a high percentage of water or SO_3 are absorbed. There are two methods of simulating the plant heat exchangers, the more simple of the two, when limited information is available on the exchanger is to thermally balance the exchanger, in this case three temperatures are known and the fourth is calculated. The second method is more difficult, but is essential

SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

Fig 6: **NORAM's custom built dynamic process simulation for a metallurgical acid plant**



Source: NORAM Engineering

to obtain an accurate and working acid plant simulation. This method requires calculation of the existing exchanger's physical design to obtain the shell and tube film coefficients as a function of gas flow. This technique will allow the exchangers to be provided with two temperatures and able to calculate two temperatures, accurately, with changing gas flows. Modelling the exchangers this way also allows the user to obtain more information and insight into controlling the exchanger bypasses and optimizing plant temperatures.

To model the converter beds either a simple conversion model can be used or an equilibrium model with a specific approach to equilibrium. However, any rigorous predictions or calculations concerning the catalyst conversion should be obtained from catalyst suppliers as they have accurate proprietary catalyst models. The final step in polishing the model is comparing the simulation results with actual plant operation.

Outputs and value

One of the most valuable benefits of the simulation is the power to test different operating conditions in the model to see how the plant would react, without actually having to put that possible stress on the existing equipment. By running different scenarios in the model, optimum operating conditions and control strategies can be determined to maximise sulphuric acid production, or minimise pressure drop/energy consumption, or in some cases maximise steam production in the plant. By testing different operating cases for example by changing the inlet SO_2 concentration or increasing gas flow a sensitivity analysis can be performed on a number of outputs including acid production. In this way the most economical methods for acid production capacity increases can be determined. The simulation will also allow the user to identify bottlenecks in the plant and see what equipment is being pushed to its limits. When attempting to increase plant capacity this is a necessity as the simulation will show what capacity increases can be obtained, and what equipment would need to be upgraded to reach those capacities. Along the same lines by comparing an accurate simulation with current operations may reveal areas of poor equipment performance such as plugged exchanger tubes or poor catalyst performance. All of these simulation benefits can provide high value to a sulphuric acid plant operation, however getting to these valuable simulation outputs is not easy. It requires a great deal of work and understanding of acid plants and the physical properties that dictate the components behaviour within that plant. For this reason a qualified consultant may be required for assistance in producing a sulphuric acid plant computer simulation.

Dynamic modelling

In a steady state simulation all the inputs to the plant such as component flows, temperatures, pressures etc. are steady and therefore the outputs are also unchanging or at steady state. The next level of simulation, a dynamic model, greatly increases the complexity of the program. In a dynamic simulation the sulphuric acid plant is modelled to represent fluctuating operating conditions in real time. This is a powerful tool as it can be used to model changing inlet conditions such as fluctuations in SO_2 concentration and flow rates that are commonly seen in metallurgical and spent acid regeneration plants.

Dynamic modelling can be used to set up advanced process controls as the simulation predicts changing process conditions as process parameters are changed. A dynamic model can also be used to simulate plant preheating conditions to determine the optimum gas bypass configurations to minimise plant heat up times.

This is very useful and beneficial to a plant operator however, the level of detail and complexity of the model increases exponentially in the leap from steady state to dynamic.

All the information needed for a steady state simulation is also required for the dynamic model plus:

- thermal mass of all equipment
- residence times
- valve and damper details
- information about process controls.

As with the steady state models there are commercial packages that can be used to create dynamic models. An alternative option is a user-created dynamic simulation which can be created in different operating platforms including Microsoft Visual Basic or Matlab. Fig 6 shows an example of a NORAM custom built dynamic process simulation.

In summary, the simulation of sulphuric acid plants is routinely done by NORAM engineers using a proprietary program developed and improved for over 25 years. The program takes into account the appropriate gas and acid physical properties and incorporates detailed exchanger, blower and converter catalyst characteristics. The results are used to prepare equipment designs and used in plant debottlenecking studies. The simulation output forms an integral part of its process flow diagrams.

Outotec process simulators

Outotec offers both steady state and dynamic process simulations. These tools can be based on commercial software (e.g. Aspen) or fully developed by Outotec.

While steady state simulators are mainly used for process design or production/operation review (e.g. change of feedstock) dynamic simulations are used in a wider range. This includes utilisation as a training simulator, which can help operators to familiarise with the process itself or adjust to a new flow sheet. A dynamic simulation can also serve as an optimisation tool for the DCS prior to start-up of the real plant. This allows e.g. validation of DCS logics, controller loop testing and configuring as far as development of operating procedures.

The basic feature of a dynamic simulation is that changes in parameters and set points are immediately reflected in the response of the simulator. By inclusion of the same DCS user interface from the real plant the dynamic simulation is providing a virtual plant with the same look and feel as the real one. A dynamic simulation is also suitable for start-up and shutdown procedures which is not possible with steady state simulations and will facilitate start-up of the real plant. Further, the simulation of failure scenarios allows matching specific training requirements, e.g. the right behaviour in case of acid cooler leaks or failure of certain equipment.

With these functions a dynamic simulation is used by Outotec for operator "classroom" training prior, during and after plant commissioning.

Advanced process control systems

New or modernised high efficient sulphuric acid plants are often designed to operate within a smaller operational window or with complex cross linkages between different areas of the chemical facility to allow for optimum energy recovery. Even if a plant is designed without these process constraints the remote area location often found for green field projects or existing plants limits the availability of skilled and experienced operational personnel. In addition, higher personnel mobility leads to higher fluctuation and less opportunity for an operator to gain sustainable experience and specialise in sulphuric acid plant operation.

To improve the safety and reliability of the plant operation, Outotec has developed an expert system (PORS = Plant

Fig 7: **PORS system for sulphur burning plants**

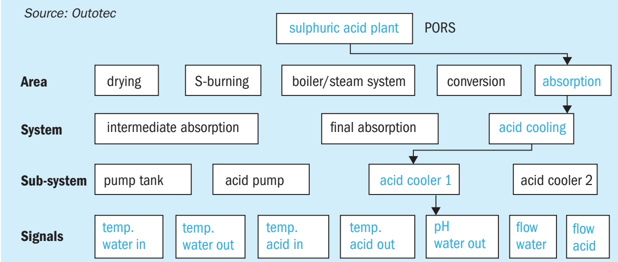
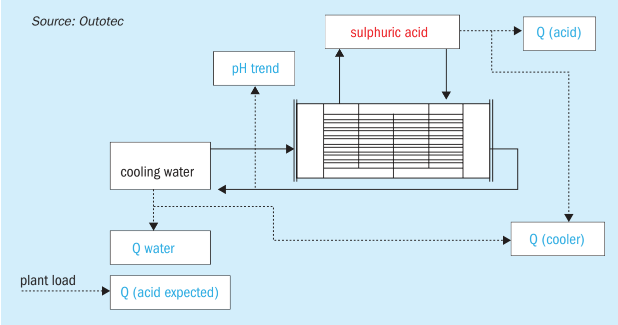


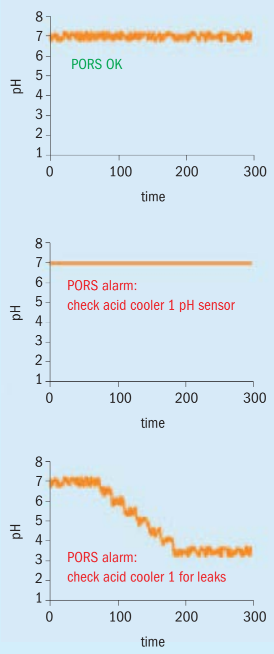
Fig 8: **PORS – sub-system acid cooler**



SULPHUR
ISSUE 359
JULY-AUGUST 2015
BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

Fig 9: **PORS – sub-system acid cooler, trend monitoring**



Source: Outotec

Operation, Reliability and Safety System), which can guide and support operators in their work and create awareness for potential operational issues.

Usually large amounts of data are collected and made available through existing instrumentation in the plant, but not used in depth to stay clear of failures or unplanned shut downs. Through digitalisation (adding value to the digital content by combining it with Outotec's process know-how) PORS provides additional information about the process, plant and individual equipment.

The system is designed to be a stand-alone solution. It is based on Outotec's proprietary ACT platform which receives in one-way communication all required process parameters and measurements from the DCS commonly through the OPC interface. The results are displayed through its own user interface to the operator. It can be an integral part of a new installation or retrofitted at existing plants, covering the entire process chain with all sub-areas with several modules, as shown in Fig. 7.

The following section describes the way the PORS system is working for a sub-system of the absorption area, the acid cooler module.

Module: acid cooler monitoring

Monitoring of the acid coolers is crucial for successful operation of sulphuric acid plants as failures in acid coolers, most probably in the form of leakages, will happen during the lifetime of the plant. If the failure is detected in time and the right measures are taken the damage can be mitigated and operation can continue after a relatively short shutdown for tube plugging or other maintenance and repair activities. However, if such failure is not detected in time, the range of damaged equipment can stretch from just a single cooler to several items of equipment. In the worst case this leads to repair measures for the plant, which will not allow operation for an extended time.

Fig. 8 shows a basic flow sheet of an acid cooler, with acid being cooled on the shell side in a counter current flow to cooling water on the tube side. The bases of this module are heat and mass balance calculations, performed for both sides of the heat exchanger. In conjunction with process information obtained from the DCS, for example:

- cooling water flow rate
- cooling water inlet temperature
- cooling water outlet temperature
- acid flow rate
- acid inlet temperature
- acid outlet temperature

and by using Outotec's physical properties database which is included in the PORS system, transferred heat on the water as well as on the acid side will be computed. Both heat quantities should be identical, as long as heat transfer is not disturbed by e.g. acid leaking into the water side.

Both results are compared by a special algorithm taking into account inaccuracies in measurements and other plant specific factors. During normal operation with a healthy cooler the comparison algorithm delivers equal values for both heat quantities and no alarm will be displayed. In the case of a difference in the heat quantities, an alarm will be displayed with additional information on the affected equipment including identification of possible reasons for the alarm.

Other possibilities to detect a cooler leakage include the strict monitoring of the pH or conductivity of the water side, as these values will rapidly change if acid is allowed to mix with the water side. This very straightforward way of detection is supported by the PORS system through a sophisticated trend monitoring system.

Fig. 9 shows an example of the operating mode of this monitoring system. The cooling water pH value trend is observed with focus on quick changes as well as for constant values, as both can represent a problem in the plant. If no or only very minor changes in the pH are measured, this can often be caused by a faulty pH sensor. Without proper pH measurement, the risk of not detecting an acid leak is extremely high; therefore a warning will be displayed with the advice to check the affected pH sensor. As anticipated, a steep drop or other anomalies will cause an alarm of the PORS system as well, as this is a potential sign of an acid cooler leak with acid being allowed to penetrate into the cooling water side.

Besides comparing heat quantities and monitoring trends for detection of possible leaks, further monitoring of the acid cooler performance is incorporated in this module. The performance of a heat exchanger can deteriorate over time as a result of fouling, i.e. accumulation of deposits on heat transfer surfaces. Fouling of the cooling water side, represents additional resistance to heat transfer and causes the rate of heat transfer to decrease. The heat quantity transferred can be calculated as a function of log mean temperature difference, the heat exchanger area and the resulting heat transfer coefficient.

Based on this calculation, the actual heat transfer coefficient will be calculated and compared to historical values, which are stored by the system for different plant loads. If the exchanger efficiency drops below a predefined value, a warning will be displayed to enable planning of cooler maintenance during the next shut down.

The PORS expert system is not limited to monitor acid coolers, but considers the entire plant with a range of functions focussing on safety relevant plant areas, such as acid dilution, boiler with associated high pressure steam equipment as well as low pressure steam generation (HEROS). Environmental and maintenance related areas are also covered for the whole plant.

CONTENTS
What's in issue 359
COVER FEATURE 1
Phosphate demand for acid
COVER FEATURE 2
America's refining renaissance
COVER FEATURE 3
Acid process simulation
COVER FEATURE 4
Reaction furnace linings

SULPHUR
ISSUE 359
JULY-AUGUST 2015
BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

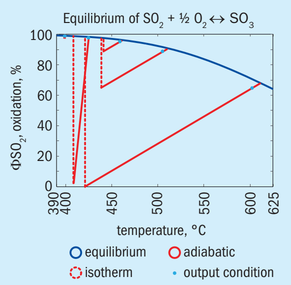
Mosaic/MECS operator training simulator

Mosaic is currently in the process of installing and commissioning two new heat recovery systems (HRS™) on its sulphuric acid plants at its New Wales facility. Recognising the importance of proper training for major process changes, Mosaic partnered with DuPont and MECS, Inc. (MECS) to build a fully customised operator training simulator (OTS) to provide a "best-in-class" training experience for their operations team. The OTS development focused on satisfying four key criteria: realistic "look and feel" (fidelity), relevant emergency scenarios (including start-up/shutdown), testing/validating capabilities, and cross training potential. Mosaic, DuPont, and MECS subject matter experts collaborated openly to develop, test, and validate the model. This ensured the model behaved in a way that agreed well with the actual process, and allowed the Mosaic team to become familiar with the OTS software well in advance of the final product delivery. The virtual plant model was developed using DuPont™ TMODS (DuPont's proprietary dynamic simulation software), and leveraged technical information such as P&IDs, PFDs, and DCS graphics screens. Time to develop and refine the model was approximately 8 months.

Initial training was delivered in October 2013, and involved lead operators who would eventually become the OTS trainers. All embedded emergency scenarios were covered, with many deployed in "hidden" mode (the student was unaware of which scenario was in effect). This proved to be a strong method of testing an operator's ability to recognise, identify, and respond to a given scenario. Students were impressed at how well the OTS maintained their interest, behaved in a realistic manner, and provided an opportunity to experience situations they may have only read about. One operator commented, "We got over ten years' experience in eight hours."

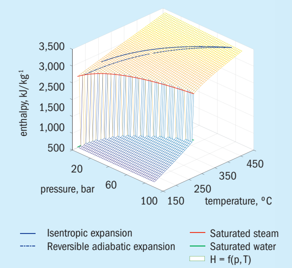
The final result was a training tool that not only is technically superior to conventional training, but one that is well-positioned to deliver results, both immediately and in the long run, due to the strong partnership between Mosaic, DuPont, and MECS. The team is also collaborating on another customised OTS for the non-HRS plants at the New Wales facility.

Fig 10: Conversion of SO_2 to SO_3



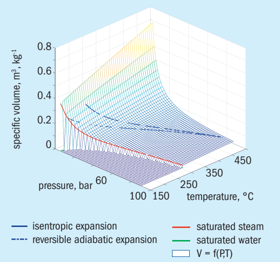
Source: Hugo Petersen

Fig 11: Steam turbine h-p-T curve for real and ideal process



Source: Hugo Petersen

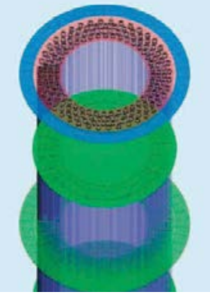
Fig 12: Steam turbine v-p-T curve for real and ideal process



Source: Hugo Petersen

Fig 13: Tube sheet and tube arrangement

Source: Hugo Petersen



Hugo Petersen simulation system

The interlinking of dynamic process simulation with equipment not only increases the reliability of design, but also the possibility to optimise plant concepts for cost efficiency.

The following account describes part of Hugo Petersen's simulation system which has been developed to decrease the development life cycle, increase the quality of engineering and reduce susceptibility to human error.

Hugo Petersen's simulation system comprises:

- mass and energy balance module (MEBM)
- equipment design module (EDM)
- process control system (PCS)

Mass and energy balance

Mass and energy balances are the basis of process design. The law of conservation is valid for each unit which means: (Input + Generation) – (Output + Consumption) = Accumulation.

Hugo Petersen engineers have developed reusable modules which describe the mass and energy balance for specific process units. These could be a heat exchanger, a reactor, an absorption column, a steam turbine or some other equipment.

The complete process plant can be realised in a sequential-modular-program, which consists of reusable basic modules and solves stepwise module-by-module. The processes which involve some feedback are initialised with plausible values and solved iteratively by the recycling of information.

To ensure a better overview the modules can be arranged in subsystems, like conversion unit, absorption unit or steam unit. The cascading of subsystems is also possible.

Model-based design with Matlab® and Simulink® is used to realise this approach. Key aspects of the process are visualised in simulation (Figs 10, 11 and 12). The process optimisation time is reduced by a factor of 5 to 10 in comparison to a spreadsheet based approach.

The simulation program is able to export the simulation results to a Microsoft® Excel® spreadsheet for all downstream users. The tool used for data export is Spreadsheet Link™ EX. The report can be customised to customer needs, suppliers and other users.

Equipment design

The next step in the development life cycle is equipment design. This could occur in the same simulation environment as the mass and energy balance.

For this case a mass and energy balance module (MEBM) will be replaced by an object for equipment design module (EDM). An EDM includes more details than a MEBM which means more time intensive computing.

Fig. 13 shows calculation results of the in house gas-gas-heat exchanger module by Hugo Petersen represented in the form of a tube sheet. This module not only includes all process parameters but also all construction parameters of a radial heat exchanger with multi radial arrangement of tubes. The module parameters could be changed during simulation runtime, which is a big advantage for heat exchanger design. Now the simulation describes not only mass and energy balance of process plant but also the dynamic performance of the process. It is also very easy to compare different heat exchangers in its operating point to choose the best one, and further compare different operating points for selected heat exchanger to ensure the correct choice.

Further, simulation of a group of heat exchangers in series, parallel or a combination network is much easier. It is also realised in the complete process environment and includes all process feedbacks and construction details.

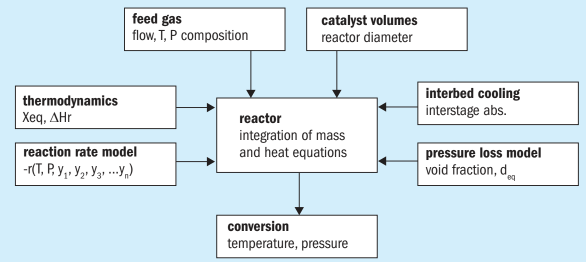
Process control system

Stable operation of a plant could be improved by simulation of process control system. The supplementary activity which engineers have to do is to combine the control system model with plant model and test the functionality of control algorithms.

Model-based design is used for smooth information exchange. Control engineers and process engineers collaborate together on the same simulation model which decreases potential for human error.

They study dynamic and steady state behaviour of a plant in normal and in critical situations, simulate start-up and shutdown procedures and carryout risk assessment for the plant.

Fig 14: Haldor Topsoe reactor software for converter simulations



Source: Haldor Topsoe

Haldor Topsoe numerical simulation and modelling

Numerical simulation and modelling are used extensively at Haldor Topsoe for analysis, design, development, and optimisation of catalytic reactors and processes. The use of well-proven mechanistic chemical engineering models secures that basic principles such as mass and heat balances, chemical equilibria and driving forces for transport processes are in place. However, the ability of the models to correctly predict system behaviour and performance requires accurate models for important phenomena including catalytic reaction rate, mass and heat transfer coefficients, pressure drop, dispersion phenomena etc. Haldor Topsoe continuously improves the accuracy of its model predictions by incorporating experience from lab, pilot and industrial data analysis into the sub-models of these rate-limiting processes. Both steady-state and dynamic models are used depending on the operating conditions and goal of the simulation.

Simulation of SO_2 converters

The behaviour of the SO_2 converter will affect most parameters within the sulphuric acid plant, everything from the SO_2 emission to temperatures and production figures. Consequently being able to accurately simulate the SO_2 converter is crucial not only to predict the effect of a change on the SO_2 conversion but also for most other parameters within the plant. This also means that an accurate model for the SO_2 converter is a crucial piece of the puzzle for simulating the sulphuric acid plant as a whole.

Requirements for a good model

To achieve an accurate model for an SO_2 converter, several sub-models are required. The converter model must include thermodynamic models in order to estimate the equilibrium for different conditions, kinetic models to estimate the reaction rate at different conditions and catalyst and pressure loss models to estimate the pressure drop over the catalyst beds. The SO_2 converter model combines the different sub-models with input on the plant configuration and feed gas to simulate the resulting temperatures, pressures and SO_2 conversion, see Fig. 14 for a schematic drawing of the input and outputs.

Using the model to find optimum conditions for the plant

Haldor Topsoe combines an accurate SO_2 converter model with good knowledge of the different catalyst types to find the optimum set of conditions and catalyst for the specific set of constraints and demands at the individual plant. For instance, one can see that with standard potassium-promoted catalyst (VK38) reducing the inlet temperature in a first bed from 420°C to 390°C will increase the catalyst volume requirement dramatically and will thus not be feasible for most plants, see Fig. 15. The simulations, however, also present a solution to this, using cesium-promoted catalyst (VK59) in the top of the bed, as this will limit the increase in required catalyst volume (Fig. 16).

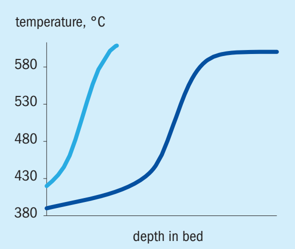
Haldor Topsoe's converter simulation can also illustrate how important it is to operate at the optimum inlet temperatures when operating less active catalyst. At lower temperatures, the bulk of the

SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

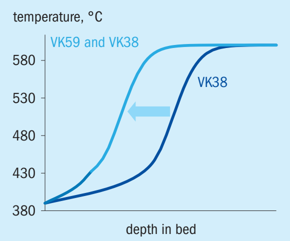
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

Fig 15: **Effect of lower bed inlet temperature on catalyst requirement**



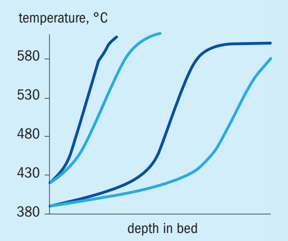
Source: Haldor Topsoe

Fig 16: **How a top layer of cesium-promoted catalyst will reduce the required catalyst volume**



Source: Haldor Topsoe

Fig 17: **Importance of using high enough inlet temperature when catalyst activity is low**



Source: Haldor Topsoe

catalyst will be used to achieve the initial temperature rise. This means that if the catalyst has lower activity, there might be insufficient catalyst left for the main conversion and the total bed conversion will drop dramatically. If the inlet temperature is higher, the bulk of the catalyst will contribute significantly to conversion and loss of activity, although still important, will have a smaller effect (Fig. 17). By using the SO_2 converter model, Haldor Topsoe can thus continuously predict and optimise the bed temperatures in the plant as the catalyst deactivates.

Pressure drop development and gas flow distribution

Apart from being used in the full scale SO_2 converter model, the pressure loss models can also be employed together with separate models for dust deposition to predict the pressure drop development as dust deposits in the catalyst beds. Based on these simulations, it is possible to predict the effect of using different catalyst shapes and sizes on pressure drop development (Fig. 18).

Haldor Topsoe can also utilise the pressure loss model together with computational fluid dynamics (CFD) simulations to predict gas flow distribution into a catalyst bed. This evaluation is relevant at low bed heights and high inlet gas velocities, where performance can be affected. As an example, one such simulation showed that for a low pressure drop scenario, the increase of SO_2 emission was around 10% compared to the normal pressure drop scenario. A CFD simulation can also be used on it its own to model the mixing of gas streams to ensure even gas composition and temperature.

Process layout and equipment sizing

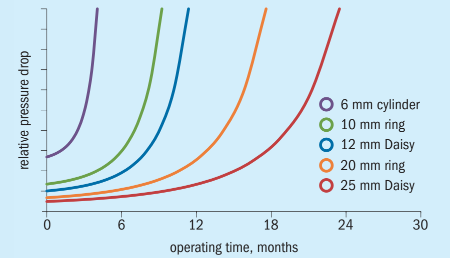
Sulphuric acid plants are typically designed by setting up steady-state heat and mass balances for the plant, and equipment is sized from steady-state models of the individual unit operations. A proprietary process simulation tool called GHEMB has been developed and perfected in Haldor Topsoe over the last decades. The GHEMB program (short for general heat and mass balance) is a conventional sequential modular simulator with unit operation modules and thermodynamic packages for simulation and design of catalytic processes (Fig. 19). GHEMB contains specific state-of-the-art reactor modules along with standard unit operations such as heat exchangers, addition and splitting of streams, flash operations, multistage separation processes, boilers, deaerators and many more. GHEMB has access to pure component data and an extensive collection of thermodynamic models for prediction of non-ideal gas and liquid mixture properties and phase equilibria. Good and experimentally validated thermodynamic models are of major importance in the case of the non-ideal SO_3–H_2O–H_2SO_4 system for correct prediction of e.g. dew point, acid strength, vapour pressure and heat evolution.

Compared to commercially available process simulators, the continuous development and expansion of the Haldor Topsoe GHEMB simulator has provided a very strong technical foundation for design of catalytic processes. The in-house expertise secures full control of the calculation methods and enables expansion when new or special catalysts, unit operations and technologies are introduced. More important, all the experimental data and experience from lab, pilot and industrial scale are built into the relevant thermodynamic models or rate-limiting mechanisms of the calculations to provide the best possible quantitative prediction of the system. This is key to achieve good equipment design, high process reliability and efficiency. One example is the proprietary Haldor Topsoe WSA condenser, in which sulphuric acid and water vapours are condensed to concentrated sulphuric acid in vertical glass tubes. For this condenser, rigorous mathematical models of mass transfer, heat transfer and chemical reaction combined with thermodynamics validated experimentally in our lab form the basis of equipment design and process performance. The excellent ability of the models to predict e.g. temperatures and acid strength as functions of condenser size and geometry is due to the specific transport coefficient expressions for e.g. mass and heat transfer, which have been derived from pilot plant experiments and industrial experience.

Modelling of transient operation

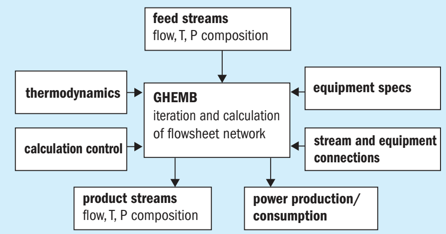
Steady-state models are not always adequate for design and prediction of plant performance during start-ups, shutdowns and changes in feed flow rate or composition. Sulphuric acid catalysts have for example a significant absorption capacity for sulphur oxides, which during transient operation will affect the reactor temperatures and the SO_2 conversion. Haldor Topsoe has therefore developed dynamic models for the transient operation of an SO_2 converter and the proprietary WSA condenser and validated them against lab, pilot and industrial data. The dynamic

Fig 18: **Simulated effect of different catalyst shapes on pressure drop development due to dust deposition**



Source: Haldor Topsoe

Fig 19: **Schematic drawing of the Topsoe GHEMB process simulator**



Source: Haldor Topsoe

models have been implemented in a commercial dynamic process simulator, enabling full closed loop simulation of a complete WSA plant including all the main process steps. Thereby, dynamic simulations can efficiently be used to evaluate operating scenarios and procedures with respect to the risk of sulphuric acid corrosion or equipment failure due to excessive temperatures, equipment sizing, control strategies in the design phase and analysis of plant performance and strategies during start-up, shutdown, and changes in the feed gas composition and flow.

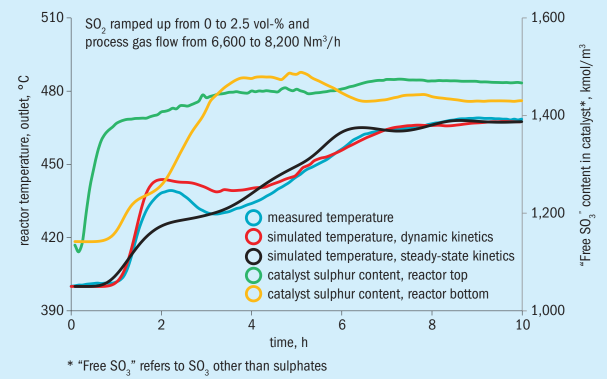
Reliable predictions are essential when using dynamic models to forecast behaviour of industrial plants. The ability of the transient reactor model to predict the behaviour of industrial reactors on the basis of data from a plant's distributed control system during a start-up is exemplified by Fig. 20. Here, a comparison of the measured and simulated exit temperatures from a first bed of an industrial adiabatic multiple bed SO_2 converter are shown. The SO_2 concentration is ramped up from 0 vol-% to 2.5 vol-% over six hours. The importance of including the dynamic behaviour of the sulphur content of the catalyst is illustrated by the fact that the measured temperature peak at two hours can only be modelled when the absorption and desorption of sulphur oxides are taken into account. The temperature peak is caused by the exothermic absorption of sulphur oxides in the catalyst. The simulated sulphur content in the catalyst melt increases in the upper part of the reactor when SO_2 is fed to the reactor and about 1½ hours later in the bottom part of the reactor when the intermediate region has been sulphatised. The sulphur content in the catalyst is temperature dependent i.e. at steady state, more SO_3 is bound in the top of the catalyst bed because the lower catalyst temperature allows a higher concentration of SO_3 in the catalyst melt.

Due to its ability to predict the sulphur content of the catalyst, the transient reactor model is also applicable for special process equipment such as reverse flow SO_2 oxidation reactors, which are used in some industrial sulphuric acid plants. With emission limits becoming tighter, more focus is also put on emissions during transient operation, and thus dynamic simulation can be used to optimise the design and control of the plant under unsteady operation, such that the emissions can be in compliance with the emissions allowances without requiring installing additional tail gas treatment. ■

References

1. Lee G, Cooper G, Mahecha-Botero A and Nikolaisen K (NORAM Engineering): "Steady state and dynamic simulation of sulphuric acid plants", AIChE Clearwater Conference (June 2014).
2. Pubillones M and Sheffield D (Mosaic), Dericotte D, Zotti M and Horne J (DuPont and MECS): "Case study on Mosaic's use of MECS® sulphuric acid plant with heat recovery system (HRS™) operator training simulator (OTS) for operator training at Mosaic's New Wales facility", AIChE Clearwater Conference (June 2014).
3. Bräuner S, Daum K-H, Schüdde J and Storch H (Outotec): "Process simulation and modelling improve performance by digitalisation".
4. Yazdi AF, Thorbole T and Schulze A (Hugo Petersen): "Simulation of sulphuric acid plant" (June 2015).

Fig 20: **Simulation of start-up of a first bed in an industrial SO_2 converter**



* "Free SO_3" refers to SO_3 other than sulphates

Source: Haldor Topsoe

SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

Limiting factors on reaction furnace linings

SRU operators are experiencing increasing demands for improved reliability due to significant changes in emission regulations and penalties, more severe operating conditions, high cost of repairs and the consequential impact a reaction furnace failure can have on other operating units in refineries. Management is finally paying more attention to these issues; however, before the SRU problems can be properly addressed they first must be fully understood.

Many companies have suffered from refractory issues in reaction furnaces. The same issues regarding premature refractory failure are repeated time and again all over the world. The impact to the plant may include the following:

- premature and/or frequent maintenance repairs or lining replacements required between or during planned outages
- longer downtimes due to extra refractory work requirements
- extended start-up times or even failures due to dryout issues
- shell breeches and the safety and environmental issues associated with this extreme failure
- loss of production capability of related units during unexpected or extended reaction furnace outages.

In other words, less run time, less reliability, higher costs and, worse, less profit. Many operating companies today are only too aware of these issues but are unaware of how to correct them.

There are reasons the same failures occur repeatedly and there are ways to significantly improve these situations. Refractories are often considered a commodity that anyone can design, supply and/or install; making refractories almost an afterthought.

In actuality, SRU linings are complex structures that require careful consideration. These units operate under some of the most severe service conditions in a refinery and the consequences of getting it wrong up front then brings in the added costs and frustrations of dealing with sub-standard design, materials of construction, or workmanship for the entire working life of the SRU or until lining improvements are implemented.

Fig 1: **Typical extreme refractory failures**

Under certain conditions, all reaction furnaces are capable of melting any refractory made today. Refractory specialist Thorpe Speciality Services Corporation bases its lining recommendations on an optimised lining approach. Linings must be designed for the real world operating conditions for reaction furnace service which encompasses start-ups and shut-downs, natural gas firing, O_2 enrichment, hydrocarbon slugs, operational errors, thermal excursions or complete unit overheating from poor burner mixing or damaged burner components. It is not a matter of "if" but "when" a thermal event stresses the lining. Every unit should be evaluated for its size, geometry, thermal profiles, etc. in an effort to optimise the lining to better endure these events.

Project considerations

Many of the problems with today's refractory lining systems actually begin in the project phase. With refractory, there are normally numerous contributory issues combining to eventually result in a failure or need for repair, sooner than is necessary.

Project structure

How a project is structured can have a significant impact on how decisions are made and therefore on the final end product and its performance. The refractory specifications are normally established by the licensor early in a project and are used to determine vessel and duct sizing, etc. Unfortunately, due to the extreme variations in size, geometry, and changing operating requirements for these units, such specifications may be inadequate. Getting refractory knowledgeable people involved early in the project is dependent on how the project is structured and is essential in mitigating problems that can further develop. If the project has divided the refractory components (design/supply/installation) between a licensor, mechanical erector(s), various equipment OEMs, vessel fabricators and local installers, the communication path and responsibility trails are often too long to effectively assure optimal lining designs and installations. Too often inappropriate companies are involved in the refractory process.

Problems are typically the result of the project team having limited knowledge of the complexity and importance of the refractory system as they focus primarily on a low cost and schedule. To assure the success and reliability of the lining, Thorpe believes the refractory design, supply and installation should not be fragmented, and the refractory company should be involved at the very beginning of the design phase.

Lack of refractory knowledge

Several factors contribute to the lack of an industry-wide, thorough understanding of the diverse and complex issues associated with sulphur reaction furnaces. It is important to recognise that owners, manufacturers, designers and installers have become more dependent upon improved monolithic (ie. castables, plastics, etc.) refractory lining systems in recent decades. The significant improvement over the last 25 years in monolithic product formulation, installation knowledge and equipment, has contributed to the replacement of many brick applications with monolithic linings throughout the industrial markets. There has been a corresponding loss of understanding of brick systems. This is particularly true in refineries where either monolithic materials or ceramic fibre based products are used in most other units outside the SRU. Since it is generally accepted that brick linings are the best choice for thermal reactors there has arisen a "disconnect", a preferred product form that has experienced a declining user base.

With the loss of brick design and installation skills, it is easy to understand why owners/EPC/licensor/OEMs, for which refractories are only a small component to the entire SRU process, are not aware of the details involved in this critical, specialised part of the unit. Most owners/EPCs/licensors/OEMs do not normally have a true refractory design engineer, familiar with SRU linings, on staff. The lack of proper refractory design knowledge combined with having to compete for projects on a price basis, results in the limited need to consider improved methods. Most refractory specifications focus primarily on the individual materials to be used without sufficient regard for how those materials must be integrated for the specific application to meet performance expectations. It is the systems' performance that is critical, not the individual materials.

Lack of customer feedback

In an attempt to defend the EPC/licensor/OEMs from some of these comments, it should be noted that many are very good, quality conscious companies and individuals operating on the firm belief they are providing the best linings possible. Part of the problem between belief and reality is that most times customers do not give proper feedback to the original project participants. Thorpe has seen numerous occasions where failures occurred well within the warranty period but the plant proceeded to perform repairs without contacting the original responsible parties. This makes for a more economical repair compared to getting the original parties notified, mobilised to inspect, time to evaluate the failure, etc. all before beginning the actual repairs. This results in a continuation of poor designs or processes from project to project by the original suppliers who are unaware they had a problem.

What needs to change?

Higher priority on the refractory process

To optimise lining life and performance it is strongly suggested to think about refractories sooner in the project rather than later. If reliability is important, the refractory linings should be considered as an integrated system requiring careful consideration through all phases of the entire project instead of passing this important function down the project food chain. Ideally the lining design, material supply and installation would be a single source supply and responsibility in order to prevent miscommunications and misunderstandings. As these functions are normally divided and each step bid out independently, it may require restructuring the project and owner education to allow for a single-source evaluation and award. Overall, since these linings should be brick construction, the evaluation process should focus on companies that emphasise and are active in industries and units involving complicated brick construction, but also including active participation in brick design and construction in SRU linings. The demanding nature of these units makes it imperative that awards be based on the knowledge and ability of the refractory company rather than the low dollar proposal or to a "good ol' boy" network system.

Better understanding of reality

The burner systems in reaction furnaces, whether for low temperature gas plant operations or for refinery related units with or without O_2 enrichment, can (and do) melt any refractory made today. Designing for only the theoretical operating range should not be acceptable. Optimising the system to better survive those upset conditions is the only way to get the best reliability and longest refractory life with the lowest life cycle cost.

Demand an engineered system

One of the biggest misconceptions in the marketplace is that if it is on a drawing, then the lining is engineered. If so, one can definitely argue the quality and depth of the engineering on some of the drawings utilized. Many of these should be labelled "bill of material" or "refractory placement" drawings which would be more accurate. Material science does apply to refractories just as it does to the steel components. There are physical material properties that when understood against the operational demands of these systems, can be applied to thermally and mechanically balance the system to optimise the lining performance. An engineered system will address and control many aspects of the system which goes through many changes on its way to a potential of say 1,650°C. Much of the true engineering of a self-supported brick system is performed behind the scene and is not obvious to the untrained person looking at the drawing. To illustrate the point, a few of the concerns that need to be addressed to optimise a lining system are discussed.

Thermal balance of the entire system

While the refractory lining system is designed to protect the steel shell from high temperature corrosion and metal failure, it is the exterior weather shroud (often inappropriately called a rain shield or shroud) that protects the shell from low temperature corrosion. Both systems, in unison, are designed to protect the vessel shell from high and low temperature

CONTENTS
What's in issue 359
COVER FEATURE 1
Phosphate demand for acid
COVER FEATURE 2
America's refining renaissance
COVER FEATURE 3
Acid process simulation
COVER FEATURE 4
Reaction furnace linings

SULPHUR
ISSUE 359
JULY-AUGUST 2015
BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

Fig 2: **Full thermal protection shroud**

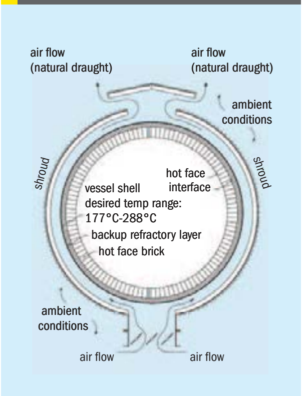
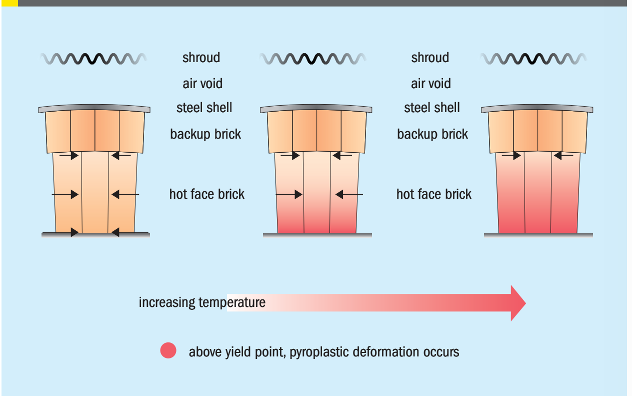


Fig 3: **Design issue for hot face brick**



corrosion. To those unaware, it seems natural to separate these two items (the refractory and the external shroud) in the initial construction. Often the two systems are designed by completely different companies (assuming an external shroud was even used). However, the external shroud can have a significant effect not only on the vessel shell temperature, but also on the thermal profile through the refractory lining. This thermal profile can have a significant effect on the ability of the refractory lining components to perform under the extreme stresses and temperatures to which they are exposed. These systems should be designed by the same engineer familiar with the dynamics of both systems and the interaction between these systems.

Proper lining thickness

Determining the ideal lining thickness to optimise performance is a complicated process. The importance of this step is often overlooked. Often, generalised rules of thumb or a similar sized unit is used from a past job that appears to have been successful and as long as a simple thermal calculation seems to show a proper shell temperature; this process stops. However, lining thickness is a function of many factors, some of which are; vessel diameter, thermal profile through the system, mortar quality and design, brick shape, physical properties of lining materials, etc. Determining proper lining thickness is usually an iterative process as the design engineer balances the effects of the complete thermal system to stresses in the refractory lining and how to control or moderate those effects within the properties of the materials utilised.

Hot load strengths

For unsupported (unanchored) brick linings, consideration of the hot load strength of the refractory products is critical and is the beginning point for designing these systems. Generally the unrestrained thermal expansion of the lining will be approximately three times as much as the vessel shell. When heat is applied, the lining goes into severe compression. If the thermal profile through the lining is excessive, it will plastically deform under the stress resulting in what is referred to as "hot load deformation". So essentially, hot load deformation occurs when the temperature of the material exceeds the point at which it will be able to resist the compressive stress to which it is subjected. While there can be other contributory issues, the evidence of hot load deformation is seen when units are inspected after a service campaign in the form of open joints overhead, sagging brick, or complete collapse of rings overhead.

Minimising deformation is a critical component of an overall design. Most specifications do not even address these issues or are misdirected by attempting to make references to specific manufacturers' brand names (or equals) or other physical properties that may have no bearing on the design. One example is specifications for alumina content. The error is assuming that higher alumina content automatically translates into higher hot load strengths. This is sometimes a result of looking at the melting temperature of the individual brick product and not understanding that materials weaken before they melt; i.e., these properties are not directly related to each other. A severe, high temperature, long duration testing regimen clearly shows there are significant differences in these supposedly competitive high alumina bricks and also show, for example, that the highest alumina (99%) bricks are not good for typical usage in reaction furnaces. Field experience has also proven this to be true. Direct testing for the needed properties should be required.

Brick keying action

Due to lining movement as a result of thermal expansion/contraction, it is essential that the individual brick shapes have the necessary "keying action" to keep them from slipping out of position. One must remember that gravity is pulling down on the overhead brick 24/7. If there is not enough keying action or taper on a brick, it will slip out. Should this happen, the entire ring will become unkeyed and the likely result is more brick falling down creating a larger hot spot and typically a shell breech.

Utilising standard brick ring tables will provide a design engineer many options to simply turn a circle, but will not tell them which combinations are best for the application. Choosing the correct brick shapes with the proper amount of keying action requires an experienced designer familiar with the brick shape options, their benefits and disadvantages combined with the need of the specific application.

Fig 4: **Classic examples of high temperature deformation**

Controlling brick movement

Unrestrained, brick will continue to move as the unit is thermally cycled with the end result being large open joints, hot spots or collapse or failure of the immediate area of the lining. On the other hand, an excessive amount of restraint will overstress the lining and the vessel shell resulting in possible damage to both. Controlling brick movement requires knowledge and experience to utilise the correct balance between restraining brick movement by use of the selective brick shapes in the correct places while relieving the expected stresses with properly placed and designed expansion relief.

Summary

Improved reliability and performance is possible for these units, even for full time oxygen enriched, high temperature operations. First one must realise the importance of the refractory linings and then raise and maintain the visibility (the coordination) of all aspects involving refractory. Once this is accomplished, detailed attention should be given at every step of the project, from start to finish, using the following three keys to reliability:

Engineered lining design

Qualifying a designer cannot be based on how old they are or how many drawings they have generated. Careful consideration must be given to:

- familiar with real world operating conditions of the unit
- full understanding of the thermomechanical issues of the lining
- skilled in complicated brick construction techniques
- able to model the complete external/internal thermal systems
- familiar with information critical to the installation crews
- clear understanding of the critical material properties needed for the specific lining design.

Proper material selection

Not only is proper material selection critical, but also long duration high temperature testing to confirm that specific material properties will meet design stress expectations, particularly for the hot face brick materials. Typical ambient QA/QC testing of the other lining materials is normally sufficient.

Experienced installation crews

Not all refractory installers are knowledgeable and skilled at complicated brick construction for SRU reaction furnaces. Careful attention should be paid to the skill level of the installers, the use of appropriate equipment and installation procedures to assure that only experienced crews are involved in the installation of these linings.

A case history

The Suncor Edmonton Refinery situated in the Strathcona County near Edmonton, Alberta, Canada, processes feedstock from the oil sands of northern Alberta. The refinery processes 142,000 bbl/d to produce products including gasoline, diesel and jet fuel.

The sulphur recovery unit (SRU), commissioned in 2008, consists of two identical two-stage air-based Claus trains (305 t/d) joined to a common selective oxidation SUPERCLAUS® stage (406 t/d).

The SRUs have been operated on average at 152 to 203 t/d inlet sulphur feed equivalent, with the reaction furnace normal

Fig 5: **Brick slippage due to insufficient keying action**

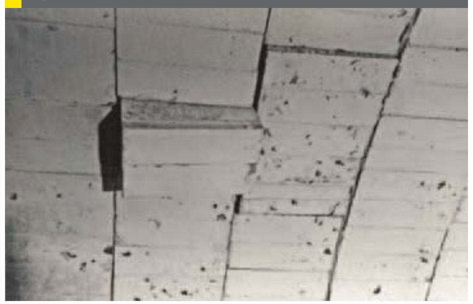
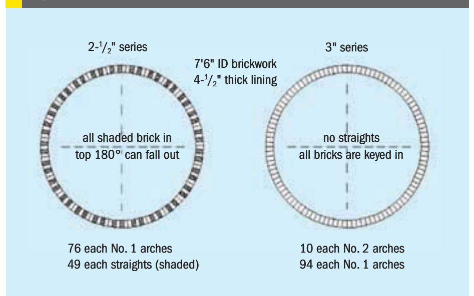


Fig 6: **Sample ring combinations from standard guides**



SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

Fig 7: **Controlling brick movement**

Drawing on left illustrates improperly oriented brick on the dished head and the result of unrestrained brick movement on the bullnose ring (center picture). Drawing on right illustrates properly oriented head brick resulting in an anchored bullnose ring with expansion relief designed into the outlet throat.

operating temperature in the 1,288°C to 1,343°C range.

The original installation of the reaction furnace was lined with a hot face castable lining and a backup insulating castable lining. The anchor system for the SRU reaction furnace refractory includes metal clips and tiles. The clips were constructed of cast alloy (25 Cr -12 Ni) ASTM A447.

After a little more than two and a half years of operation the SRU units were shut down for a routine inspection during the 2011 spring turnaround. While not expecting to perform any refractory repairs, it was discovered both units had suffered severe degradation of the refractory linings and required extensive repairs before the plant could safely restart. Due to the extensive damage found in the choke ring, the top half section of the refractory in the furnace was removed, finding that the anchor clips were corroded due to high temperature sulphidation. This type of corrosion was also found on the shell with worse severity in the area around the manway, but without major impact on wall thickness at any location on the shell. The choke ring and top half of both furnaces were replaced in kind to allow time for a complete lining system redesign.

To improve the SRU reliability and safety by reducing the potential for a shell breach due to refractory lining failure, a project was initiated to re-design the reaction furnace linings and to improve the main burner turndown capability and control.

Thorpe was contracted to design, supply material and install the new refractory linings for both SRU 1 and 2 which occurred during the refinery 2013 spring turnaround. The new refractory installation consisted of a two brick layer design to replace the original full castable lining.

Refractory lining failure factors

- **Metallic anchors:** castable refractory linings need to be anchored to the shell for support and are problematic in SRU applications as their integrity is compromised by their exposure to high temperatures and acid gas.
- **Refractory impurities:** bonding systems in high alumina castables inherently have impurities, which at the high temperatures and reducing environment of sulphur plant reaction furnaces can be reduced to components with lower melting points compromising the strength of the lining.
- **Volumetric changes:** mineralogical transformations cause volumetric changes in unfired monolithic refractory forms that are disruptive to refractory integrity.
- **Installation deficiencies:** quality of a castable refractory lining is dependent on field mixing variations and quality of the dry-out process.
- **Rapid rate of temperature change:** operational history showed that rapid temperature changes were present during cold start-ups, hot start-ups, shutdowns and when switching between natural gas and acid gas firing exceeding the recommended maximum rate of 70°C/hour.

Jacobs perspective

Jacobs was awarded the supply of licensor technology and engineering design of the SRUs. They completed the design basis memorandum (DBM) and were then awarded the FEED and detailed engineering phases. Bid packages were developed based upon the Jacobs design which included a two layer brick system and weather shield, but the refinery refractory specifications were added later before bids were solicited. The refinery refractory specifications were general and not specific to SRUs, and were castable based standards; therefore the lining package was changed to castable. Although one bidder did offer a brick option, this was not considered as it was 10% higher in cost. None of the bidders, all considered experts in their field, expressed any concern with the castable design. The detail design of the refractory was performed by the selected vendor. As this was viewed as their specialty, Jacobs and the refinery had little to no input on the final refractory or weathershield details.

Thorpe inspection findings

Thorpe was not involved in the SRU units when originally installed but were called in to perform a refractory inspection in 2011. During and after this inspection, Thorpe found many issues associated with the lining design that is common in industry today. Some of the common errors found across the industry that also appear in the original linings for this project are highlighted below.

Operating design conditions

Believing theoretical operating conditions are appropriate for refractory design is a common error. Reaction furnaces have a long history of operating outside of design conditions for many reasons. Some of these include poor burner mixing (whether due to poor burner design, heat damage or corrosion to burner internals), abnormal feedstream composition, difficulties that arise with natural gas standby, loss of quench steam, startup/shutdown situations and operator error. The lining design should be robust enough to endure most of these upset events. This lining was not optimised for high temperature operation from many perspectives.

Fig 8: **Damaged versus new anchor clips at choke ring**

Anchor clip in service *New anchor clip*

Taking shortcuts

Compromising reliability to reduce cost or accommodate skill level of refractory installers is another common error. Due to the high cost of the refractory materials needed for these units and the labor intensive demands of their installations, these shortcuts knowingly or unknowingly, can lead to significantly lower costs but result in poor reliability. Some of these shortcuts may include decreasing lining thickness, use of inappropriate refractory product forms (monolithic, brick, etc.), use of supposedly "equal" material that is not actually "equal" for this service, differences in installation techniques, etc.

Also contributory to some of these issues is an overall change in the marketplace. For many less severe applications industry wide, older brick systems have been converted to the use of monolithics for their lining systems (plastic, castable, etc.). This is due to significant improvements in the last 25 years to the materials, installation techniques and equipment and attention by inspectors for those applications. The result for any unit requiring complicated brick systems for reliability (such as reaction furnaces) is that many engineers/contractors have lost the skill sets to properly design/install complicated brick linings such as these and revert to utilising what they know; monolithics.

Lining system

Reaction furnaces operate at high temperatures in a severely reducing atmosphere with other gases involved (hydrogen, sulphur, etc.) that can and do affect the refractory material properties and contribute to premature lining failures. While monolithic materials can perform adequately for a length of time in these units at lower temperatures, they suffer many disadvantages when compared to properly designed self-supported brick systems. Thus, regardless of the stated maximum service limit of the individual materials utilised, the lining system was highly compromised in this application. In this case, a properly optimised system would have allowed hundreds of degrees increase in operating temperature range.

External thermal protection system

Many in the industry today still consider this to be a simple "rain shroud", but it is so much more. The shroud effectively "moderates" ambient weather events that would otherwise affect vessel shell temperatures. Maintaining proper thermal control of the vessel shell can prove impossible without a full and properly designed shroud and an understanding of all of the factors involved in this system. This is especially true in colder climates such as Canada. Adding to the problem is the fact that the shroud is normally designed and supplied completely independent of the refractory system. In Suncor's case, corrosion was found on the vessel shell due to a combination of issues with the refractory lining and the external thermal protection system. This higher shell temperature can also affect the performance of the refractory lining by de-rating the effective service limit of the lining system.

Lessons learned

Specialised refractory knowledge and experience

The refractory lining must be treated as an engineered specialty item with a high level of attention.

A qualified refractory design engineer/company specializing in SRU linings should be selected. Normal in-plant refractory contractors typically do not have the skills to be considered for this function.

The refractory design engineer/company should be engaged no later than the FEED stage.

Main burner turndown and operability

Should be capable of achieving startup/shutdown ramp rates of 100°F/hour to avoid adversely affecting the refractory system yet not damaging the burner metallurgy in doing so.

Refractory standards and specifications

Currently there are no industry accepted design specifications for SRU refractory linings. A knowledgeable design engineer/company is critical to long term success.

Applying a general refractory standard not specific to SRUs can lead to a false sense of security and result in inadequate lining installations.

Operational experience feedback

It is important that the owner notify the original parties involved of problems during operation to so they can learn and improve their services to avoid repeating inadequate designs.

Project team comments

Bid packages containing design points (lining thicknesses, materials, etc.) limit the liability of those quoting those linings. Many bidders knowingly, or unknowingly, use these guidelines to provide a proposal matching what was asked for and to limit their own liability. This does not typically lead to notifications of concern by the bidder to the owner as this is also an acceptance of responsibility if corrected. Good or bad, the project team gets the lining they request.

It is crucial that a line of communication be established early in the project with the key stakeholders on the project team (including licensor) to enable review and then acceptance or rejection of any proposed furnace refractory design changes (mechanical, material, thickness, etc.) before proceeding further. ■

Acknowledgement

This article is a condensed version of the Brimstone Sulfur Symposium papers "Understanding today's limiting factors on reaction furnace linings by A. Piper and J. Proctor of Thorpe Specialty Services Corporation, presented in Vienna in May 2013; and "Limiting factors on reaction furnace linings part 2 – A case history", by D. Koscielnuk and M. van Son of Jacobs Comprimo, M. Young and S. Maldonado of Suncor Energy Inc. and A. Piper and J. Proctor of Thorpe Specialty Services Corporation, presented at Vail in September 2014.

CONTENTS

SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

Editor: RICHARD HANDS
richard.hands@bcinsight.com

Technical Editor: LISA CONNOCK
lisa.connock@bcinsight.com

Contributor: MEENA CHAUHAN
meena.chauhan@integer-research.com

Publishing Director: TINA FIRMAN
tina.firman@bcinsight.com

Subscription rates:
GBP 440; USD 880; EUR 680

Subscription claims:
Claims for non receipt of issues must be made within 3 months of the issue publication date.

Subscriptions Manager / enquiries:
MARIETTA BESCHORNER
Tel: +44 (0)20 7793 2569
Fax: +44 (0)20 7793 2577
marietta.beschorner@bcinsight.com
Cheques payable to BCInsight Ltd

Advertising enquiries:
TINA FIRMAN
tina.firman@bcinsight.com
Tel: +44 (0)20 7793 2567

Agents:
Japan: (also subscription enquiries)
KOICHI OGAWA
O.T.O. Research Corporation
Takeuchi Building
1-34-12 Takadanobaba
Shinjuku-Ku, Tokyo 169, Japan
Tel: +81 3 3208 7821
Fax: +81 3 3200 2889

Previous articles from *Sulphur* from 1995 to the present are available digitally in PDF format. To make a purchase, or for a list of available articles, please see: www.bcinsight.com

ISSN: 0039-4890

Design and production:
JOHN CREEK, DANI HART

Mixed Sources FSC

Printed in England by:
Buxton Press Ltd
Palace Road, Buxton, Derbyshire, SK17 6AE

BCInsight

Published by: BCInsight Ltd
Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

Advertisers' index

Advertiser	Page	Contact	Fax / Email
Blasch Precision Ceramics	31	Mr Jeff Bolebruch	1 518 436 0098
Enersul Limited Partnership	OBC	Ms Pat Wories	pwories@enersul.com
Fluor Corporation	IFC	Mr Thomas Chow	1 949 349 2898
Hugo Petersen GmbH	19	Mr Axel Schulze	49 611 962 9098
Jacobs / Chemetics	9/23	Mr Andrew Berryman	1 604 737 4483
MECS Inc.	7	Mr Kirk Schall	Kirk.m.schall@mecsglobal.com
MECS Inc.	17	Ms Andrea Trapet	Andrea.c.trapet@mecsglobal.com
Merichem Company	39	Mr Brett Stephen	bstephen@merichem.com
Sandvik Process Systems	5	Ms Gundula Eckhardt	49 711 5105 28 208
Solvadis GmbH	13	Mr Eberhard Zorn	49 69 5700 7534
Sulphur 2015 Conference	IBC	Ms Kay Rowlands	Kay.rowlands@crugroup.com
Weir Minerals Lewis Pumps	47	Mr Ken Black	1 314 843 7964

Next issue: September/October 2015

Distribution at:
Sulphur 2015 Conference, Toronto, Canada

- **Sulphur recovery technology trends**
- **The European sulphuric acid industry**
- **Sulphur content in fuels**
- **Sulphur fertilizers**
- **Direct Sour Gas Combustion**

Closing date for advertisement space booking is 9 September 2015
For further information and to book advertisement space contact:
Tina Firman, Publishing Director: tina.firman@bcinsight.com
Tel: +44 (0)20 7793 2567 Fax: +44 (0)20 7793 2577

SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31

Don't forget the next issue of Sulphur September/October 2015

SULPHUR
ISSUE 359
JULY-AUGUST 2015

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com