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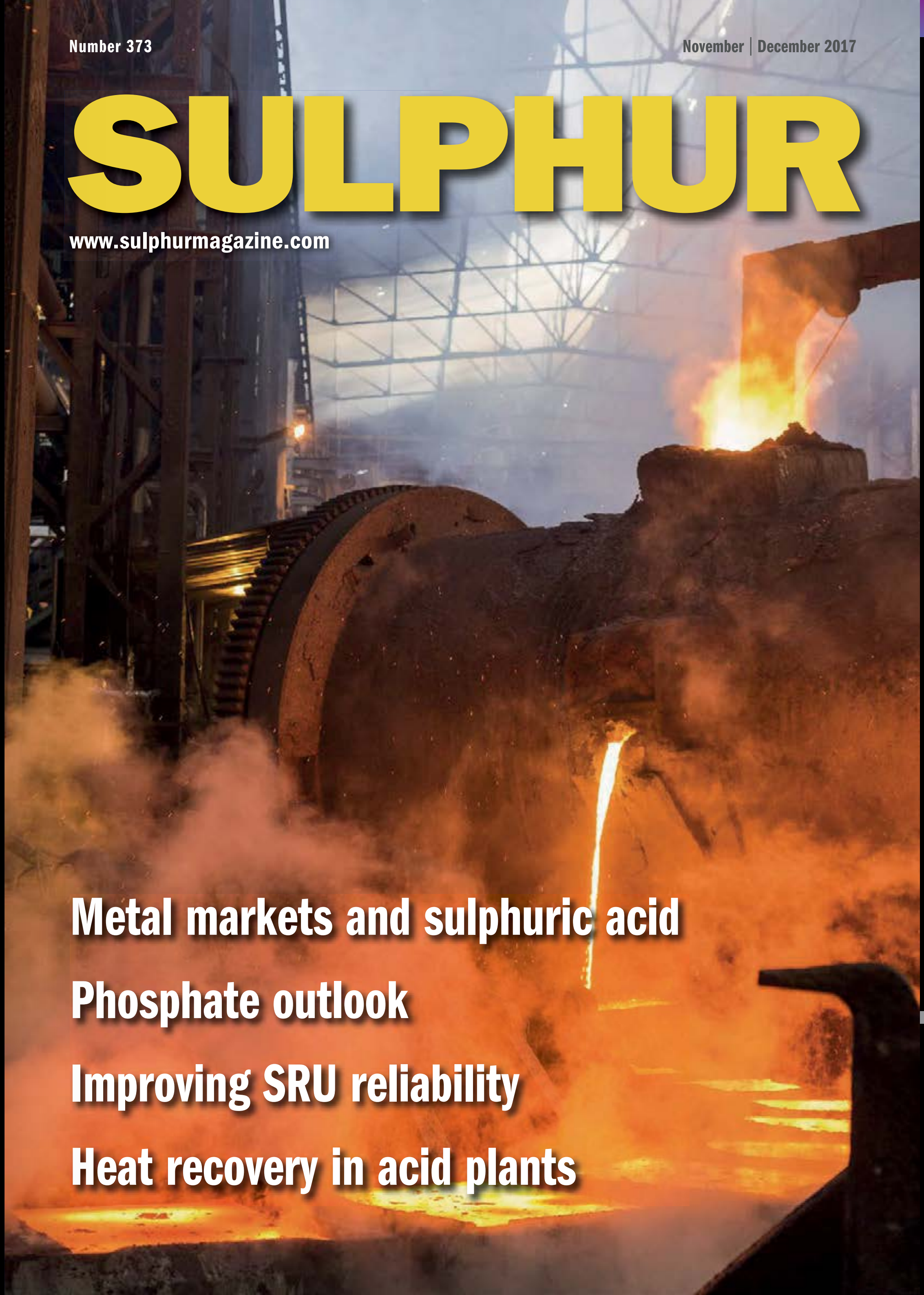

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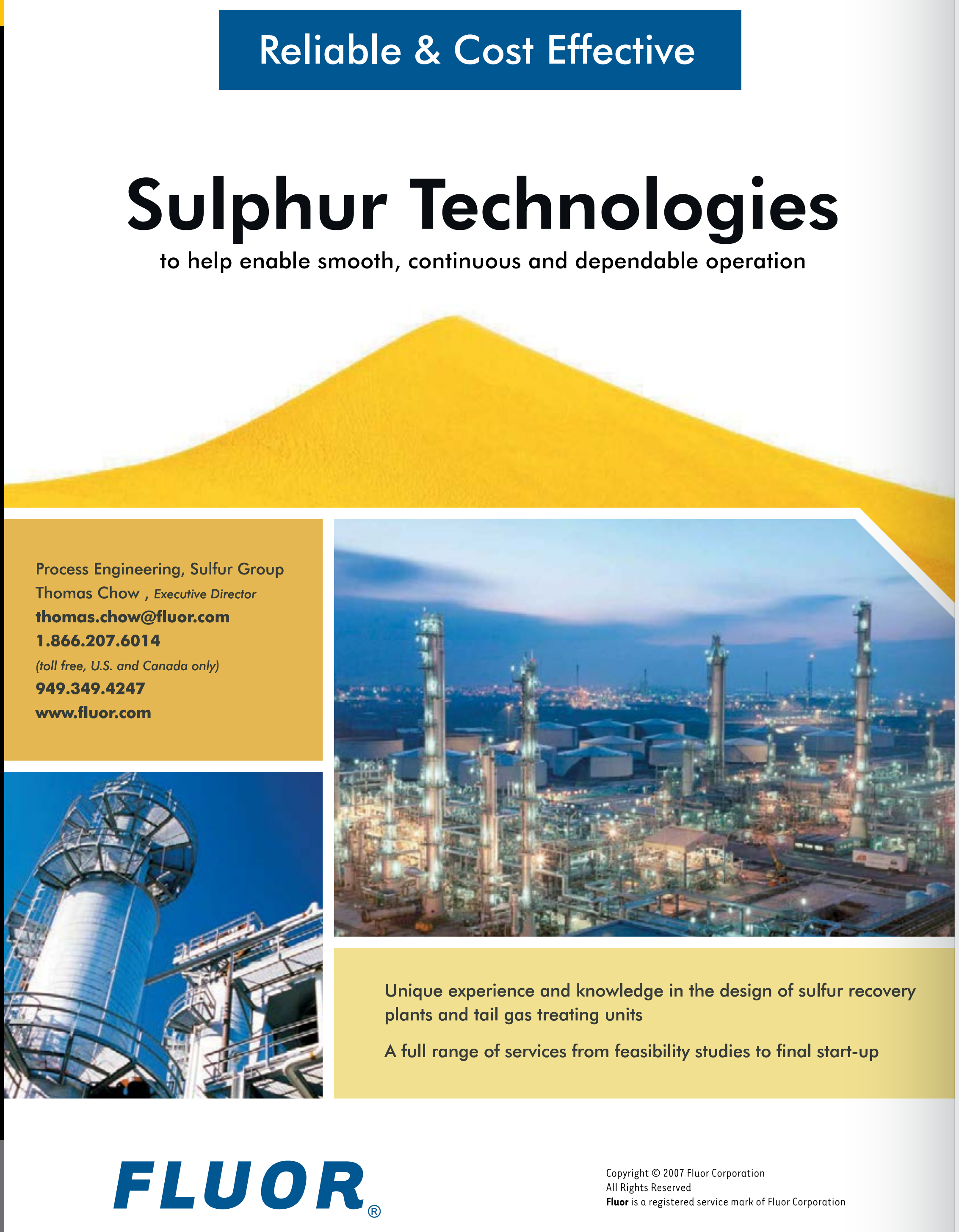

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Phosphate markets

Continuing boost to sulphur demand.

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Improving performance and reliability.

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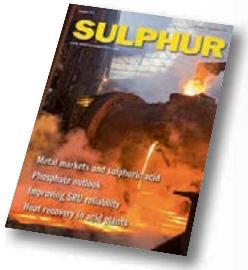
When is a bull market a bubble?



> Market fundamentals continue to point in the opposite direction...

Sulphur markets seem to have been on their own idiosyncratic trajectory in the past few weeks. While major indicators like Adnoc's monthly contract price had been moving up gently, form $100/t to $110/t to $120/t, a few days ago Qatar set its November price at $174/t, while prices in China have been skyrocketing, heard to be over $200/t and even $210/t for some delivered rates, and even Vancouver prices have touched $180/t, a level not seen for three or four years. As always, the sulphur market constantly defies expectations – as recently as May prices were around the $70-80/t range in most major markets. What is going on?

While there have been some developments in the US market, like the impact of Hurricanes Irma and Harvey on Gulf refinery production and the wildfires in California, and some have discussed whether the new Heartland forming plant in Canada will impact on availability out of Vancouver, the culprit this time definitely seems to be China, where prices began rising at the end of September, and where they have continued to leap upwards in increments during October. Several factors seem to have coincided to produce a local shortage and a scramble for additional tonnes of sulphur which has had a knock-on effect on all major markets.

The beginning may have been seen back around May-June, when demand in China ticked higher as refineries produced less than expected. At the same time, phosphate producers who were not able to source sulphuric acid appeared to be burning more sulphur. While China's imports decreased by 10%, stocks at ports dropped by 500,000 tonnes from May to September. With the expectation of a further environmental clampdown on emissions in 2018, phosphate producers were also rushing to build inventory and running at higher than usual rates. Couple this with less availability from the US and Russia and suddenly there are the makings of the kind of bull run in sulphur prices we have not seen for some time. No doubt the rising oil price, hitting a two year high at $60/barrel as OPEC production cuts finally start to eat into the surplus inventory and drive prices higher, has also been psychologically significant.

Market fundamentals continue to point in the opposite direction, however, and so it seems likely that this flurry in sulphur pricing, as unexpected and exciting as it may be, is just a short lived bubble and not the start of something bigger. In the longer term, additional large volumes of supply are due from the Barzan project in Qatar and the long-delayed re-start of the sulphur recovery units at Kashagan in Kazakhstan, the latter adding up to 1 million t/a. Nevertheless, given that both of these projects have now been pushed back into 2018, for the moment, the bubble appears to still be with us. Enjoy it while it lasts! ■

Richard Hands, Editor

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Price trends

MARKET INSIGHT

Oliver Hatfield, Director, Fertilizer Research Team, Integer Research (in partnership with ICIS) assesses price trends and the market outlook for sulphur.

SULPHUR

Recent sulphur prices have been surprisingly robust, due to a combination of primarily unpredictable events. In September the price of sulphur at f.o.b. references at Vancouver and the Arab Gulf averaged around $105 per tonne, having traded in a $80-90 per tonne range for many months previous. We have to go all the way back to early 2016 to find the last time f.o.b. prices reached three figures. Prices for sulphur delivered to China averaged $133 per tonne in September. The rally continued through October and at the end of the month, the Chinese delivered reference exceeded US$200 per tonne with exporters from the Middle East realising $150-165 per tonne for spot business. Chinese domestic sulphur prices increased by around $35 per tonne in the fourth week of October alone.

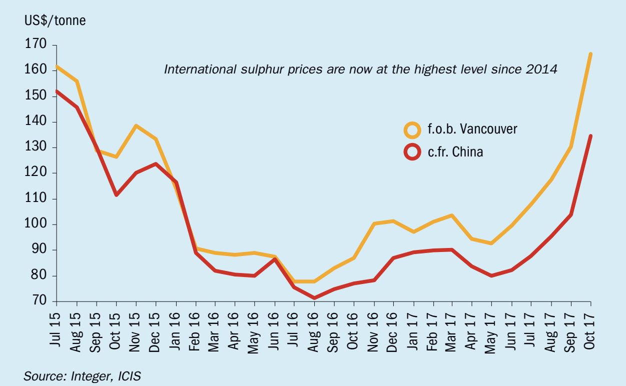
Several factors contributed to the uplift. In China, there has been a rush of activity over the last few months. Chinese buyers are reported to have raised purchases in connection with the impending addition of environmental taxes which are scheduled to be imposed in calendar year 2018. Producers of phosphate and other sulphur consuming downstream operations are presumably buying up more sulphur in order to work their plants harder until the end of 2017, temporarily avoiding these taxes. China's new environment tax includes charges of 5 yuan per tonne of coal waste, 1.2 yuan per unit of atmospheric pollution, 1,000 yuan ($150) per tonne of hazardous waste and 1.4 yuan per unit of water pollution. Chinese industry is also fearful that already announced punitive environment taxes could be raised further at the Chinese Communist Party Congress taking place in October.

Some of the key indicators for the Chinese market present a mixed picture. Chinese sulphur inventory levels had been declining steadily from around 1.5 million tonnes in May 2017, to just over 1 million tonnes at the end of September. They have since climbed by around 200,000 tonnes. It's likely that the decline in stocks contributed to bullish sentiment, encouraging buyers and traders to secure relatively scarce sulphur volumes. Chinese import volumes on the other hand are actually lower in 2017 on a year to date basis to September, totalling 8.6 million tonnes against 9.4 million tonnes over the same period in 2016. However, import activity has accelerated in the most recent quarter. For the first half of 2017, Chinese sulphur imports totalled 5.5 million tonnes, 16% lower than the same period in 2016. For Q3 2017, imports were 3.1 million tonnes, compared to 2.8 million tonnes in Q3 2016.

Sulphur availability from Russia has also been squeezed. Harsh weather has led to earlier than usual closures to rivers and waterways, which are essential to internal sulphur shipments through the country. This has reduced sulphur volumes for export, leaving sulphur buyers in North Africa and beyond short of product. Austrofin Gazprom could offer no sulphur material from Russia for the fourth quarter of 2017 and was forced to cancel contracts for the period, while Q3 shipments were delayed due to storms. OCP and Austrofin Gazprom are important partners and with Russian export volumes cut short, OCP is likely to need to increase spot activity in the last quarter of 2017.

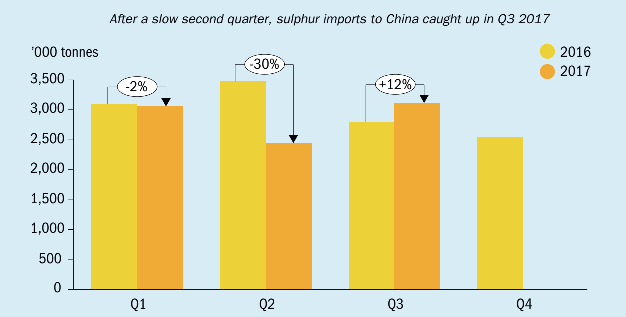
The US Gulf f.o.b. price increased to a range of $130-140 per tonne at the end

Fig 1: **Month average spot sulphur prices, July 2015 to October 2017**



Source: Integer, ICIS

Fig 2: **China quarterly sulphur imports, 2016 to 2017**



Source: Integer, GTIS

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of October, increasing by around $40 per tonne in the final week of the month, reflecting the movement of prices in line with other locations. Having been disrupted the earlier Hurricane Harvey impact, US Gulf shipments to regular destinations like Brazil were getting back to normal in October. While values for solid sulphur have escalated rapidly, prices quoted for liquid sulphur have lagged behind with the contract price at around US$75 per tonne at the end of October, more or less unchanged for the month. Mosaic then reported at the end of October that it had agreed Q4 2017 contract prices at $110 per long ton delivered, significantly below spot sulphur prices elsewhere.

Brazilian demand for sulphur continues to be relatively robust. Imports for the first three quarters of 2017 reached 1.6 million tonnes, nearly 200,000 tonnes ahead of the same period in 2016. Despite weather disruptions, 2017 shipments to Brazil from the US were more or less on a par with the previous year at around 580,000 tonnes.

SULPHURIC ACID

The global sulphuric acid market balance remained tight moving in to the fourth quarter of the year, supported by ongoing supply constraints, but there were signs that the rally was coming to an end. Supply availability from most major sources remained tight due to a combination of turnarounds and unplanned outages while the recent spike in sulphur prices limited opportunities to fill supply gaps with burned acid.

In Europe, there was relatively limited spot business, due to a lack of supply availability. For Mediterranean sellers, the US$30-40 per tonne f.o.b. price range lasted through September and most of October, but by the end of the latter month, indications were around $5 per tonne lower. The escalation in sulphur prices meant sellers of acid based on burned sulphur were unable to find buyers at high enough prices to cover costs. Toward the end of October, some Q4 contracts were reported to have been concluded at increases in the range of €3-5 per tonne.

Price gains made during Q3 started to ebb away in the Chilean market by the end of October, with the $78-85 per tonne c.fr. price range seen for most of September and October dipping to $65-75 per tonne. Import volumes to Chile for the year to August 2017 were relatively robust reaching 1.6 million tonnes, compared to 1.1 million tonnes over the same period in 2016. Expectations are that total volumes will reach around 2.1 million tonnes for calendar year 2017. Attention is starting to shift to likely price levels for 2018 annual contracts. Expectations are that prices will rise significantly compared to the $27-33 per tonne range agreed for 2017, with some talking up levels as high as the $60s. However, with the bull run seemingly plateauing at the end of October, such ambitious price ideas seem likely to be reined in, particularly as 2018 import volumes are predicted to be lower and closer to the 1.7 million tonnes recorded in 2016.

A significant contributor to price inflation during 2017 has been a lack of supply availability in the NE Asian market due to a cluster of maintenance turnarounds, notably in Japan. The market balance in this region has remained tight, with prices f.o.b. Japan/South Korea trading in the $30-40 per tonne range through September and October for spot business. However, prices were high enough to dissuade buyers and consequently the market has been relatively quiet. The potential for Chinese sellers of burned acid to enter the market were stifled by rising sulphur prices, so most Chinese sellers preferred the more attractive domestic market. NE Asia contract negotiations for the third quarter were protracted, and remained unsettled until the end October when an increase to a range of $20-40 per tonne c.fr. was agreed, compared to $18-30 per tonne previously. For Q4 contracts, discussions are starting on the basis of a rollover.

Elsewhere in Asia, the PASAR operation in the Philippines which suffered an earlier unexpected outage due to power failure after an earthquake remained out of action. The force majeure declared earlier remained in place but by early October the plant had restarted and was reported to be gradually ramping up. ■

Price indications

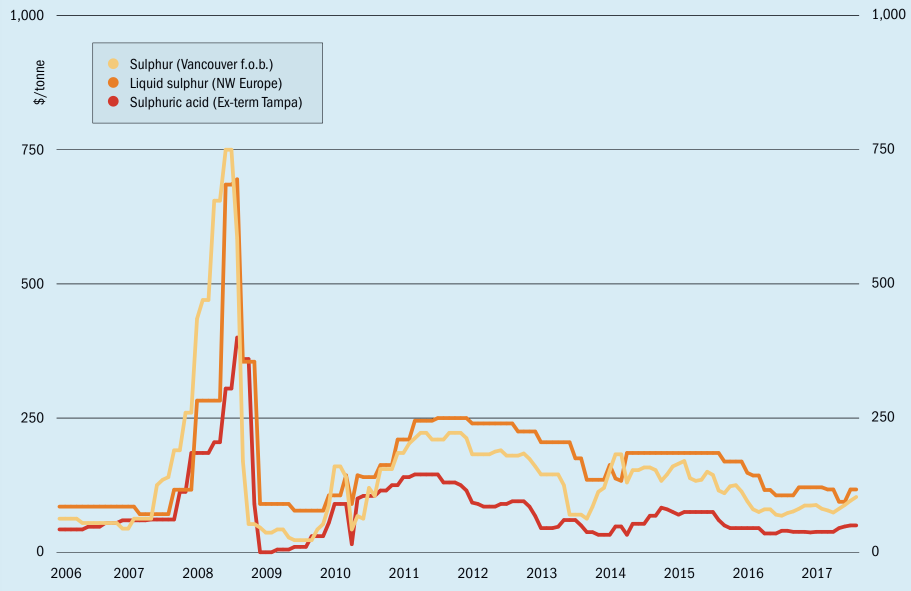
Table 1: **Recent sulphur prices, major markets**

Cash equivalent	May	June	July	August	September
Sulphur, bulk ($/t)					
Vancouver f.o.b. spot	74	81	88	96	103
Adnoc monthly contract	82	82	87	102	110
China c.fr. spot	91	97	105	135	135
Liquid sulphur ($/t)					
Tampa f.o.b. contract	70	70	74	74	74
NW Europe c.fr.	117	94	94	117	117
Sulphuric acid ($/t)					
US Gulf spot	38	45	48	50	50

Source: various

Market outlook

Historical price trends $/tonne



Source: BCInsight

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- The current tightness is likely to persist until the end of 2017. Thereafter, we expect the tension to begin to unwind due to a combination of short term factors and supply fundamentals.
- The enthusiasm for buying from China seen recently seems increasingly likely to subside. As we move in to 2018, Chinese import demand is expected to soften significantly as downstream producers, faced with higher environmental taxes, implement postponed turnarounds and maintenance. In addition, various Chinese domestic projects will lead to greater volumes of sulphur production, reducing import dependency.
- Similarly, Russian sulphur stocks are likely to start the spring at a higher level in 2018 due to the earlier than normal river closures this year. Consequently spring 2018 export availability would be higher.
- The Kashagan project in Kazakhstan, remains a focal point, with the potential to sell 1 million t/a of sulphur to export once it reaches capacity. However, ongoing delays continue. Latest reports from partners in the project indicate that it will only begin to ramp up in the first half of 2018.
- The delayed Rasgas Barzan project in Qatar is now not expected to start up until the end of 2018 at the earliest.

SULPHURIC ACID

- Metals, TiO_2, and sulphur prices continue to offer support but we would expect NE Asian sulphuric acid export volumes to increase in December 2017 as operations normalise post planned outages.
- The turnarounds in NE Asia that have limited availability in that market are likely to be concluded by the end of 2017, at which point export availability should normalise. Nevertheless, sellers of acid in South Korea and Japan are reported to be sold out until Q1 2018.
- The restart of the PASAR operation in the Philippines is likely to boost availability in the SE Asia market, easing recent supply shortages there.
- Sulphur prices continue to rally, and it seems most likely that prices will remain robust until the end of 2017 at least. This should provide support to the sulphuric acid market. With delivered sulphur prices hitting $200 per tonne at the end of October on a spot basis in some markets, this is likely to eliminate arbitrage opportunities for burned acid sellers.
- In the US, the market looked to be getting back to normal after Hurricane Harvey disrupted operations, but there are now additional uncertainties due to reported US smelter disruptions and downstream phosphate production volume adjustments.
- In China, greater interest in imports of sulphur have contributed to the ramp up in sulphur prices, with buyers keen to avoid impending environmental charges coming in 2018. The impact on Chinese sulphuric acid volumes is mixed, with August 2017 year to date exports reaching 330,000 tonnes, compared to 36,000 tonnes for the same period in 2016. At the same time, Chinese acid imports have shrunk from more than 1 million tonnes in the year to date August 2016 to 850,000 tonnes in 2017. ■

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Sulphur Industry News

INDIA

Coke gasification plant to start up by end of the year

Reliance Industries says that the company's new petroleum coke gasification plant at its Jamnagar Refinery complex will be on-stream by the end of 2017, ramping up into the first half of 2018. The plant, claimed by Reliance to be the largest petcoke gasification plant in the world, is expected to produce 2,000 t/d of sulphur at capacity. Even the large-scale refinery at Jamnagar will not be able to produce sufficient petroleum coke to feed the plant, and Reliance says that it is looking to import high sulphur petcoke from elsewhere in India or even as far afield as Saudi Arabia. The gasifier will produce power, hydrogen and other process streams for the refinery. ■

EGYPT

MECS scrubbing technology for Zohr gas field

DuPont Clean Technologies (DuPont) has signed a contract with Kinetics Technology (KT) for Eni's giant Zohr deep water gas field in the Egyptian exclusive economic zone of the Mediterranean Sea. Under the contract, DuPont will deliver the technology license, engineering and proprietary equipment for two MECS *DynaWave*® wet gas scrubbing units while KT will provide the related onshore gas plant units in Port Saïd with Claus and tail gas treatment units (TGTUs). This will allow the new Zohr project to meet stringent environmental requirements on sulphur dioxide emissions, in all operating cases.

"This is the second large contract DuPont has been awarded in Africa in recent months, coming closely on the heels of delivering equipment for another Claus TGTU off-gas scrubber, alkylation unit and spent sulphuric acid plant for the Dangote Oil Refinery Company in Nigeria," Yves Herssens, global market leader MECS® DynaWave® reported. "We are delighted to help Eni to comply with air emissions regulations using DuPont technology that is highly efficient and fully flexible."

Licensed by DuPont, MECS® DynaWave® scrubbers are designed to work with a variety of reagents and handle multiple functions in one vessel. As such, the process makes it possible to quench the incinerated gas and remove potential particulates while absorbing the remaining acids from the Claus TGTUs. The technology also offers the flexibility of bypassing the sulphur recovery unit (SRU) or the SRU tail gas system during maintenance and repairs, so operations can continue without interruption.

Over the last 40 years, the MECS® DynaWave® technology has been successfully installed and used at more than 400 sites around the world in different industries. In the oil and gas industry alone, DuPont Clean Technologies, which licenses both the DynaWave® scrubber technology and the BELCO® EDV® scrubber technology, has more than 150 successful wet scrubbing references around the globe. The large nozzles and open vessel design of the DynaWave® scrubbers result in units that are virtually plug proof and able to handle any possible sulphur particulate entrainment. This results in higher on-stream time and lower maintenance and operational expenditures for the operator.

QATAR

Grant to study sour gas corrosion in pipelines

The Qatar Shell Research and Technology Centre (QSRTC) and its research partners have been awarded three National Priorities Research Program (NPRP) grants by the Qatar National Research Fund (QNRF), totalling approximately $2 million. QSRTC will collaborate locally and internationally on three projects to develop solutions designed to address industrial-related corrosion issues and water treatment. Two three-year projects will target the issue of corrosion; the most prevalent cause of failure in many oil and gas infrastructures, particularly those exposed to harsh environments. It is responsible for about 70% of the repair and replacement needs in pipelines and piping. In partnership with Qatar University (QU) and Imperial College, London, QSRTC will develop new sensor technology for real time, online monitoring of 'under deposit' corrosion risks in wet sour gas pipelines.

Another project, in partnership with Texas A&M University at Qatar, the Qatar Environment and Energy Research Institute, Ecole Normale Supérieure de Chimie de Lille in France, and Université de Montreal in Canada, will use multi-scale computational modelling to unveil corrosion mechanisms and investigate prevention. Dr Marwa Al-Ansary, Research and Development and Technology Manager at QSRTC, and Dr Nicholas Laycock, Senior Materials and Corrosion Engineer at Qatar Shell, will serve as the primary industry investigators and consultants on both projects. The third project will develop and evaluate nano-particle-based biocatalysts to treat process water in collaboration with the University of Delft in the Netherlands.

QSRTC is the main tenant of the Qatar Science and Technology Park, established in 2008 to develop and deploy technologies which support the Qatar National Research Strategy. Since 2015, QSRTC has collaborated on five projects that have received QNRF funding in support of the government's Qatar National Vision 2030.

UNITED ARAB EMIRATES

KBR awarded FEED contract for Hail/Ghasha

KBRsays that it has been awarded a project management services contract (PMC) by the Abu Dhabi National Oil Company (Adnoc) for management of the front end engineering design phase of the Hail and Ghasha Development Project in Abu Dhabi. KBR will also perform PMC services for the detailed engineering phase of the sour gas project under a contract awarded by Occidental of Abu Dhabi Ltd. which is jointly managing the project with OMV Offshore Abu Dhabi GmbH on behalf of Adnoc. Under the terms of the contract, KBR will provide project management consultancy services over the coming two years. The Hail and Ghasha Project, one of the largest sour gas projects that Adnoc is developing, is forecast to produce about 1 billion cubic feet of sour gas per day. The infrastructure requirements include a minimum of eleven offshore artificial islands to be designed and constructed.

"KBR is very pleased to be awarded this important project in support of Abu Dhabi's Gas Infrastructure Improvement Plan," said Jay Ibrahim, KBR President, EMEA. "This contract demonstrates KBR's ability to establish strong local partnerships as well as our global oil and gas capabilities for greenfield project developments in any location across the globe".

NIGERIA

Dangote sets "firm completion date"

The Dangote Oil Refinery Company says that it has set December 2019 as a "firm completion date" for the massive new refinery and petrochemical complex which the company is developing in the Lekki Free Zone near Lagos. The refinery is expected to be the world's biggest single-train facility, upon completion, with a price tag put at $9 billion. The refinery aims to reduce Nigeria's imports of refined fuels, in spite of being Africa's largest oil producer, by doubling the country's refining capacity. It will produce Euro-V quality gasoline and diesel, as well as jet fuel and polypropylene. Annual refining capacity will be 10.4 million t/a of gasoline, 4.6 million t/a of diesel and 4 million t/a of jet fuel. It will also produce 690,000 t/a of polypropylene, 240,000 t/a of propane, 32,000 t/a of sulphur and 500,000 t/a of carbon black feed.

Engineers India Ltd was awarded the engineering, construction and procurement contract for the refinery. Additional processing units a DuPont *STRATCO*®alkylation unit and the MECS sulphuric acid regeneration (SAR) unit.

NETHERLANDS

Jacobs signs licensing deal with Paquell

Jacobs Engineering Group Inc. has signed a sulphur recovery technology licensor agreement with Paquell, a joint venture between Shell Global Solutions and Paques BV. The agreement allows Paquell to use Jacobs' *THIOPAQ O&G* technology in refineries and gas treating facilities worldwide. The biological process integrates gas purification with sulphur recovery in a single unit, removing mercaptans and hydrogen sulphides from a gas stream and converting them into biologically formed sulphur. In a statement, Jacobs noted that the deal positions it as the only gas treating and sulphur recovery licensing company to license the technology to low capacity sulphur facility owners.

"Refining and gas treating facility owners and operators require reliable technology that delivers low CAPEX and OPEX, provides high sulphur recovery efficiency and minimises environmental impact," said Andrew Berryman, Jacobs Mining & Minerals and Speciality Chemicals senior vice president and general manager.

CANADA

Start-up for Sturgeon refinery be end of year

North West Refining says that its new C$9 billion Sturgeon plant in Alberta will be on-stream by the end of 2017. The refinery, co-owned by Northwest Redwater Partnership and Canadian Natural Resource Ltd, will process 80,000 bbl/d of oil sands bitumen at the end of its first phase, producing 40,000 bbl/d of diesel as well as other products, aimed towards the US west coast. It is Canada's first new refinery in 33 years.

CHINA

China looking to ban petrol and diesel cars

China, the world's biggest car market, plans to ban the production and sale of diesel and petrol cars and vans. The country's vice minister of industry said it had started "relevant research" but that it had not yet decided when the ban would come into force. "Those measures will certainly bring profound changes for our car industry's development," Xin Guobin told Xinhua, China's official news agency. China made 28 million cars last year, almost a third of the global total. Both the UK and France have already announced plans to ban new diesel and petrol vehicles by 2040, as part of efforts to reduce pollution and carbon emissions. China wants electric battery cars and plug-in hybrids to account for at least one-fifth of its vehicle sales by 2025.

URUGUAY

Court refuses to seize phosphate shipment

In late August, a court in Uruguay rejected a request from the Polisario Front, which claims the independence of the Western Sahara from Morocco, to seize a 300 tonne shipment of Moroccan phosphate which had originated from the port of Boucraa in Western Sahara. The dispute was the latest in several attempts by Polisario to impound phosphate shipments from Boucraa. In June the Panama Maritime Court also rejected a similar plea, but a South African court had previously upheld the impounding of a 55,000 tonne phosphate shipment bound for New Zealand, and in July Morocco's Office Cherefien des Phosphates (OCP) declined to take the matter to trial. In a statement issued on July 13th, OCP described the court's decision as "judicial over-reach [which] threatens the freedom and security of international trade". It said it had notified the court registrar that it will not participate in the trial, adding "we have reluctantly come to the conclusion that participating in any trial before this forum would give further credit to a process without any legal legitimacy."The company further denounced the South African decision as a "political piracy", "an eminently political decision" and "a gross abuse of power", and said that it would "continue to explore every option under international law to recover our rightful property." ■

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OMAN

Al Hadeetha considering first Gulf copper smelter

Al Hadeetha Resources, a 70:30 joint venture between Australia-based Alara Resources and local firm Al Hadeetha Investment Services, says that it plans to start construction of a copper concentrate plant by the end of the year, subject to the company getting a mining license from the Public Authority for Mining. The copper concentrate plant will be located at Washihi, 160 km southeast of Muscat, and is expected to start operations in 2018. It will process 1 million t/a of copper ore to produce 30,000 t/a of concentrate. A 75 km buried pipeline from Nizwa to the mine site will transport 2,400 cubic metres of water. The total project cost is estimated at $270 million.

Justin Richard, chief executive officer and managing director of Alara Resources, told the Mining Investment Middle East and Central Asia Conference that Al Hadeetha Resources has three exploration licenses (Washishi, Mullaq and Al Ajal) and has also applied for a mining license. Alara also has two other joint ventures in the country; Daris Resources LLC, which has an exploration license and has applied for two mining licenses, and Alara Resources (Oman) LLC, which has also applied for an exploration license, but has yet to receive permission. He also added that his company is also looking at the possibility of building a copper smelter.

"There is no smelter in the Gulf region now. Oman had a copper smelter, which was closed down. There is enough copper concentrate here for setting up a smelter. Copper concentrate is also produced in Saudi Arabia, which is shipped outside the region," Richard said. ■

SAUDI ARABIA

Wa'ad al Shamal begins shipping DAP

According to project partner Mosaic, the Ma'aden Wa'ad Al Shamal Phosphate Company (MWSPC) has produced its first tonnes of diammonium phosphate. The announcement follows the successful start-up of the ammonia plant last year at Ras Al Khair. Mosaic says that only one train is currently up and running at MWSPC's granulation plant in Ras Al Khair, but once all four trains are online later this year, the joint venture is expected to produce approximately 3 million t/a of DAP, MAP and NPK fertilizers. Mosaic says that it will be one of the lowest cost phosphate producers in the world.

MoU signed with PhosAgro

In other news, Ma'aden has signed a memorandum of understanding with Russia's PhosAgro, agreeing to share best practices and knowledge related to technical aspects of production, environmental protection, and workplace health and safety. The firms will also take measures to support their long-term sustainable development, participating in initiatives to ensure the reliability and stability of supply of phosphate-based fertilisers to agricultural producers across the world.

PhosAgro CEO Andrey Guryev said: "We welcome cooperation with another one of the world's leading producers of phosphate-based fertilisers. PhosAgro and Ma'aden both place great importance on sustainability and stability, both in terms of developing our businesses and in terms of the important role we play in supporting food security at the domestic and international levels. This landmark memorandum of understanding is an important achievement for both of our companies and will help, among other things, to ensure greater discipline to secure the stable supply of phosphate-based fertilisers to customers around the world."

Ma'aden president and CEO Eng. Khalid bin Saleh Al-Mudaifer said: "We are happy to cooperate with PhosAgro, and look forward to the opportunities that sharing knowledge and best practices can bring both of our companies. Like PhosAgro, Ma'aden is committed to ensuring discipline and stability in the supply of high-quality phosphate-based fertilisers. This will ultimately benefit all of our stakeholders, helping to enhance the sustainability of global food security."

PERU

Jacobs to provide sulphuric acid technology for copper refinery in Peru

Southern Peru Copper Corporation (SPCC) has awarded Jacobs Engineering a contract to provide engineering, procurement and construction (EPC) services for its No. 1 Acid Plant upgrade project. SPCC operates one of the world's largest copper smelting/refinery facilities at Ilo, 965 km south of the capital, Lima. Under the terms of the lump sum EPC contract, Jacobs will modify the existing acid plant, decreasing its sulphur dioxide (SO$_2$) emissions while increasing sulphuric acid capacity using the company's proprietary Chemetics sulphuric acid technology.

"Our successful relationship with Southern Peru Copper Corporation (SPCC) spans more than 20 years," said Jacobs Mining & Minerals and Speciality Chemicals Senior Vice President and General Manager Andrew Berryman. "We will provide our innovative Chemetics acid plant technology for this project, complementing the two existing plants our teams previously executed at the site, to further reduce SO$_2$ emissions."

In addition to the No. 1 Acid Plant project, Jacobs says that is also performing a feasibility study for SPCC in Lima for its power distribution system which will enable the company to support future demand.

AUSTRALIA

Port Pirie smelter begins commissioning

Nyrstar NV says that it has achieved "a significant milestone" on its Port Pirie smelter redevelopment with the commencement of hot commissioning. In a statement the company also confirmed that the conversion of the lead smelter to a multi-metal refinery would cost A$ 660 million. Nyrstar says that the key aspects of the redevelopment include the replacement of the existing sinter plant with an oxygen enriched bath smelting furnace and replacement of the existing sulphuric acid plant with a new plant with greater capacity and upgraded technology. The acid plant will take the off gas from the Outotec Ausmelt TSL Furnace after being cleaned and conditioned, and will convert the sulphur dioxide contained in the gas to concentrated sulphuric acid. The capacity of the acid plant will increase significantly from the current approximately 200 t/d to approximately 1,000 t/d (330,000 t/a).

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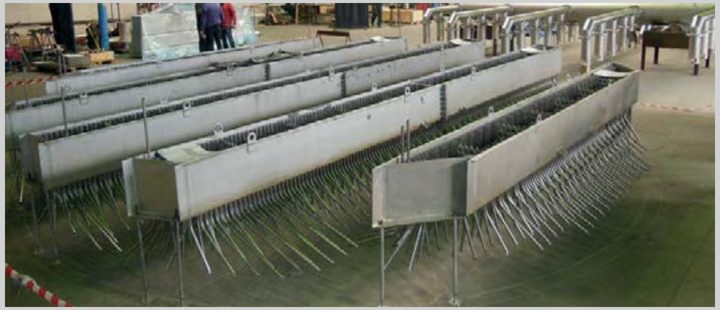


CORRECTION

The photo which was published in *Sulphur* 370, May/June 2017 as Figure 18 on page 39, in the article on sulphuric acid equipment should be replaced by the photo (left) of a NORAM trough distributor prior to installation inside of a NORAM acid tower.

TUNISIA

Phosphate production down 18%

Tunisia's phosphate production fell by 18.% in the first nine months of 2017 to 3.1 million tonnes compared with the same period last year, according to figures from state-run Phosphate Gafsa. The fall was due to protests in the south of the country. In May president Beji Caid Essebsi ordered the army to protect phosphate, gas and oil production facilities after protests aimed at disrupting output broke out in the Gafsa region. The government had targeted doubling its phosphate production to 6.5 million t/a in 2017 after output returned to its highest monthly level since 2010 in 1Q 2017. Tunisia produced 8 million t/a of phosphate in 2010. The low production levels have led Tunisia to lose some foreign markets such as India and Brazil and the country has focused on exporting phosphates to Europe.

UNITED STATES

Satco to build new acid terminal in California

Sumitomo says that is has agreed a land lease agreement with the port of Stockton, California on the US west coast. The agreement was made via the company's subsidiary the Tampa-based Sulphuric Acid Trading Company, Inc. (Satco), which is owned by Swiss-based Interacid Trading – itself a wholly owned subsidiary of Sumitomo. The land will be used for the construction of a new sulphuric acid tank terminal at that port, comprising a 30,000 tonne sulphuric acid tank, diluting facilities and freight car/truck shipping facilities. Sumitomo puts construction expenses at about two billion yen ($17.7 million). Construction is scheduled to begin by the end of 2017, and operation should start in early 2019. Sumitomo says that the port of Stockton, 100 km east of San Francisco Bay, is a key import/export port, annually handling four million tonnes of cargo, primarily fertilizer, grain, cement, steel materials, and coal. West Coast demand for sulphuric acid is expected to increase in future, particularly for agricultural, mining and industrial use, and the terminal will be the only sulphuric acid receiving terminal on the US west coast. Sumitomo says it will seek to sell more than 200,000 t/a of sulphuric acid to customers via Satco, which will operate the terminal. In California, sulphuric acid is widely used to improve soil. Faced with chronic water shortages recently, the state has been steadily introducing drip irrigation methods that allow for highly efficient water distribution, and sulphuric acid is being used to adjust irrigation water quality to make it suitable for drip irrigation.

Mosaic to idle concentrates plant "indefinitely"

During the announcement of the company's third quarter 2017 results, Mosaic also announced that it will be idling its Plant City, Florida concentrates plant for an indefinite period of at least one year. The company says that the move is "to ensure minimal market disruption" from new phosphate capacity additions, including Mosaic's own Saudi Arabian joint venture at Wa'ad Al Shamal. Mosaic says that the net result is expected to be higher phosphate margins overall and lower capital requirements. The company also said that it "expects to serve a significant portion of its distribution business and other Indian customers more effectively with phosphate production from its Saudi Arabian joint venture" and that it will focus its US production towards the North and South American markets, where it has logistical advantages.

RUSSIA

SNC-Lavalin to deliver sulphuric acid plant package for Acron

SNC-Lavalin has been awarded a contract by Novgorodskiy GIAP, a subsidiary of Acron Group, for the development of engineering design packages and licensing services for a fertilizer project at Dorogobuzh in the Smolensk region of Russia. SNC Lavalin says that the scope of the contract covers pilot tests and engineering services, the development and delivery of basic engineering packages, and working documentation for the construction of the fertilizer facilities, including sulphuric acid, phosphoric acid, and granulated NPK plants at the site.

"We are honoured to have been awarded this contract," said José J. Suárez, President, Mining & Metallurgy, SNC-Lavalin. "This new contract award is testament to our recognized expertise and of our ability to support our clients globally in multiple sectors."

Nornickel promises to lower SO_2 output

Nornickel, which operates a nickel processing facility on the Kola Peninsula in northern Russia, has promised to reduce its emissions of sulphur dioxide, which have caused considerable friction with neighbouring Norway and Finland. Nickel is mined and concentrated at Zapolyarny, and then pelletised. The pellets are then taken to the smelter in the town of Nikel on the Norwegian border where the nickel matte is melted. The matte is then transported to Monchegorsk on the Kola Peninsula where the smelter makes pure nickel ready for the market. The three sites between them are estimated to emit 100,000 t/a of sulphur dioxide to atmosphere.

In response, Nornickel has presented its Sulphur Project to address the issue of sulphur dioxide emissions, targeting a 75% reduction. By the end of 2017, Nornickel plans to choose one of the two sulphur dioxide capture and recovery technologies to be implemented going forward. SNC-Lavalin has been asked to prepare a detailed design for the production of elemental sulphur at the Nadezhda Metallurgical Plant. The company is also considering sulphuric acid production with subsequent neutralisation. The Sulphur Project will cost up to $2 billion.

BRAZIL

Fire at Vale acid plant

A fire disrupted operations at a Vale Fertilizantes plant in Brazil's southeastern state of Minas Gerais. The fire occurred in the water cooling tower of the site's sulphuric acid plant at the Uberaba facility and was under control within an hour, according to the company, no employees were hurt and the cause of the fire is under investigation. Brazilian regulators approved Mosaic's purchase of Vale Fertilizantes in August.

CHINA

Environmental crackdown leads to fall in acid output

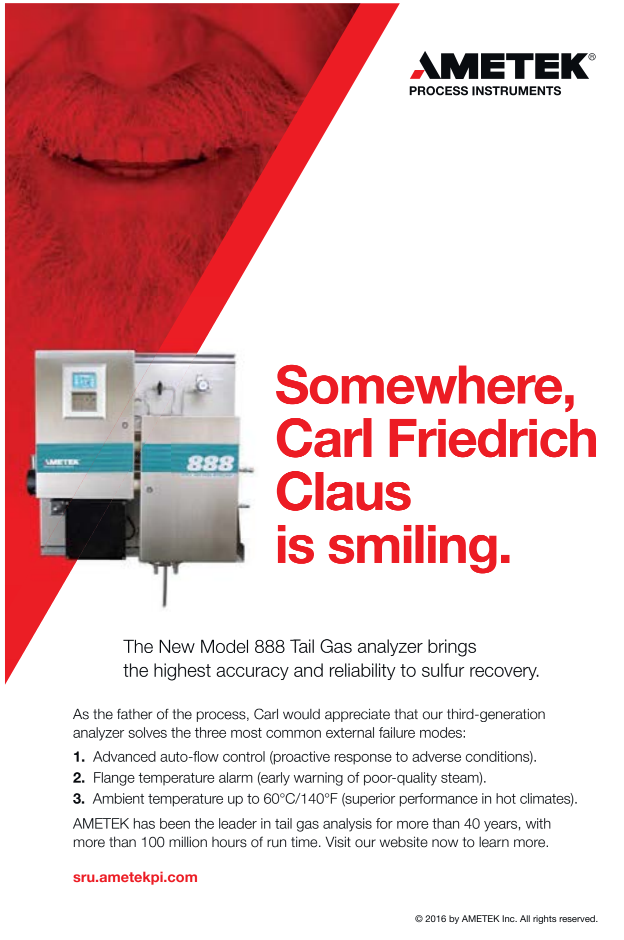
China has launched an aggressive campaign to curb smog in its northern regions, promising to close more factories and enforce bigger emission cuts in coming months, along with random spot checks to ensure targets are met. Smelters of copper and other nonferrous metals have faced closures because of the crackdown. Lead has been particularly hard hit, with 80% of illegal secondary smelters shut down since the second half of last year, according to research group Antaike.

This follows a bumper year in 2016 for Chinese smelting and copper refining capacity, with copper concentrates imports rising to 17 million t/a in 2016, up 28% year on year. However, the figure for the first half of 2017 showed only 3% growth due to tightening global concentrates availability, and led instead to a focus on importing copper scrap – with imports up 14% percent to 2.4 million tonnes for January-August, according to the International Copper Study Group.

INDIA

Tata Chemicals to sell Haldia plant to Indorama

Tata Chemicals has entered into discussions with Indorama Corporation to sell its phosphate fertiliser business at Haldia and the associated fertilizer trading business for 4-5 billion rupees ($60-75 million). Once completed, the deal will see Tata Chemicals exit the fertiliser business completely – last year the company sold its urea plant in Babrala, Uttar Pradesh, to Yara International. The Tata Chemicals Haldia plant has a production capacity of about 1.2 million t/a, and produces diammonium phopshate (DAP) and NPK fertilisers, sulphuric acid, phosphoric acid, and sodium tripolyphosphate crop nutrition. ■



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Jack Cohn

The Sulphur Institute (TSI) says that **Jack Cohn**, senior vice president & industry unit leader at Savage Services Corporation has assumed responsibilities as chairman of the board. Cohn's appointment follows a new assignment for Mike Lumley, former vice president of Shell Sulphur Solutions. Rob McBride, president and CEO of The Sulphur Institute praised Lumley for his tenure as TSI chairman and vice chairman: "We appreciate Mike's leadership and direction he provided the Institute while serving as vice chairman and chairman over the last 18 months. We welcome Jack, who is no stranger to TSI; the staff looks forward to working with him as chairman of the board."

Cohn previously served as TSI's chairman of the board from 2012 to 2013. "It is an honour to once again serve the sulphur industry as TSI's Chairman," said Cohn. Cohn will continue to spearhead many initiatives already underway at TSI, including plans to demonstrate its value to members in not only North America, but also further developing its interests for European members and expanding into Central Asia, the Middle East and North Africa.

Orbital Gas Systems has appointed **Jacob Tivey** as its trace measurement specialist, based in the company's Houston office. Tivey will serve as part of Orbital's research and development team, involved in the company's research into adsorption phenomena. He will apply his knowledge to existing Orbital technology, aiming to set the new standard for trace gas measurement. Tivey is a graduate of the university of Birmingham, UK, with a foundation degree in engineering fundamentals, as well as a bachelors and masters degree in chemical engineering. He is a member of the Institute of Chemical Engineers (IChemE), and is working towards gaining chartership. He has also had work published and presented at the ISA symposium in Pasadena, California."

Blasch Precision Ceramics, has announced that **Uday Parekh** will join Blasch Precision Ceramics to represent the company as Senior Global Director, Energy and Chemicals. In this role, Mr. Parekh will aid in the expansion of Blasch's coverage within these industries, increasing the company's bandwidth and technical knowledge, and enabling a closer customer relationship to facilitate the development of new technologies and solutions.

"With this appointment, we further position the company to deliver sustainable, competitive advantages to existing and new customers globally," commented Jack Parrish, Blasch Precision Ceramics Chief Operating Officer. "The combination of our experienced personnel, innovative culture, strong engineering and product development teams, and state of the art manufacturing facilities ensure that our customers realize the best possible performance in their challenging applications."

Uday has close to 30 years of experience in the petroleum refining and chemicals industries with several years leading the applications development and technical sales areas at Air Products. This includes his extensive oxygen enrichment expertise and resultant critical environments in Sulphur Recovery Units (SRU), FCCUs and sulphuric acid. Blash says that his experience in hydrogen derived from Air Products' premier position in hydrogen supply will help customers improve the reliability of their hydrogen and syngas manufacturing facilities through the deployment of Blasch's *StaBlox* product line. In addition, he was previously vice president of Sales and Marketing at Goar, Allison & Associates, Inc. (GAA), a leading SRU technology licensor.

Trammo Inc. has appointed **Sarah Terrell** as senior vice president and product manager of Sulphuric Acid and as a member of Trammo's executive board. Terrell joined Trammo in 2011 as sulphuric acid manager and in 2014 was promoted to vice president of trading.

"Sarah is a veteran of the sulphuric acid business. Prior to joining Trammo, she was director of trading at Keytrade AG, product manager at SATCO and purchasing manager at Noranda in Chile. Terrell will be heading an experienced team of trading, chartering and logistics personnel," Trammo's CEO Brent Hart said. ■

Calendar 2017/18

NOVEMBER 2017

6-9

Sulphur 2017, ATLANTA, Georgia, USA
Contact: CRU Events
Tel: +44 20 7903 2167
Email: conferences@crugroup.com

13-15

European Refining Technology Conference, ATHENS, Greece
Contact: Sofia Barros, Senior Conference Producer & Project Manager,
World Refining Association
Tel: +44 20 7384 7944
Email: sofia.barros@wraconferences.com

FEBRUARY 2018

25-28

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

MARCH

11-13

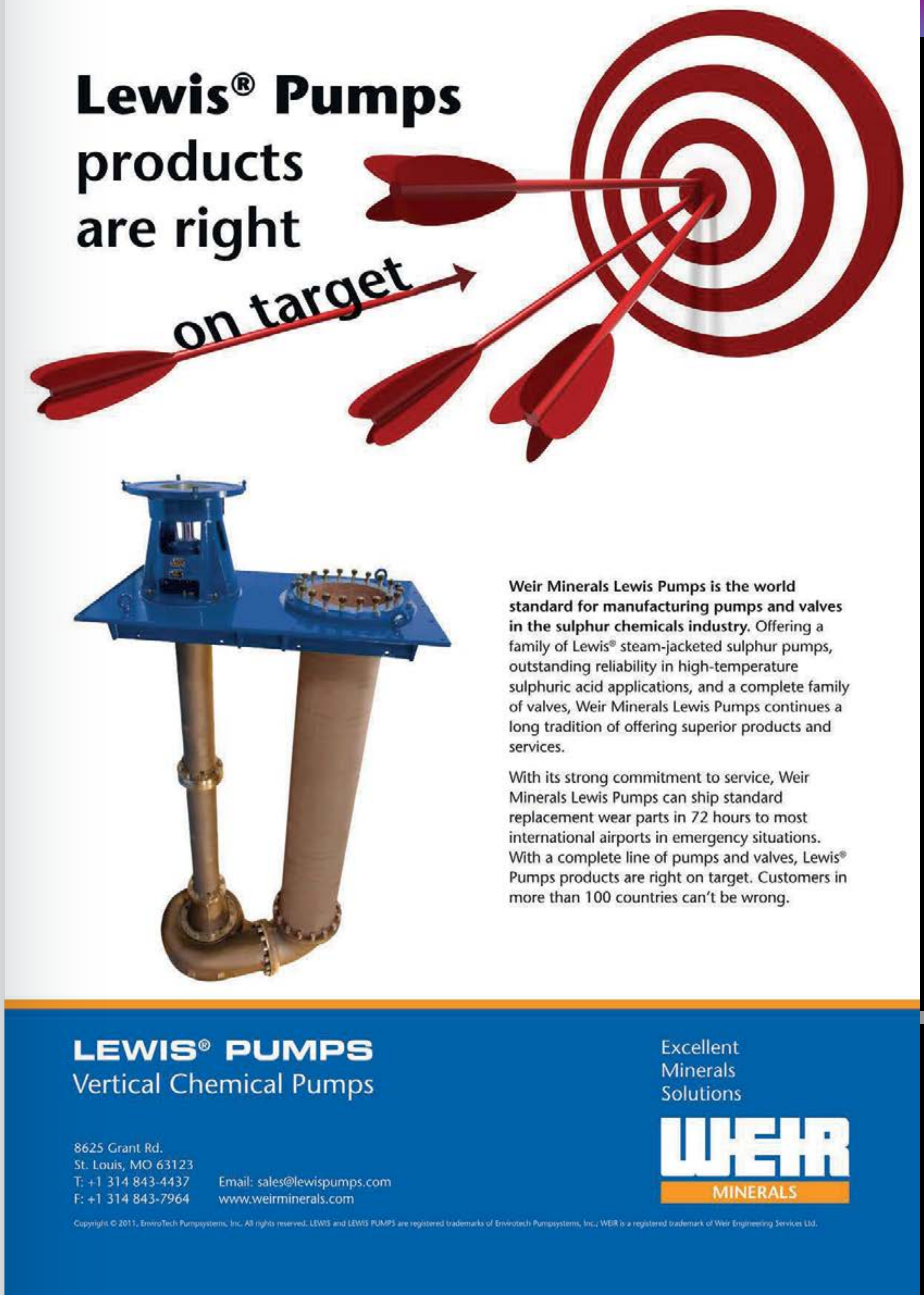
AFPM Annual Meeting,
NEW ORLEANS, Louisiana, USA
Contact: American Fuel and Petrochemical Manufacturers (AFPM)
1667 K Street, NW, Suite 700,
Washington, DC 20006, USA
Tel: +1 202 457 0480
Email: meetings@afpm.org
Web: www.afpm.org

12-14

Phosphates 2017,
MARRAKESH, Morocco
Contact: CRU Events
Tel: +44 20 7903 2167
Email: conferences@crugroup.com

26-30

SOGAT 2018,
ABU DHABI, UAE
Contact: Dr Nick Coles, Dome Exhibitions
Tel: +971 2 674 4040
Email: nick@domeexhibitions.com



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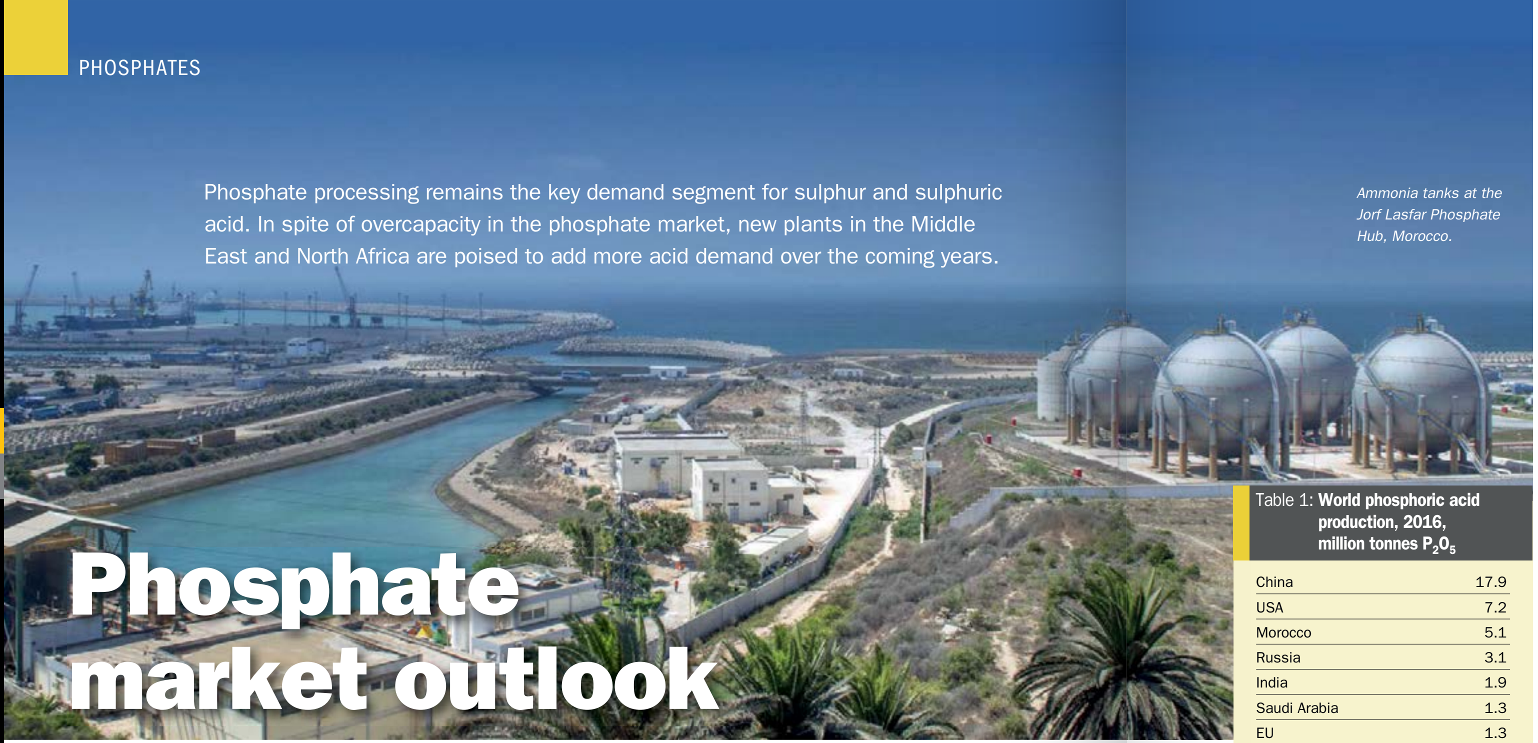


Phosphate processing remains the key demand segment for sulphur and sulphuric acid. In spite of overcapacity in the phosphate market, new plants in the Middle East and North Africa are poised to add more acid demand over the coming years.

Phosphate market outlook

Ammonia tanks at the Jorf Lasfar Phosphate Hub, Morocco.

While its industrial uses, particularly for metals processing, are a large slice of sulphuric acid demand, as detailed elsewhere in this issue, the processing of phosphates, mainly for fertilizer use, continues to represent the majority of sulphuric acid demand – something around 55%, of which 90% is accounted for by fertilizer demand.

Demand – agriculture

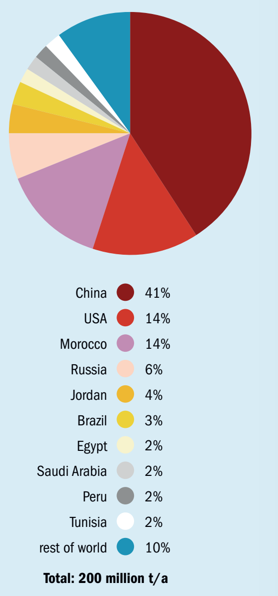
Phosphate fertilizer demand is set by the pace of the global agricultural economy and world demand for food. As global population increases, so demand for food also increases, and while the rate of population increase has slowed, global population is nevertheless forecast to rise from its present estimate of around 7.2 billion to 9.2 billion in 2050, according to the United Nations. At the same time, the amount of arable land available for planting is actually falling slightly due to urbanisation, while calorie intake per capita continues to increase as diets change in the developing world. This phenomenon is particularly strong in China and India, due to the increasing prevalence of meat, dairy, and oilseeds in diet, all of which are increasing the demand grain, animal feeds and agricultural production in general. 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 hence demand in these areas is also forecast to increase.

Only one possible mitigating factor is working in the opposite direction, and that is the tendency of countries with higher application rates of fertilizer to try to use fertilizer more efficiently, in a more targeted way. This is a particular issue for China, where very high fertilizer application rates have led to issues with fertilizer leaching into watercourses, and the Chinese government has decided to cap fertilizer use by 2020, including phosphates. Overall, world phosphate demand grew by 35% from 2005 to 2014, from 48 million tonnes P_2O_5 to 65 million tonnes P_2O_5, and most of this incremental demand came from China. However, this growth rate of about 4% per year has slowed since 2014, and is forecast to increase more modestly in future, at about 2% per year.

Supply – phosphate rock

Phosphate fertilizer begins its life as phosphate rock. Phosphate rock deposits are found worldwide, but production is concentrated in a relatively small number of mining countries – as Figure 1 shows, 90% of all production comes from the top 10 producing countries, and nearly 7% from just the top three producers – China, the US and Morocco. Mined production has been boosted by new mines in Saudi Arabia and Morocco, Jordan and Brazil, while production has fallen in Tunisia since the Arab Spring, due to ongoing industrial disputes.

Fig. 1: **Phosphate rock production, 2016**



Source: IFA

Table 1: **World phosphoric acid production, 2016, million tonnes P_2O_5**

China	17.9
USA	7.2
Morocco	5.1
Russia	3.1
India	1.9
Saudi Arabia	1.3
EU	1.3
Brazil	1.2
Tunisia	0.9
Jordan	0.8
Israel	0.6
Others	3.5
Total	**44.8**

Source: IFA

Sulphur and sulphuric acid consumption generally follows mined production, as phosphate rock is large and bulky to transport, and it is usually easier to import sulphur than export phosphate rock or concentrates. However, there is a traded market of around 27 million t/a of phosphate rock – around 14% of total world production. This is down from the figure of around 20% a decade ago as phosphate rock producers, particularly Morocco, have sought to capture a greater share of the downstream market for processed phosphates. Nevertheless, Morocco remains for now the largest exporter of phosphate rock, at around 8 million t/a, followed by Jordan, Peru, Egypt and Russia. The major importing country is India, which imports around 7 million t/a of phosphate rock; India maintains a considerable domestic phosphate industry in spite of relatively low mined production.

New production totals 23 million t/a of phosphate rock capacity added between 2016 and 2021, according to IFA figures. Morocco accounts for 6 million t/a of this, and Saudi Arabia 5 million t/a, and there is also more rock output due from Tunisia, Algeria, Egypt, and Jordan. Outside the Middle East and North Africa, Brazil, Peru, Senegal, Russia, Kazakhstan and Canada are also looking at new production. Some production cuts are forecast in China.

Supply: phosphoric acid

Most phosphate rock is processed with sulphuric acid to produce phosphoric acid. This can then be combined with other products to produce finished fertilizers. The largest slice of phosphoric acid demand comes from combination with ammonia to produce monoammonium phosphate (MAP) and particularly di-ammonium phosphate (DAP). Phosphoric acid can also be used to treat phosphate rock to produce the phosphate rich triple superphosphate (TSP). Phosphoric acid production is thus the major source of phosphate demand for sulphuric acid, although there is also a lesser but still significant slice due to direct fertilizer production from phosphate rock and sulphuric acid, so-called single superphosphate (SSP), more on which below.

World phosphoric acid production in 2016 is shown in Table 1. This total has increased by about 30% since 2000, but most of that growth occurred from 2007-2013, and almost all of it happened in China, where capacity virtually tripled. At the same time, there has been a slow run-down of capacity in North America and, more recently, major boosts to production in the Middle East and North Africa. From 2001-2012, demand for phosphoric acid outstripped supply, leading to a run of high prices, but Chinese capacity building pushed the market into surplus from about 2012 onwards.

New phosphoric acid capacity is expected in Morocco, where OCP plans to build 2.6 million t/a (P_2O_5) between 2016 and 2021 at its Jorf Lasfar Phosphate Hub. Saudi Arabia is in the process of commissioning its 1.5 million t/a phosphoric acid plant at Wa'ad al Shamal. In spite of its overcapacity, there are still more phosphoric acid plants under construction in China, totalling some 1.5 million t/a, from 2016-19. There is an open question as to what will happen to Chinese excess capacity, as detailed below. Other new expansions are expected in Russia at PhosAgro and Eurochem, totalling 350,000 t/a, and in Brazil, with another 200-400,000 t/a, depending on the timing of various projects. Overall, global phosphoric acid capacity is forecast to increase by 7 million t/a P_2O_5 to just over 64 million t/a. At the same time, phosphoric acid demand is only forecast to increase by 4.1 million t/a to 48.8 million t/a P_2O_5, leading to a large overhang of excess capacity.

Morocco

Morocco holds an estimated 75% of the world's reserves of phosphate, and state-run Office Cherefien des Phosphates (OCP) represents 5% of the country's GDP, 20% of its exports and about half of all government revenues. While OCP is already the world's largest phosphate rock producer, a few years ago it embarked on an ambitious $16 billion expansion programme which aimed to not only double its phosphate rock capacity by 20205 but also to massively expand its downstream phosphate processing capability to achieve a greater market share. This programme takes the form of 25 million t/a of new mining at existing mines near Khouribga and Gantour, and the development of a new mine at Meskala, as well as six new beneficiation plants; three at Kouribga, and one each at Gantour, Meskala and Laayoune, together with two slurry pipelines to bring the concentrate to processing plants at the coast, from where the finished phosphates can be exported.

The downstream processing will happen at two 'phosphate hubs' at Safi and Jorf Lasfar. The first phase of the development has added four pairs of MAP/DAP plants at Jorf Lasfar. Three of these plants are now fully commissioned – the most recent in March 2017 - and the fourth one is under commissioning at present and is expected to be producing at full capacity by early next year. These four plants have added 2.25 million t/a of P_2O_5 capacity in Morocco. A further six pairs of MAP/DAP plants are planned in Phase 2, out to 2025, adding another 2.7 million t/a of phosphoric acid capacity (P_2O_5 terms) at Jorf Lasfar, together with an additional 1.2 million t/a at Safi. Each of the 10 MAP/DAP complexes at Jorf Lasfar also includes a 1.5 million t/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 15 million t/a to Morocco's sulphuric acid production and 5 million t/a to the country's requirements for sulphur.

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In order to market this vast volume of phosphates, Morocco has taken a variety of steps, including diversifying into more speciality products, and setting up joint venture NPK plants in African countries – OCP already has more than 60% of the African phosphates market.

Saudi Arabia

Saudi Arabia has also taken a major strategic decision as regards phosphates, in its case to diversify its economy away from oil. Last year, the oil sector accounted for 42% of Saudi GDP, 90% of export earnings, and 87% of budget revenues, and in a low oil price environment the country has been haemorrhaging foreign currency reserves, which have dropped form $737 billion in 2014 to $487 billion in July. Saudi Arabia's Vision 2030 plan, launched last year, hopes to triple non-oil revenues by that time, and mining is one of the sectors that has been already long been identified as an opportunity.

The fruits of this have come from the Saudi Mining Company (Ma'aden), which together with Sabic operates the Ma'aden Phosphates Company, producing 11 million t/a of phosphate rock from mines at Al Jalamid and downstream MAP and DAP production at Ras al Khair on the coast. Now a new 2.6 million t/a DAP plant at Ras al Khair is starting up as production begins at Wa'ad al Shamal, where Ma'aden and Sabic are in partnership with major US producer Mosaic, which has a 25% stake in the project and a corresponding share of the offtake. The new, lower cost source of phosphates – Mosaic's first venture outside the US – has allowed it to rationalise some of its less profitable US operations, and may be a cue for further reduction in US output.

Sulphuric acid production for Saudi Arabia's phosphate production is expected to be about 5 million t/a at full capacity, requiring 1.5 million t/a of sulphur. This figure can be met from domestic production, but will reduce Aramco's exports of sulphur proportionately.

China

China has made the running in the phosphate market for some years now, and is likely to continue to do so. The key question is: what will happen to Chinese overcapacity in DAP? According to CRU figures, China has an estimated 21-22 million tonnes P_2O_5 of capacity in MAP, DAP, TSP and NPKs, and a further 2.5 million t/a of purified acid and feed phosphate capacity. Domestic consumption for fertilizer use is about 10.5 million t/a P_2O_5 and has been in decline since it peaked in around 2010-13. China's cap on fertilizer application from 2020 will help ensure that this process continues, or at least that there is no increase. Production has run at around 17 million t/a, with most of the excess exported, contributing to the depressed global MAP/DAP markets. There have been capacity closures in China, but mostly the industry has been content to operate at low production rates of 60-80% of capacity. However, there are signs this may be changing. There has also been a steady rollback of subsidies to the industry, in terms of gas, electricity and rail freight prices and VAT exemptions. There are also increasing environmental concerns over gypsum stacks. The industry has begun to diversify, into downstream NPK production or merchant grade phosphoric acid for industrial uses and feed phosphates, but around 3.5 million t/a of capacity remains at high risk of closure, according to CRU.

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 are various plans to expand domestic phosphate capacity. Yara, in conjunction with Galvani, has an MAP and dicalcium phosphate project due to come on-stream at Serra do Salitre in 2018, which will bring domestic phosphate capacity to 3.7 million t/a P_2O_5. In addition, Vale, Copebras and MBAC all have phosphate projects under development, although start dates have been moved back, and for the moment Salitre is the only certain one.

Table 2: **Phosphoric acid capacity increases, 2017-2021 (million t/a P_2O_5)**

Morocco	+2.6
Saudi Arabia	+1.5
China	+1.5
Egypt	+0.5
Russia	+0.4
Brazil	+0.4
India	+0.1
Tunisia	+0.1
World	**+7.1**

Source: IFA

India

India is the world's major importer of phosphates. Imports of DAP are expected to be higher than 6 million t/a this year. Phosphate demand fell in 2016, and has only recovered this year to a similar position to 2015. However, changes to the subsidy regimen there are expected to see an increase in demand in future. The Indian government is moving to pay agricultural subsidies directly to farmers, rather than producers (who then offer discounted products). India has had a progressive problem with nutrient imbalance over the years due to the cheapness of urea compared to other fertilizers. While the new system may not cure that, it is anticipated that phosphate demand will increase. DAP demand may increase by 2.3 million t/a to 2021.

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 single superphosphate (SSP). 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. In 2015 some 25 million tonnes (4.2 million t/a P_2O_5) of SSP were produced and consumed. This is a significant fall – by about 0.5 million tonnes P_2O_5 – over the figure for 2013, and SSP consumption has in general been dropping, especially in China, where it is being replaced by MAP and DAP. Consumption had risen in India and Brazil – in India due to the high cost of DAP – but as DAP markets have fallen, so SSP consumption has fallen back again.

Impact on acid demand

Taking all of the phosphoric acid capacity increases discussed above, as Table 2 shows, a total of just over 7 million tonnes P_2O_5 is due to come on-stream by 2021. This represents the equivalent of 21 million t/a of additional sulphuric acid demand, most of it in the Middle East and North Africa. 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. ■

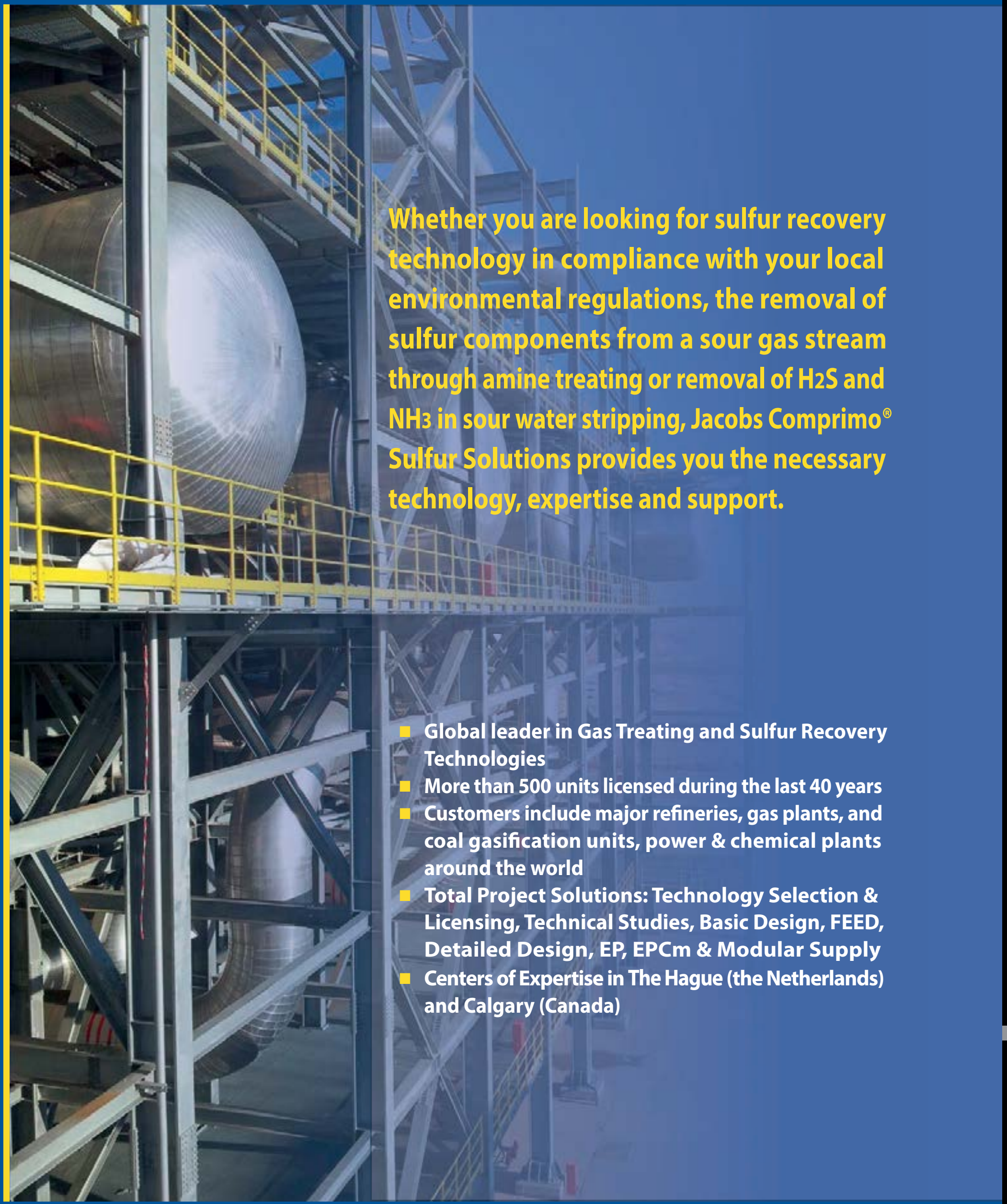

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PHOTO: ANDINA

Sulphur in South America

Left: *The Las Bambas copper mine, Peru.*

Changing patterns of leaching and smelting in Chile and Peru's copper industries, the growth of Brazil's phosphate fertilizer demand and troubles in oil major Venezuela are contributing to changing supply and demand patterns across the continent.

South America's sulphur industry ranges from sulphur production from refining, consumption in fertilizers and sulphuric acid generation and consumption from the region's extensive copper smelting and leaching operations. The region had been forecast to be a major rising star in the global economy, but the past few years have seen the economy stagnate during 2015 and even contract by 1% during 2016. This year is forecast to see a modest return to growth of 1%, and in 2018 this will reach 2%, but the long-term prediction is for only 2.6% growth. Low commodity prices on which the region depends and political instability in some of the major economies have taken their toll.

Of the continent's 420 million people, approximately half live in Brazil, which is also by far the region's largest economy, accounting for 80% of the region's GDP.

Sulphur production

Sulphur production in South America comes almost exclusively from oil refining. Here the two main refiners are Brazil and Venezuela, which between them operate two thirds of the continent's refining capacity. However, while Brazil has been expanding its oil and gas sector, Venezuela's output has stagnated due to lack of investment. Table 1 shows refinery capacity in South America. Also shown are refinery throughputs last year, and it is immediately obvious that in spite of the region's continuing deficit of refined products – forecast to widen to 860,000 bbl/d for diesel and 910,000 bbl/d for gasoline respectively by 2020 – its refineries run at relatively modest operating rates. This is because of a mismatch between refinery configuration and domestic demand product mix; many of the refineries have lagged well behind their North American counterparts in terms of upgrading and desulphurisation capacity.

A further issue has been the slow descent of Venezuela into political chaos, as low oil prices have bankrupted an economy that has been used to spending freely, and which has few other sources of foreign revenue. Although Table 1 shows Venezuela refinery operating rates averaging 53% for 2016, this year the figure has been much lower, closer to 40%, and the country's main refining complex at Paraguana has been at only one third capacity, contributing to intermittent fuel shortages in the country which have themselves exacerbated social unrest. Lack of investment and maintenance have led to intermittent output and frequent shutdowns. Ambitious plans to expand Venezuela's production from the Faja de Orinoco – the oil sands belt across the centre of the country – have been put on hold. Venezuela remains the region's largest sulphur producer – its oil is heavy and sour (averaging 2.4% sulphur by weight), and even at low operating rates it still – just – produces more than neighbouring Brazil. It is also the only significant sulphur exporter in the region, but production now runs far below its peak of 950,000 t/a in 2006. The only bright spot this year has been an announcement from Hyundai that it has been in discussions with the Venezuelan government to accelerate work in the Puerto la Cruz Deep Conversion Project, a heavy/very heavy oil upgrader at Anzoategui, 300km east of Caracas, which was said to be 80% complete a few months ago. Once complete the refinery will be able to process 210,000 bbl/d of Orinoco oil sands oil instead of the 180,000 bbl/d of light/medium oil that it currently processes, and this should boost Venezuela's sulphur output by 150,000 t/a as and when it is completed and running at capacity.

Table 1: **Refinery capacity in South America, 2016**

Country	No. refineries	Capacity (bbl/d)	Throughput (bbl/d)
Argentina	8	657,000	511,000
Bolivia	3	63,000	n/a
Brazil	16	2,289,000	1,831,000
Chile	3	258,000	263,000
Colombia	5	421,000	239,000
Ecuador	3	210,000	150,000
Peru	6	253,000	185,000
Uruguay	1	40,000	n/a
Venezuela	10	1,303,000	698,000
Total		**6,259,000**	**4,490,000**

Source: BP

Currently it is due to begin operations next year, but it is already years late and billions over budget, and given the current situation in Venezuela, it is anyone's guess when it might actually be up and running.

Brazil, by contrast, has been expanding its refining capacity in the past few years, flush with new oil from offshore discoveries. However, around 99% of this capacity is in the hands of the state oil company Petrobras, which is only now emerging from the major 'Lava Jato' corruption and money laundering scandal which has heavily impacted upon the company's credibility and which led it to slash its ambitious expansion and investment plans for 2017-21. Rising construction costs have also put back some refinery upgrades. For the sulphur industry, the abandoning of the Premium I and II refineries at Maranhao in 2015 has removed 230,000 t/a of potential new sulphur production. The company's new chief executive has concentrated on cutting the company's vast debts instead, but Brazil nevertheless says that it intends to boost oil output to 3.4 million bbl/d and refining capacity to 2.8 million bbl/d by 2021. The Rnest and Comperj refineries are now back on track after the projects were suspended in 2014 in the wake of the scandal, although Comperj is not now expected to be completed before December 2020. The Rnest project includes an emissions abatement unit which will process I. Part of this project includes a sulphur emissions reductions unit which will allow the facility to process 650,000m3 of sulphur-rich process gas and which will generate 700 t/d of sulphuric acid from a Topsoe WSA unit. This is now expected to be on-stream in 2018.

Sulphur demand – fertilizers

Most sulphur demand in South America goes into fertilizer production, and here the giant is Brazil. Brazil produced 5.1 million tonnes of phosphate rock in 2016, and has the world's 12th largest reserves of phosphates, at 270 million tonnes. Brazil consumed 5.1 million tonnes P_2O_5 of phosphate fertilizer in 2016, recovering 13% from a depressed 2015, and while this figure was lower than the peak in 2014, it still represents an average growth rate of 6% this decade. Phosphate fertilizer production in Brazil totalled 0.6 million t.a P_2O_5 of mono-ammonium phosphate (MAP), 0.4 million t/a of triple superphosphate (TSP), and 0.9 million t/a of single superphosphate (SSP), leaving a 3.2 million t/a gap which is filled with imports, mainly of MAP. Brazil's demand for phosphates is forecast to rise at an average rate of 2.2% per annum going forward, with the prospect of new phosphate production coming from Galvani's Serra do Salitre project in Minas Gerais, mining 1.2 million t/a of phosphate rock, and producing 350,000 t/a of MAP (tonnes product). Other phosphate projects include Anglo at Catalao and Galvani at Santa Quiteria, with more MAP and TSP production in the 2019-2020 timeframe.

Peru's estimated reserves of phosphate rock are actually three times that of Brazil and ninth in the world. Peru was not a phosphate rock producer, however, until very recently (2010), when the Bayovar phosphate mine opened in the extreme northwest of the country. Since then, phosphate rock production in Peru has increased rapidly, and reached 3.9 million t/a in 2013. However, Bayovar, run by Brazil's Vale, is a coastal location and is set up to export phosphate concentrate, mainly to other locations in the Americas. There is no phosphoric acid production or other downstream fertilizer production at the site. Consequently, Brazil continues to be the main consumer of sulphur for sulphuric acid production, balanced by only 200,000 t/a coming from refinery sulphur production.

Sulphuric acid – smelting and leaching

Moving south, Chile and Peru have the lion's share of the world's deposits of copper. Chile has about 30% of the world's copper reserves, and Peru another 10%. Chile also produces about 30% of the world's copper – 5.6 million tonnes in 2016, of a total mined output of 20.2 million t/a. Peru produced 2.4 million t/a and was the world's second largest producer. Production rose 35% in Peru last year, due to increases at the MMG's Las Bambas mine, and Freeport-McMoRan Inc.'s Cerro Verde mine, the largest in Peru. But Peru has much bigger ambitions than this; a recent study counted 18 major new and growth copper projects in Peru, including expansion at Southern Copper's Toquepala and Chinalco's Toromocho mines. In theory, Peru's copper production could reach 4.8 million t/a by 2021.

While both counties operate both copper leaching and copper smelting plants, traditionally Chile has concentrated more on leaching operations, and hence been a major importer of acid to operate its solvent extraction/electrowinning (SX/EW operations), while Peru has been primarily a smelter and a net exporter of acid, mainly to Chile. According to Cochilco, the Copper Commission of Chile, Chile consumed 7.4 million t/a of sulphuric acid in 2016, and produced 5.7 million t/a from its smelters and sulphur burning acid plants, with the 1.7 million t/a remainder imported, 70% of it from Peru, but with other major volumes from Japan, Korea and Mexico. But Chile's production of acid has increased by 1 million t/a since 2007 while consumption peaked in 2012 at 8.4 millon t/a, and has since been falling due to declining copper mine grades, cutbacks in SX/EW capacity, and expansions in copper smelting. Imports of acid fell over the same period from 3.2 million t/a to 1.7 million t/a. Cochilco is forecasting that Chile's acid imports will continue to fall, and by 2020 the country will become a net acid exporter, changing the dynamics of the region.

At the moment, smelter acid production dominates Peru's sulphuric acid market, and the country produces around 1.6 million t/a and consumes only 0.6 million t/a of sulphuric acid, with the rest being exported, mainly south to Chile. However, while smelter acid production continues to increase incrementally, two copper leaching projects could see Peru's acid surplus largely wiped out. Southern Copper's Tia Maria project has been much delayed and faced a lot of local opposition to the project, but the government said last month that it would allocate a key construction permit in 1Q 2018. Rio Tinto's La Granja project has likewise been on hold due to low copper prices and local opposition. These two projects together could take Peru's acid production to 1.5 million t/a, bringing acid exports down to only 300,000 t/a, but at the moment there is no firm start date for either project. Likewise there is no new smelter capacity on the cards for Peru in spite of the expected rise in copper production. Indeed, the Doe Run smelter at La Oroya is currently facing permanent closure, and President Kuczynski's attempts to attract investment in a new project in the south have not drawn much interest so far.

Meanwhile, of the other countries in South America, only Brazil also produces significant volumes of acid from smelting – around 700,000 t/a, all of which is consumed domestically by the fertilizer industry. Brazil also imports another 0.4 million t/a of sulphuric acid.

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Metal markets and acid production


PHOTO: KGHM

The Glogów smelter, Poland.

Low prices for copper and nickel have dramatically scaled back mining projects, especially on the leaching side, but smelter capacity continues to increase in China and Indonesia.

Out of total global sulphuric acid production of around 260 million t/a, the amount represented by metallurgical acid was just under 80 million t/a in 2016, 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, but smelting of sulphide ores is an oxidative process which generates sulphur dioxide. In the past much of this was simply released to atmosphere, but increasing evidence of the damage that sulphur dioxide can do to human health and the environment has led to it increasingly being captured and converted into sulphuric acid.

Conversely, metal oxide ores are often treated with sulphuric acid to recover the metal as a soluble sulphate. This leaching process is a major consumer of sulphuric acid, accounting for just over 10% of all acid demand in 2016, and the balance between leaching and smelting, and the state of the metal markets that they feed into, are key determinants in the supply of sulphuric acid.

Copper

Copper is the main driver of both smelter acid production and consumption for leaching. Copper demand is mostly for electrical wiring, industrial machinery, electronic products, transportation and similar fields, and so is closely correlated with industrial production. Most incremental demand over the past 20 years has come from China's industrialisation, and due to the long timescales of copper mine development, as China's industrialisation has slowed dramatically from about 2010, so copper markets have been pushed towards greater and greater surplus. Major producers had been holding back on cutting production and scrapping new projects in an attempt to force the competition to do so instead, and hence copper markets had been on a downward trajectory for most of this decade. The production cuts came in 2015, with a number of projects curtailed and mines idled. Because they have tended to be towards the higher end of the cost curve, it has tended to be mining projects which relied on acid leaching rather than producing copper concentrate, and so this has had the effect of boosting acid supply. It has also had the desired effect on copper markets, however, where prices had touched bottom in late 2015 at around $4000/t, half of their value a few years earlier, and since then the general trend has been back upwards, peaking at $6,970/t on the London Metal Exchange in September 2017. There has been a slight softening since then, as metal markets have taken stock and decided that this price is too exuberant for a market that still has ample supply – China did not make production cuts this year, for example. Nevertheless, the price rise has pushed many projects back into the black financially, and mining activity is picking up again.

Nickel

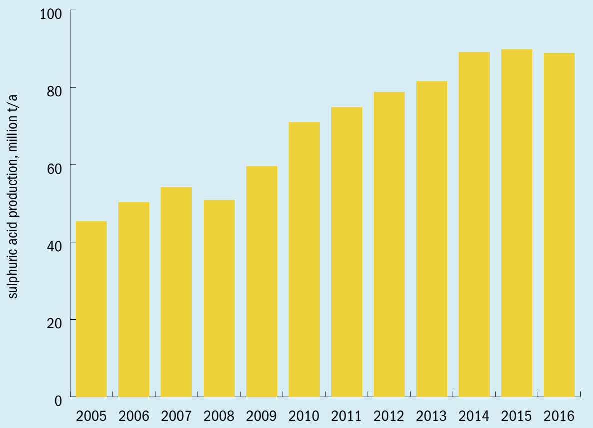
Nickel is, like copper, closely tied to industrial growth. Just over two thirds of all nickel (68%) is used in the manufacture of stainless steel, and the rest goes into other alloys (16%), nickel plating (9%), casting (3%) and nickel-cadmium batteries (3%). As with copper, China has come to dominate the market, consuming 52% of all nickel in 2016. And as with copper, overcapacity has brought markets low earlier this decade as China's industrial demand slows.

However, nickel has some wrinkles compared to copper – nickel production had historically been from sulphate ores which required smelting and generated acid. While the market for nickel is much smaller than copper (around 2 million t/a as opposed to 24 million t/a), nickel ore grades are lower, so smelting can generate more sulphur per tonne of metal than it does for copper (up to 8 tonnes of acid per tonne of nickel, compared to typically 3 tonnes for copper). However, a shortage of available sulphate ores has led to greater concentration on more readily available but lower grade laterite (oxide) ores. Some of these are processed via leaching, but nickel is chemically bound more tightly than copper and so nickel leaching is far more difficult than copper. This means that either it requires higher temperatures and pressures to force the leaching operation (so-called high pressure acid leaching, or HPAL), or else, if done atmospherically, either a bacterial agent to assist or simply longer time frames (heap leaching). HPAL, which consumes several million t/a of sulphuric acid, has suffered from high costs and operability problems, and this has led to the increasing prominence of pyrometallurgical processes, particularly ferronickel and so-called nickel pig iron (NPI) production, both of which are nickel-iron alloys which can be used (only) in stainless steel production. NPI has come to represent 20% of the nickel market, mainly in China, and new nickel smelting and leaching projects are very few and far between.

Zinc and lead

Zinc and lead production produce the remainder of the world's smelter acid. While demand for both metals is roughly comparable at around 11-14 million t/a, lead has a much higher rate of recycling, from e.g. old lead-acid batteries, which represent about 70% of all demand for lead, especially for scooters, and lead's fortunes are closely tied to the transportation sector. Zinc is mainly used in galvanising of steel (50%), and the manufacture of brass and bronze alloys and die casting, and is closely linked to construction and urbanisation. As with copper and nickel, China has driven world markets this decade, and represents around 45% of all consumption of both metals.

Fig. 1: **China's sulphuric acid production, million tonnes/year**



Source: National Bureau of Statistics of China

China

As noted above, China has come to be the major global market for metals and has expanded its own metals mining and processing industries accordingly to cope with this. This has had a knock-on effect on acid production; Figure 1 shows the growth in China's sulphuric acid industry, and the spurt of growth between 2005 and 2012 can be clearly be seen. Chinese sulphuric acid production was 88.9 million t/a in 2016, and although this was actually a fall of 0.8% on 2015, it means that China now represents 36% of the world's sulphuric acid output. As well as non-ferrous metal smelter expansions, China has also increased its sulphur burning acid capacity to process phosphates for the rapid growth in its diammonium phosphate (DAP) production.

Smelter acid capacity has come 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. According to the International Copper Study Group (ICSG), China has four out of the five largest copper smelters, and nine of the 20 largest. The five largest alone collectively represent 3.15 million t/a of copper smelting capacity, or about 12% of global copper capacity. Chinese copper production from smelters reached 7 million t/a in 2015, representing 21 million t/a of sulphuric acid production. However, while China has built to overcapacity in many industrial areas, copper production is one of the few areas where domestic refined production has lagged behind demand, and China has had to make up the remainder with imports.

Chinese copper demand continues to increase, and the government projects in the current Five Year Plan that it will rise from 11.5 million tonnes in 2015 to 13.5 million tonnes in 2020 – an annual growth rate of 3.3%. While this is considerably down on historical trends of around 9% year on year from 2010-15, it nevertheless has provided a much-needed boost to the global copper market. China is still in a programme of import substitution with its copper smelter capacity, and hence it is continuing to build new copper smelters even though the pace of Chinese industrialisation has slowed considerably and copper consumption has plateaued for the time being. Chinese smelter acid capacity increased by a tremendous amount over the 2010-15 period – an estimated

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4 million t/a of copper or 12 million t/a of acid. A further 5.0 million t/a is expected to come on-stream over the 2016-2020 period. Something like 70% of all new smelter acid capacity is being added in China over the next few years. Looking to the medium term future, this increase in smelter acid production is projected to lead the Chinese acid market into surplus by 2020, and by 2025 there could be a 1.5 million t/a acid surplus for China in spite of potential pressure on pyrites and sulphur-burning capacity to switch.

Indonesia

The other country that is rapidly building smelter capacity is Indonesia. Here the reason is to try and move downstream from simply mining and exporting copper concentrate and nickel ore to China to processing it at home and capturing more of the value chain. Indonesia's government has tried to do this via the relatively blunt instrument of a ban on exports of ore and concentrate. While there has been some pushback on this on the copper side from Freeport, which operates the Grasberg mine and owns 25% of Indonesia's original copper smelter at Gresik, it seems to be having a major effect on the nickel side. Most of the nickel processing plants are pyrometallurgical however. There is a 150,000 t/a (tonnes nickel) ferronickel plant starting up this year, and Indonesia is also investing heavily in nickel pig iron production - Glencore has forecast that this will reach 225,000 t/a of nickel by 2019. The reduction in ore availability from Indonesia is likewise impacting on Chinese NPI production. The concentration on pyrometallurgical processes means that there will be no new acid from Indonesia's nickel processing.

On the copper side, the government's attempt to force Freeport to build a new $2 billion smelter on Papua have not so far borne fruit, and Freeport is holding out for a guarantee from the government that it will continue to be able to export copper concentrate from Indonesia. Consequently new smelter acid capacity from Indonesia still looks to be modest over the medium term time horizon.

New supply

At the moment, China still looks to be the major source of new smelter acid, with over 5.0 million t/a of new capacity coming on-stream during the current Five Year Plan (2015-20). New investments in SO_2 capture at existing smelters in Africa have seen acid output increase in recent years in Namibia, where the Tsumeb smelter can produce 300,000 t/a of sulphuric acid at capacity, and at Chambishi, Kansanshi and Mufulira in Zambia – Kansanshi adds another 1.0 million t/a of acid capacity. In Botswana, the BCL copper-nickel smelter at Slebi-Phikwe has been upgraded to capture more SO_2 but has not been operational since 2015. Norilsk Nickel is now in talks to buy the smelter and re-open it.

In North America, there is actually 100-300,000 t/a less acid availability from Canada, which is a major acid exporter to the United States, now that Vale has completed refurbishments at Subdury. The US may make up for this with smelter expansions at Miami, Arizona for Freeport.

Environmental improvements at smelters in Russia will also lead to additional acid production at Svyatogor from 2018. Norilsk Nickel has chosen to produce sulphur rather than sulphuric acid because of the remoteness of the site and lack of demand for acid locally, and Nornickel on the Kola Peninsula near Finland is considering whether to produce acid or sulphur from its own environmental improvement. Kazakhstan is also looking towards boosting domestic concentrate processing.

New demand

In Mexico, there is fresh demand from the ramp-up of the El Boleo copper, cobalt, zinc and manganese mining and processing operation. There is both a smelter and a SX/EW hydrometallurgical processing facility which will produce a total 62,000 t/a of copper at capacity. The smelter started up before the SX/EW plant and hence the site managed 400,000 tonnes of acid exports in 2015, but as SX/EW processing has expanded so acid availability from El Boleo has fallen.

Other changes, as we note in or article elsewhere this issue, are occurring in South America. Chile, which produces 30% of the world's copper, is tightening environmental regulations, prompting investment in upgrading the country's existing smelter capacity. At the same time, falling ore grades in the existing SX/EW plants are leading to something of a run-down in processing there. Chile consumed 7.4 million t/a of sulphuric acid in 2016, and produced 5.7 million t/a from its smelters and sulphur burning acid plants, with the 1.7 million t/a remainder imported, 70% of it from Peru, but with other major volumes from Japan, Korea and Mexico. But Chile's production of acid has increased by 1 million t/a since 2007 while consumption peaked in 2012 at 8.4 million t/a, and has since been falling. Imports of acid fell over the same period from 3.2 million t/a to 1.7 million t/a. Cochilco is forecasting that Chile's acid imports will continue to fall, and by 2020 the country will become a net acid exporter, changing the dynamics of the region.

Peru meanwhile, which produces about 10% of the world's copper, is aiming to double this to 20% via an ambitious expansion programme. Peru produced 2.4 million t/a of copper in 2016 and was the world's second largest producer, with production 35% up on 2015 due to increases at the MMG's Las Bambas mine, and Freeport-McMoRan Inc.'s Cerro Verde mine, the largest in Peru. There are some 18 major new and growth copper projects in Peru, including expansion at Southern Copper's Toquepala and Chinalco's Toromocho mines. In theory, Peru's copper production could reach 4.8 million t/a by 2021.

Currently Peru produces 1.6 million t/a of acid and consumes 0.6 million t/a, exporting most of the rest to Chile. But Peru's future availability of acid depends upon the potential several major projects. On the SX/EW side; Southern Copper's much-delayed Tia Maria project has faced a lot of local opposition, but the government said last month that it would allocate a key construction permit in 1Q 2018. Rio Tinto's La Granja project has likewise been on hold due to low copper prices and local opposition. These two projects together could take Peru's acid production to 1.5 million t/a, bringing acid exports down to only 300,000 t/a, but at the moment there is no firm start date for either project.

Meanwhile, the smelter at Ilo, with 1.7 million t/a of acid capacity, has faced persistent battles with the government over emissions, and was threatened with closure in 2013. A deal now seems to have been struck which will see the SO_2 emission limit change held in abeyance in return for $350 million of environmental improvements. 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. While a re-start for La Oroya looks unlikely, improvements at Ilo could lead to higher acid output. ■

From HF to sulphuric acid alkylation

DuPont has introduced new technology for converting HF alkylation units into sulphuric acid alkylation units, while also achieving significant capacity increases. By significantly minimising capital expenses and maximising alkylate production, the DuPont™ ConvEx℠ HF alkylation conversion technology makes HF conversion projects much more attractive to refiners than in the past.

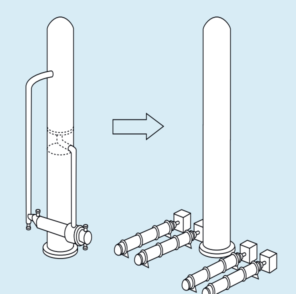
With a ban on hydrofluoric acid (HF) being considered in some parts of the US and significant doubt around the long-term viability of HF alkylation technology, refiners must consider whether additional investment in existing HF alkylation units is wise. Although HF conversion to sulphuric acid alkylation has been considered by refiners for many years, due to the risks associated with the use of HF, several factors have led to refiner inaction to date. These factors include: the perceived high cost of conversion and the lack of economic value from a conversion.

DuPont has been listening to the concerns and constraints of HF alkylation refiners and, based on this feedback, has introduced the DuPont™ ConvEx℠ HF alkylation conversion technology, the first cost-effective solution that enables refiners to convert volatile and toxic HF alkylation units into safer sulphuric acid alkylation technology, while significantly increasing the design capacity of the existing HF alkylation unit. To provide refiners with an economic incentive for HF conversion, DuPont has taken advantage of a key difference between HF and sulphuric acid alkylation to provide an opportunity for a significant capacity increase at the same time as the conversion. In many cases, capacity increases of 100% or more are possible with minimal additional cost beyond the cost of conversion.

Conversion and expansion solutions

DuPont has developed innovative, low-cost ConvEx℠ HF conversion and expansion solutions for both major HF alkylation technologies: gravity flow reaction section and pumped flow reaction section.

Fig. 1: **HF acid coolers replaced with STRATCO® Contactor™ reactors**



Source: DuPont

The first conversion option using the time-tested STRATCO® Contactor™ reactors will match the performance of a grassroots STRATCO® alkylation unit.

The second option includes a patent-pending novel reactor, which utilises proven design elements and includes DuPont's latest reaction research innovations. This option is intended to be a lower-cost solution with a minor performance debit compared to the other option.

These two HF alkylation conversion choices allow refiners to select the solution that works best with their unit configuration and best aligns with their operational and business needs.

STRATCO® Contactor™ reactor option

The ConvEx℠ HF technology solution utilising STRATCO® Contactor™ reactors is suitable for refiners with either a gravity flow or pumped flow HF alkylation unit. The case study featured in this article employs this option for the conversion of a gravity flow HF alkylation unit.

The gravity flow HF alkylation technology uses a single, large, vertical acid settler with sieve trays and multiple acid coolers. The HF-catalysed alkylation reaction between olefins and isobutane occurs in the acid riser pipe; multiple large HF acid coolers use cooling water to remove the heat released by the alkylation reaction.

Fig. 1 depicts such a conversion where Contactor™ reactors are installed in place of the existing HF acid coolers. The reactors can also be elevated on a deck for closer proximity to the settler. This arrangement can minimise unit downtime by allowing refiners to install the new reactors while the existing HF acid coolers remain in service.

Four reactors are shown in the schematic for illustration purposes, as the actual number of reactors will be determined based on the required plant capacity. The larger STRATCO® Model 74 Contactor™ reactors can be used to reduce equipment count, minimise plot space and reduce cost.

The existing HF acid settler is shown in Fig. 2 and will be modified to function optimally in sulphuric acid emulsion service. The HF settler modifications include segmenting of the acid-rich zone to allow for acid staging and adding two stages of coalescing media for the separation of acid and hydrocarbon. The lighter hydrocarbons in the combined settler effluent are flashed across a pressure control valve prior to entering the tube bundle inlets to cool and remove the heat of reaction. The tube bundle outlet is routed to a new refrigeration section before proceeding to fractionation. The flashed vapours are

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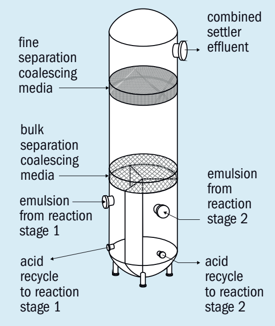
Fig. 2: **Segmented acid settler for the conversion to sulphuric acid alkylation**



Source: DuPont

subsequently compressed, condensed and returned to the reactor feed providing additional cooling and contributing a large amount of isobutane to the isobutane-to-olefin ratio. The recycle isobutane from fractionation and the refrigeration section ensures that conditions are optimum for the alkylation reaction. The converted acid settler can be segmented such that one large acid settler can function as multiple individual settlers.

Novel reactor option

DuPont recently developed a novel reactor, which utilises proprietary mixing and separation equipment. This option can also be used to convert and expand either a gravity flow or pumped flow HF alkylation unit. The existing HF acid settler is converted to a sulphuric acid alkylation reactor utilising common refinery equipment with no moving parts within the converted acid settler. It is a lower cost, yet robust design option for HF conversion.

Conversion basics

Sulphuric acid alkylation reactions are typically optimised at a reaction temperature of 7°C (45°F) while most HF alkylation units operate around 38°C (100°F). Although the heat generated by the exothermic alkylation reactions is similar regardless of the catalyst, the reaction heat released from an HF alkylation unit can be removed by cooling water, while sulphuric acid alkylation units require refrigeration to achieve the colder reactor temperatures. Both conversion options require the addition of a refrigeration section and new feed/effluent heat exchangers to achieve the desired 7°C (45°F) reactor temperature.

To protect the downstream fractionation section from corrosion and fouling, an acid coalescer and dry alumina treaters are installed. Existing HF recovery equipment in the HF alkylation unit may be repurposed for these applications. Removal of SO$_2$ from the propane product is also required in the sulphuric acid alkylation unit; however, existing equipment in the propane product treating section can typically be reused for this purpose without significant modifications.

Finally, the entire fractionation section, which is oversized for sulphuric acid alkylation, can typically be reused in its entirety with little or no changes.

Value through expansion

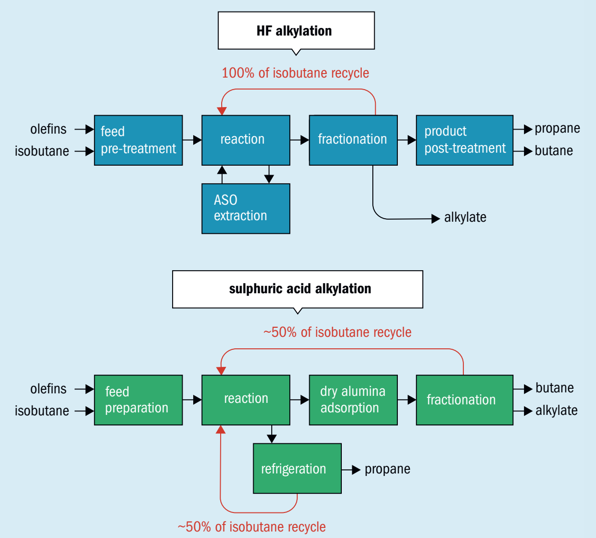
The DuPont ConvEx℠ HF conversion and expansion solutions leverage one key distinction between HF and sulphuric acid alkylation units: the relatively large fractionation facilities already present in HF alkylation units. This allows for a significant capacity increase with minimal additional investment above the conversion cost. For both processes, a high flow rate of isobutane to the reaction section is required for good performance of the alkylation unit. Maintaining a sufficient isobutane-to-olefin ratio ensures favourable kinetics to drive more reactions between olefins and isobutane and less olefin oligomerisation reactions that lead to higher acid consumption and poor alkylate quality.

A comparison of how isobutane is recycled in the HF and sulphuric acid alkylation processes is shown in Fig. 3. For the HF alkylation process, all isobutane is recycled from the fractionation section, so the distillation towers must be sized adequately to handle a large recycle stream. In the sulphuric acid alkylation process, about half of the total isobutane is recycled from the fractionation section. The other half of the isobutane required for the isobutane-to-olefin ratio is recycled from the refrigeration section, where effluent vapours are compressed, condensed and then pumped back to the reaction section as refrigerant recycle.

This difference between the isobutane recycle streams in HF and sulphuric acid alkylation units is the key to the large expansion potential. With plenty of isobutane recycling from the new refrigeration section to the reaction zone, the existing fractionation section is significantly unloaded. This allows for a substantial capacity increase of the alkylation unit without requiring extensive changes to the fractionation equipment. Additionally, since the refrigeration section will be new as part of a conversion, the incremental cost of that equipment for a capacity increase is minor compared to the overall investment of that equipment.

Another difference between HF and sulphuric alkylation is that sulphuric acid alkylation is not very sensitive to feed contaminants. The HF alkylation process, on the other hand, is very sensitive to contaminants such as water and requires feed dryers. Although water dilutes the acid in the sulphuric acid alkylation process, there is no strict requirement for water removal. In fact, grassroots STRATCO® alkylation units, where dry alumina adsorption is used, do not typically include feed coalescers or feed dryers. The dry alumina adsorption section results in a dry isobutane recycle stream, so the very small amount of water entering the alkylation unit is only from the olefin feed and makeup isobutane. Although there may be a small reduction in acid consumption if the existing HF feed dryers are used, there is no need to modify or replace them as part of an expansion and conversion to sulphuric acid.

Fig. 3: **Comparison of isobutane recycle streams in the HF and sulphuric acid alkylation processes**



Source: DuPont

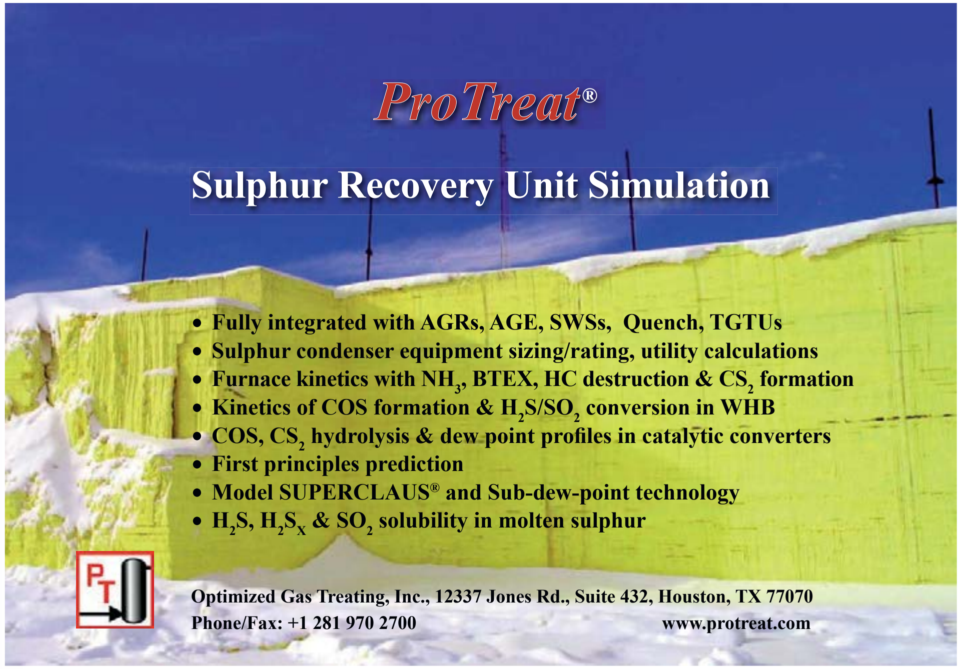
Metallurgy considerations

The primary metallurgy selection for piping and equipment in sulphuric acid alkylation units is carbon steel. In a few locations within the unit, where carbon steel is not suitable, others materials such as stainless steel, Alloy 20 and Alloy C276 are utilised. The same is true for HF alkylation in that carbon steel is acceptable in most services in the unit. However, in the services where carbon steel is not suitable in HF alkylation units, Monel 400 (a trademark of Special Metals Corporation) is typically used because stainless steel and its alloys are generally not suitable in HF acid service.

Although Monel 400 can be used effectively in low-strength sulphuric acid services, there is a sharp increase in the corrosion rate as the acid strength increases above 25 wt-% due to the fact that sulphuric acid takes on oxidising characteristics at higher strengths. Since most sulphuric acid alkylation units operate with acid strengths greater than 85 wt-%, Monel 400 does not provide good corrosion resistance where large concentrations of sulphuric acid are present.

This is not typically of great concern with regards to conversion from HF to sulphuric acid alkylation because those portions of the HF alkylation unit that contain Monel 400 are generally not reused anyway. However, because some refiners have upgraded the metallurgy in other parts of the unit, a full metallurgy evaluation is recommended.

While Monel 400 is not recommended for services where the primary fluid is high-strength sulphuric acid, hydrocarbon-continuous streams with dispersed sulphuric acid are less of a concern because the hydrocarbon can provide some protection from corrosion by the acid. This would apply to several services within the sulphuric acid alkylation unit, such as the net effluent piping.



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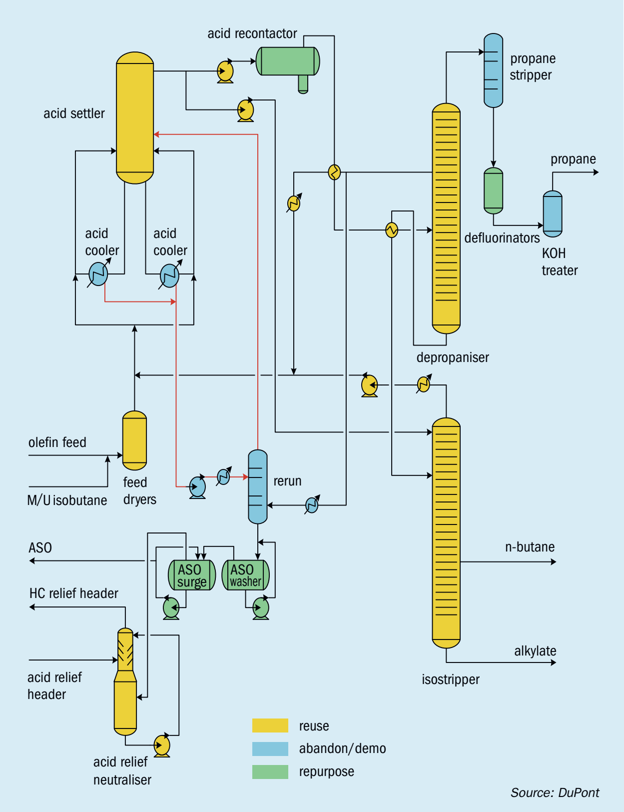
Project economics

One of the main objectives of DuPont when developing the ConvEx^{SM} technology was to deliver solutions with a step-change reduction in cost compared to other solutions on the market. Historically, the expense of converting from HF to sulphuric acid alkylation was estimated by the industry at 80% of the cost of a grassroots sulphuric acid alkylation unit of a similar size. This perceived high conversion cost and the lack of any other economic benefits deterred refiners from committing to this change By maximising reuse of existing equipment, the conversion solutions offered by DuPont are estimated to be 40-60% the cost of a grassroots sulphuric acid alkylation unit of a similar size. When considering this lower investment in addition to the opportunity to gain value through expansion of alkylate capacity, HF conversion is much more attainable than previously perceived.

Another aspect of HF conversion that can greatly impact project economics is the time required for construction, and specifically the time required for construction during a unit turnaround. Extending the duration of a turnaround and increasing unit downtime leads to higher lost opportunity costs and can be detrimental to the refinery economics. The most significant new construction required for a conversion from HF to sulphuric acid alkylation is the refrigeration section, including a new refrigerant compressor. If plot space is available near the existing unit, installation of this new equipment can occur during normal operation outside of the turnaround window. The same is true for the dry alumina adsorption section, if existing HF equipment is not available for reuse. If the installation of the majority of the new equipment can be done outside of the turnaround, it is feasible to complete the remainder of the work required for HF conversion within a typical 30-45 day turnaround window.

Fig. 4: **Case study: existing gravity flow HF unit**



Source: DuPont

Case study

This case study involves the conversion of a gravity flow HF alkylation unit with a single vertical acid settler and four acid coolers. Fig. 4 shows a simplified process flow diagram of the original HF alkylation unit and Fig. 5 shows the converted unit.

The design capacity for the original HF unit was 13,500 bbl/d of alkylate product with a feed stream consisting of MTBE raffinate. The converted unit makes 24,435 bbl/d of alkylate, representing a capacity increase of 81% as result of the conversion and expansion using the ConvEx^{SM} technology.

The existing fractionation equipment includes isostripper and depropaniser columns. After conversion, reactor effluent from the acid settler is split to both reflux the isostripper and provide the feed stream to the depropaniser. The depropaniser overhead is the propane product and the bottoms stream contains isobutane, normal butane and alkylate which is routed to the isostripper as feed. The depropaniser also yields a side stream which provides a portion of the recycle isobutane to the reaction section. The isostripper yields a n-butane product side draw and the bottoms alkylate product. The isobutane-rich isostripper overhead stream is condensed, sub-cooled and then pumped to the reaction section, providing another portion of the recycle isobutane. The refrigeration section provides additional isobutane to the reaction zone.

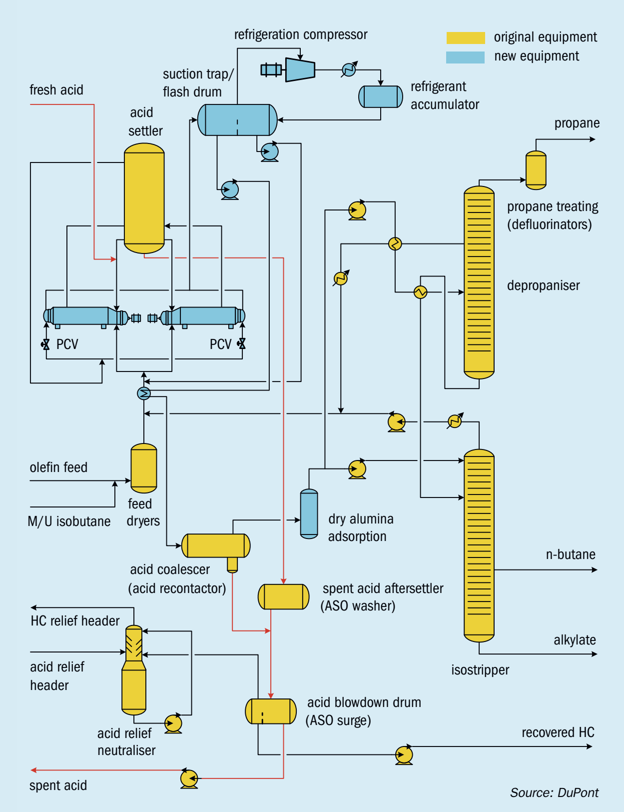
The recommended conversion solution for this case involves adding five reactors (DuPont's STRATCO® Model 74 Contactor™ reactors), a refrigeration section and feed/effluent heat exchangers. Equipment to be used for the acid coalescer, propane product treatment, spent acid aftersettler and acid blowdown drum are all repurposed from the original HF unit.

Table 1: **Case study feed and product streams**

	Olefin feed	Isobutane feed	Propane product	Normal butane product	Alkylate product
Volume flow, bbl/d	25,000	8,300	871	2,877	24,435
Composition, vol-%					
Propane	0.6	8.5	98.0	0.0	0.0
i-Butane	34.4	87.6	2.0	2.0	0.0
n-Butane	10.3	3.8	0.0	87.5	1.5
Propylene	0.0	0.0	0.0	0.0	0.0
i-Butene	0.3	0.0	0.0	0.0	0.0
1-Butene	16.7	0.0	0.0	0.0	0.0
t-2-Butene	22.1	0.0	0.0	0.0	0.0
c-2-Butene	14.8	0.0	0.0	0.0	0.0
i-Pentane	0.9	0.0	0.0	6.5	4.8
C6+	0.0	0.0	0.0	4.1	93.7

Source: DuPont

Fig. 5: **Case study: converted sulphuric acid alkylation unit**



Source: DuPont

Table 2: **Case study alkylate properties**

RON	98.5
(R+M)/2	96.5
D-86 T90, °F (°C)	<245 (118)
D-86 EP, °F (°C)	<365 (185)
Acid consumption, lb acid/gal of whole alkylate	0.25 – 0.30
Alkylate RVP, psi	6.0
Alkylate sulphur, ppm	< 2

Source: DuPont

Most modern HF alkylation units have remote HF acid storage vessels and remote HF acid blowdown drums. Depending on the location of these vessels and the requirements of the conversion solution offered, these may be utilised as spent acid aftersettlers, acid blowdown drums, suction trap/flash drums or supplemental acid settlers. Potential opportunities to reuse these vessels will be determined on a case-by-case basis.

By optimising the isobutane-to-olefin ratio and maximising existing equipment capacity, DuPont increased the capacity by over 80% while achieving a product quality at or greater than the original unit. Table 1 provides a summary of feed and product streams for the conversion solution offered for the case study.

Since STRATCO® Contactor™ reactors were used in this conversion solution, DuPont can accurately predict alkylate properties utilising proprietary correlations developed from decades of pilot plant testing and real-world empirical data. Table 2 provides a summary of predicted alkylate properties. ■

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Improving sulphur plant performance

Elmo Nasato of Nasato Consulting describes some of the key design and operating parameters that are to be considered in the sulphur recovery unit, amine acid gas unit and sour water stripper unit in order to improve performance and online reliability of the SRU.

Above: Key design features of a WHB include a thin tubesheet, proper strength weld tube/tubesheet connection and an engineered ceramic ferrule tubesheet protection system.

Current trends in the characteristics of crude oil supply, petroleum product demand, and tightening environmental regulations require continuous change in the worldwide refining and gas producing industry. Refiners and gas producers are confronted with more stringent environmental, safety and regulatory requirements that must be met while maintaining very high on-line factors in a safe and highly efficient operation.

More hydrotreating and increased processing severity are required for removing sulphur and nitrogen compounds from fuels to meet current and future environmental regulations. The increase in production of hydrogen sulphide (H_2S) and ammonia (NH_3) in combination with more stringent sulphur recovery levels, on-line factors, and safety requirements has placed new demands on the processing capability of refinery sulphur recovery units (SRUs). These developments have led to an increased understanding of root cause failure adversely affecting SRU performance and on-line time.

In theory, the SRU is a relatively simple process operating unit, but the details in design and operation of the SRU, the upstream amine acid gas unit and sour water stripper acid gas unit, are critical in maintaining very high on-line factors. In comparison to the process side of the SRU, the utility side of the SRU is frequently neglected in both the details of the conceptual design and in the normal day-to-day operation. However, the utility side frequently provides harsh reminders of its importance and need for keen attention in order to ensure reliable, safe and high on-line operation of the SRU complex.

Reliability considerations

Acid gas flaring is prohibited by law in most regions, except for very short periods of time during an emergency situation, due to the toxic sulphur dioxide (SO_2) that is generated. Redundant sulphur plants may be required and the refinery may need to curtail or limit throughput in its sulphur producing units until the sulphur plant can be repaired. This can lead to lost profits and, in some cases, fines by environmental agencies. Proven techniques exist in both the design and operation of the sulphur recovery block that will improve its reliability. These techniques have been shown to improve the on-stream factor dramatically and provide for up to the industry standard of five years between scheduled turnarounds.

As environmental regulations become more stringent, optimisation of the sulphur complex continues to be a design challenge as the industry continues to approach near 100% sulphur recovery levels. However, the challenge for operating companies is to take action to control excess emissions and maintenance costs. The goal for most operators is to eliminate unplanned shutdowns of the sulphur recovery operations. This goal has the benefit of achieving environmental compliance but also improves overall safety and economic viability through increased equipment reliability. The best practice for a SRU operation is keep the unit hot; this implies starting the unit and desirably only shutting down for scheduled maintenance turnarounds. It is thermal cycling of the SRU complex that causes the most damage and places personnel and the environment at the greatest risk.

Although the process is simple, problems do develop. Unexpected upsets and shutdowns of sulphur recovery operations cause excess SO_2 emissions and increase plant maintenance costs. Examples of resulting cost increases include: direct replacement costs for damaged equipment, labour costs for repairs, and increased costs for maintaining greater inventories of spare catalyst and critical parts.

Based on operating experience, shutdowns in the sulphur complex can be linked directly to the SRU, (TGTU) but more importantly the upstream amine gas unit (AGU) and upstream sour water stripper unit (SWS). The four typical, high-priority causes of unit failure (causes that fall in both the high probability and high consequence categories) can be categorised in general terms as follows:

- fouling problems;
- instrumentation problems;
- utility problems;
- human or procedural errors.

It is worth noting that every refinery and gas plant is unique and consequently operating reliability issues are site specific. However, in general terms the above list of four problem items is common to most locations, regardless of location, operating philosophy and/or corporate culture.

Design impact of SRU and TGU

Some of the key design features of SRUs with higher reliability include:

- Generously sized knock-out drums are provided in the acid gas feed piping to remove free liquids, which helps to minimise process upsets and equipment problems.
- To achieve high sulphur recovery efficiency and reliability in the SRU, the flow measurement and control loops must be accurately tuned and utilise V-notch control valves, size permitting. The air control loop as a minimum should use a combination of feed-forward and feedback whereas feed-forward control is based on measured feed-flow rates and independently feedback control from a tail gas air demand analyser measuring H_2S and SO_2.
- The acid gas burner must be a high efficiency burner capable of operating at high turndown and ensures complete contaminant destruction.
- The reaction furnace must be designed with a refractory system that is properly designed and installed for start-up, shutdown and normal operation. The refractory material must be compatible with H_2S, SO_2 reducing environment in order to avoid thermal and mechanical degradation. The refractory design should include a properly designed external weather shield to control the furnace metal skin temperature.
- The waste heat boiler should be designed with a thin tube sheet, proper strength weld tube/tube-sheet connections for maximum tube sheet reliability, including an engineered ceramic ferrule tubesheet protection system. Preferred generated steam pressure is 31 or 41 barg (450 or 600 psig).
- Two or three catalytic reaction stages follow the thermal stage. Indirect steam reheaters using steam as the heating medium to control of the reactor inlet temperatures.
- Properly designed, installed and maintained thermal steam tracing/jacketing system.

The design of the reactor section of the TGTU should be based on a low-temperature hydrogenation catalyst. This relatively recent development in catalyst technology increases TGTU reliability and reduces capital and operating costs. TGTU amine system performance and reliability hinge on having a good amine management program to maintain the solvent strength and purity.

SRU plant layout can have a significant impact on reliability, due to the safety, fouling and corrosion problems inherent in the Claus process. The layout should incorporate the following design features:

- Minimise the length of process pipe.
- With the exception of the reaction furnace, insure that all equipment and piping is properly insulated.
- Ensure the SRU equipment and piping is self-draining to the sulphur collection point.
- Use indirect U-tube steam reheat exchangers with steam on the tubeside.
- Lay out equipment and piping with minimum 1% slope to be completely free draining
- Minimise molten sulphur piping lengths, and slope all sulphur piping 2% if possible.

Design impact of AGU/SWS

The design of the amine regeneration unit (ARU) and SWS should incorporate the necessary equipment and features to ensure stable, reliable and efficient operation of the downstream SRU. To minimise the effects of these upstream units on the operation of the SRU it is important to minimise the hydrocarbon content of the acid gas and to provide a consistent acid gas composition.

Amine absorbers

Fouling problems in the SRU are frequently caused by hydrocarbon carryover from the AGU that results in the formation of solids in the SRU. The solids plug instrumentation ports, SRU catalytic beds, and foul heat exchangers leading to loss of control, operational difficulties, excess SO_2 emissions and, ultimately, shutdowns.

To maintain a reliable operation of the amine plant and ultimately the SRU, any operational effects of feed gas contaminants, should be avoided. This is achieved by the high efficiency separation feed gas knock-out vessel. The feed gas knock-out vessel should be designed as a high efficiency separation column, with installed inlet deflection device(s), adequate disengaging space and demister

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pads. In some situations, the knock-out drum should incorporate a water wash to remove undesirable contaminants from the feed to the amine absorber.

One of the main sources of hydrocarbon carryover in an AGU in a refinery is the hydrotreater and LPG contactor. To prevent hydrocarbon from condensing inside the contactor, the amine temperature must be 10°C (20°F) greater than that of the inlet hydrocarbon stream.

The lean amine temperature should always be higher than the hydrocarbon feed to the absorber, this prevents the condensation of hydrocarbons into the rich amine stream.

Amine regeneration unit

Minimising the hydrocarbon content of the acid gas stream from the amine regenerator requires a rich amine flash drum sized for a recommended minimum 20-minute residence time and for an operating pressure of less than 3.4 barg (50 psig). This allows the free liquid hydrocarbons to float to the surface and be skimmed off and the dissolved hydrocarbons to flash off from the rich amine.

The SRU reliability is directly correlated to the amine system performance with the amine reliability dependent on having a good amine management programme to maintain the solvent strength and purity, consisting of the following engineering and operational features:

- lean amine partial but preferential full-stream filtration to remove particulates;
- rich amine filtration (if permitted);
- lean amine slip-stream carbon-bed treating to remove chemical contaminants;
- regular sampling and analysis of lean and rich solvent concentration, heat-stable salt content, and chemical composition;
- correct selection and proper dosage of antifoam agent.

Cooling capacity should also be provided in the regenerator overhead condensing system to ensure a maximum target acid gas temperature of 50°C (120°F). Maintaining a low acid gas temperature improves the acid gas quality by reducing its water content, to the benefit of the downstream SRU.

Sour water strippers

To minimise the hydrocarbon content of the acid gas produced in the SWS, provisions for separating free hydrocarbon liquids from the raw sour water should be included in the sour water gathering system. This should include a flash drum with 20 minutes of residence time, and oil skimming nozzles on the sour water storage tank draining to a skimmed oil drum. Segregating phenolic and non-phenolic sour water should be considered, based on the end use of the treated water and the availability of make-up water. SRU performance and reliability are greatly enhanced by acid gas feeds of consistent composition and constant flow rate. To accomplish this, the SWS feed should be of a consistent composition and constant feed rate. This is accomplished by providing a well-designed raw sour water storage tank with 3-5 days' capacity for blending the individual raw sour water streams. The tank inlet and outlet nozzles must be separated to avoid direct feed of sour water through the inlet connection directly to the outlet connection.

Instrumentation

In recent years there have been significant improvements in the SRU instrumentation, especially with respect to the SRU main burner. The main burner has instrumentation that is critical to the safe and reliable operation of the SRU with certain components such as flame detection, front-end pressure measurement and ignitor systems that are included in the SRU shutdown system and burner management system. While the electronics of these devices have improved, the weak link of the system is the burner nozzle purge system. These nozzle purge systems are critical in order to allow the instrumentation to work effectively but are frequently designed and/or operated incorrectly.

In order to maintain reliable SRU operation, it is imperative to have a proper air control system that maintains the SRU operation at the tail gas analyser setpoint and provides adequate robustness for feed disturbance rejection. The control scheme should be programmed to allow for independent feed flow measurement on all feed streams to the SRU; this includes amine acid gas, sour water stripper acid gas, and all fuel gas streams. Each stream will have an air demand multiplier than can be adjusted based on composition in order to provide a feedforward air demand signal. Air demand requirement for each stream is then fed to a summation block to allow for feed forward component of air control scheme. If there is doubt with the flow measurement the flow measure can be checked/inferred based on valve positioning and valve characteristic curves. In the ideal case, maintaining the optimal air flow to the reaction furnace during start-up and shutdown procedures would be accomplished using separate air-to-feed gas ratios for all of the possible feed gases (i.e., acid gas, SWS gas, hydrogen gas (if applicable), natural gas and/or fuel gas), with the DCS then summing and controlling the total required air flow at all times. This "feed forward" method of controlling the air is typically used to control the main air and the tail gas air demand analyser, which is used to accurately monitor the tail gas H_2S to SO_2 ratio (whenever acid gas is one of the streams being processed), and to automatically adjust the trim air flow. Proper feed forward control, however, is only useful if the flow meters for all streams are reasonably accurate and if the stream compositions do not vary significantly. Similarly, the critical feedback loop is very dependent on having a well maintained and calibrated air demand tail gas analyser.

The sudden change in feed gas composition represents a significant disruption to the SRU operation. Incorporating feed gas analysis in the feedforward control loop has been widely applied using a variety of analytical techniques to make a comprehensive quantification of the components. In order to provide proper control response and disturbance rejection, the analytical method must provide a real time (< 5 seconds) analysis of the combustion components. The complication is the multiple components of hydrocarbons (HC) that can be present and that will vary and is unique to each disturbance episode. Recent developments have resulted in significant improvements that have reduced the response time by no longer attempting to define each of the HC components. Rather it has been identified that it is sufficient for control purposes to make a single measurement of total hydrocarbon (THC) content that provides a signal for the total "air demand". This has proven to be a reliable method that results in a useful and quick feedforward signal to assist in rejecting the change in composition disturbance.

A significant challenge that can adversely affect reliability in a refinery SRU operation is maintaining the instrumentation associated with handling the sour water stripper acid gas (SWSAG). The SWSAG is a difficult stream to measure accurately for flow and level because of the inherent

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problems with ammonia salt formation at temperatures below 80°C (180°F). Formation of salt will plug large items such as piping, mesh pads and condenser tubes, but is most likely to plug smaller diameter items like instrument connections such as flow meter pulse lines and transmitter connections. Thermal heat maintenance is critical on the SWSAG knock-out drum high level switches and purging of instrument lines is required. Also it is recommended to install a continuous SWSAG purge meter arrangement to provide reliable SWSAG flow measurement.

Human and procedural error

It is difficult to identify common causes for the human errors investigated. Humans are much more difficult to predict than equipment performance. Sulphur complexes appear to be relatively simple relative to most units in a refinery, however the sulphur units are very unforgiving if there is improper attention to detail. Successful operations place emphasis on cross training between process engineers, reliability improvement team members, maintenance personnel, and unit operators. The goal of the training should be to improve operational awareness and the important details in the SRU complex.

Precise and well understood procedures should include the following key items:

- troubleshooting guides indicating possible causes of equipment malfunction and failure;
- steam system monitoring especially steam traps;
- analyser calibration and monitoring;
- lists of equipment requiring vibration analysis and monitoring;
- recommended lubricants and lubrication intervals for specific equipment;
- preventive maintenance task lists for critical equipment.

A good predictive/preventive maintenance (PM) programme includes equipment prioritisation so that maximum effort is focused on the critical pieces of equipment, or those with significant impact on refinery operations and environmental compliance. Inspection checklists with PM procedures, including lists of proper settings, log sheets, and tests specific to individual equipment, should be made available to maintenance and operations personnel. This is especially true for SRU specific instrumentation such as the steam trap system, tail gas analyser and main burner flame scanners.

Utility considerations

In comparison to the process side of the SRU, the utility side of the SRU is frequently neglected in both the fine details in the conceptual design and in the normal day-to-day operation. However, the utility side frequently provides harsh reminders of the importance of keen attention in order to insure reliable, safe and high on-line operation of the SRU.

The purpose of this section is to identify the key design and operating considerations for the utility side of an SRU with the primary intention of raising the awareness of its importance, a more extensive review is available in the referenced paper[2].

The sulphur recovery unit utilities and problems associated with its operation and design include:

- steam (imported and exported);
- boiler feed water, utility water and make-up water;
- fuel and natural gas;
- nitrogen;
- instrument air;
- electricity.

In all likelihood the problems associated with utility systems have always existed but it appears that in more recent years the frequency and severity of SRU problems associated with the utility systems have increased. It is suggested that the increase and severity of these problems are most likely related, but not limited, to the following items:

- use of utilities may be intermittent;
- utilities are not instrumented to the same degree as the primary process and even when they are instrumented, their maintenance is not prioritised as highly as process systems;
- DCS system has reduced field check-out;
- high turnover/inexperienced operating staff;
- overworked/understaffed operating and technical support staff;
- limited SRU design experience;
- lack of understanding of the intent and significance of all utility requirements.

By their nature some of the utility streams are used intermittently during start-ups and shutdowns and the industry as a whole has moved to lengthening the run time between scheduled shutdowns. In the past, annual turnarounds were common, today scheduled turnarounds are typically three to four years apart. Several refineries are targeting five years between scheduled turnarounds. This change in turnaround philosophy has resulted in the start-up, shutdown and utility systems being less familiar to operating staff. It is also more likely that the operating staff has changed, and thus operating experience has been lost since the last turnaround. Furthermore, the extended run time increases the possibility that the utility systems may have been compromised since the last usage.

Another major change in the industry is the trend of replacing satellite control rooms, necessitated by pneumatic control systems, with central remote located control rooms utilising electrically based DCS control systems. In itself the DCS systems have provided terrific advancements in control strategies, process variable data tracking, overall system component (i.e. control valves, rotating equipment, motors, etc.) tracking, allowing for statistical data analysis on both the process and utility side. However, there are certain critical items, particularly on the utility side, that are not instrumented. Especially important in an SRU, the steam traps require diligent manual inspection to verify correct operation. All too frequently, the failure of a steam trap is revealed by a low temperature alarm on the process side, or a high pressure alarm on the process side, as a result of inadequate heat input due to a steam trap failure.

The safety and control features of the single remote control room based on a DCS/PLC system are very beneficial. For many locations; an unfortunate casualty of this "advancement" is that field checkout is not as common. It is not unusual to spend an entire day in a refinery SRU and not see an operator. There was an era in which a routine walk through the "metal forest" would provide a feel for the operating condition of the unit on the basis of sound, sight (i.e. sulphur rundowns, steam leaks, etc.), smell and touch.

This notion may seem nostalgic, but the modern DCS/PLC systems do not completely replace and are not as reliable as the human senses. At one time the limited amount of data provided by the control system was supplemented and complemented by the database accumulated by the human element. It is suggested that there may be too much reliance placed exclusively on the data provided by the DCS system.

Steam

Sulphur recovery units generate two products, sulphur and steam. In many cases the steam is more valuable than the sulphur. The steam is generated as a useful way of transferring the significant amount of energy generated by the Claus process in both the thermal and catalytic stages. The steam generated in an SRU can be utilised within the SRU, and the excess can be exported for heating (i.e. amine reboiler, sour water stripper reboiler, steam tracing, etc.) or to spin a turbine. In many cases, SRUs import high pressure steam, where it is not generated within the SRU, for indirect heating for feed preheaters and/or catalytic reheaters. It is the desirable and special properties of steam and water that make them so widely selected for the energy transfer role.

In many cases high pressure steam is imported to the SRU as the heating medium for heat exchangers for amine acid gas preheating, sour water stripper acid gas preheating, combustion air preheating and/or catalytic reheaters and in some cases for driving steam turbines on a combustion air blower.

Another consideration in the design and repair of SRU heat exchangers is the tube-to-tubesheet weld procedure. For the low pressure heat exchangers, such as the condensers, a seal weld procedure is acceptable. For the high pressure heat exchangers, such as the waste heat boiler, a strength weld procedure must be utilised. The proper strength weld procedure is mandatory but is too often neglected especially in field repairs.

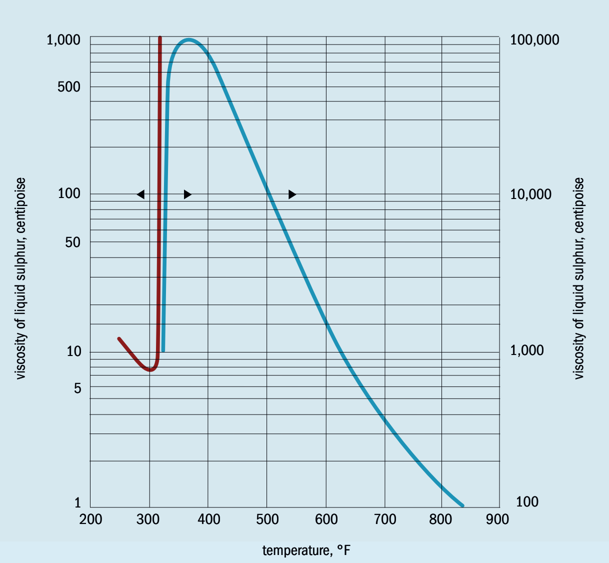
Sulphur pumps are commonly damaged because too high a steam pressure is supplied to the pump jacketing. Most vendors will recommend adjusting and controlling steam supply to a sulphur pump jacketing at 2.4 barg (35 psig) in order to avoid viscosity problems with the sulphur pump. It is common to burn out sulphur pump motors because "the sulphur would not flow, so higher pressure steam was used to help make the sulphur flow". The sulphur viscosity curve (Fig. 1) supports the need for utilising 2.4 barg (35 psig) steam and not higher than 2.4 barg (35 psig) pressure steam.

Boilers and steam systems are full of air prior to start-up. A very important requirement of getting any steam system operating efficiently is the removal of air. Air is a poor conductor of heat and thus mixtures of steam and air, for a given steam pressure, have less heat content than steam alone. This fact also means that the mixture will have an adverse effect on heat transfer rates. With higher pressure boilers, the feedwater is often passed through a deaerator before it is pumped to the boiler. The best deaerators can reduce oxygen levels to 3 parts per million (ppm) in water. Non-condensible gases, specifically carbon dioxide and oxygen are both present in steam systems. At 80°C (180°F), water can dissolve about 0.6% of its volume, of air. The solubility of oxygen is roughly twice that of nitrogen, so air which dissolves in water contains nearly one part of oxygen to two of nitrogen rather than the one part to four parts in atmospheric air. Carbon dioxide has a higher solubility, roughly 30 times greater than oxygen. Free oxygen is a normal component of a water system but it is the agitation of boiling that causes the carbonates in water to produce carbon dioxide. Both gases will cause corrosion in the entire steam/condensate system. A very important feature of a properly designed steam system is the ability to purge these non-condensibles from the steam system.

One of the critical elements in the entire steam system is steam traps. In the industry there have been significant problems with the design and far too often the steam traps are ignored in day-to-day operations. The purpose of a steam trap is to remove condensate from a steam heating system while "trapping" steam in the system. This is essential to the successful operation of the heating system. There are many different types and features of steam traps available in the market, but not all steam traps perform well in all situations[1]. The steam trap must keep the jacket system clear of condensate, continuously purge non-condensibles and accommodate the condensate return pressure. Regardless of the steam trap selected, a robust structured monitoring and maintenance plan is recommended. All traps eventually fail, and trap surveys commonly report that a third of a plant's trap population does not function properly[1]. It is mandatory that the design and installation facilitates isolation and easy removal of the steam traps while the SRU is in operation.

Corrosion is a given factor in a steam system. Corrosion attacks boiler tubes, steam mains, heat exchangers, valve components and fittings such as steam traps

Fig. 1: **Pure sulphur viscosity curve**



Source: Fanelli & Bacon

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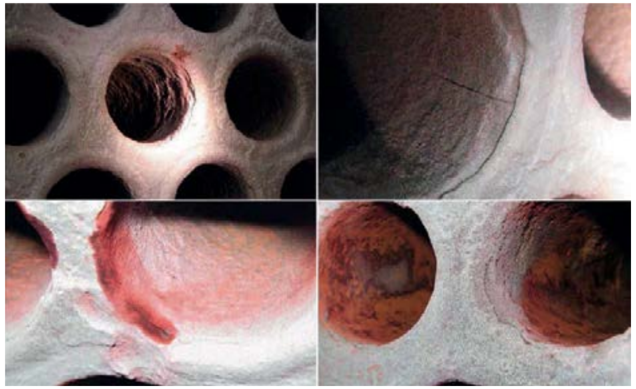

Fig. 2: Waste heat boiler tube-to-tubesheet weld failure.

(Fig. 2). The primary defence is to carefully monitor and maintain the boiler feedwater treatment system and control of the non-condensible gases (oxygen and carbon dioxide) that promote corrosion. There is a significant amount of trash and accumulated debris in both a newly commissioned and existing isolated system. It is mandatory to disconnect steam traps connected directly to the steam system, admit steam and flush the entire system until the system is blown clear. In older systems, especially those that are used intermittently, dirt, corrosion products and foreign debris will cause problems with traps, small valves, instruments and steam traps. Dirt prevents the free movement of internal parts or can get caught between valves and seat sealing surfaces leading to erosion damage. A properly designed pipe system will protect the steam traps by upstream pipe strainers.

Boiler feed/utility/and make-up waters

Many waste heat boiler failures are now linked to the boiler feed water/steam side of the exchanger. These problems have a significant impact on the SRU reliability but the current industry trend indicates a lack of awareness on the importance of boiler water/steam quality. The treatment of water for steam generation is one of the most difficult branches of water chemistry. The pressure and design of the boiler determine the quality of water it requires for steam generation.

Deposits, particularly scale, can form on boiler tubes. Each contaminant has an established solubility in water and will precipitate when it is exceeded. At the high temperatures found in a boiler, deposits are a serious problem causing poor heat transfer and a potential for boiler tube failure.

Boiler water blowdown

Boiler water blowdown is used to remove some of the concentrated water from the pressure vessel while it is under pressure. The removed water containing suspended and dissolved solids is replaced with relatively pure feedwater even though this water is treated prior to use through external processes designed to remove the unwanted substances which contribute to scale and deposit formations. Regardless of the treating efficiency, none of the treatment processes in themselves are capable of removing all substances and a small amount of solids will be present in the boiler water. The solids become less soluble in the high temperature of the boiler water and as the water boils off as relatively pure steam, the remaining water becomes concentrated with either suspended or dissolved solids.

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

There are two principal types of blowdown, they are intermittent and continuous. Intermittent is done manually and is necessary for the operation of the boiler regardless of whether or not continuous blowdown is employed. Continuous blowdown is a continuous and automatic removal of concentrated boiler water.

A problem that appears to have become more common is related to the design and the operational procedures related to the continuous and intermittent blow down. By regularly utilising both intermittent blowdown connections, sludge and debris can be removed over the entire length of the WHB. From an operational perspective, the intermittent blowdown valve(s) should be exercised on a regular and scheduled basis with good practice being considered to be daily exercise of the valves. Too frequently, the intermittent blowdown is only used based on water conductivity test results of samples collected from the continuous blowdown. Depending on the continuous blowdown location, the sample may be collected from the steam phase and this may result in a false sense of security of WHB shellside having very high water quality/purity. Poor water management will result in external tube fouling and reduced heat transfer resulting in thermal stress of the WHB tubes, tubesheets and tube-to-tubesheet welds. The unfortunate result of inadequate use of the intermittent blowdown has resulted in more frequent tube failures due to high temperature failure.

Fuel and natural gas

Most sulphur recovery units use natural gas on a continuous basis for the incinerator, but on an intermittent basis for SRU start-up, shutdown and hot standby. In the case of start-ups where new catalyst has been installed, the main burner may be fired with excess air. For all other cases and for the majority of natural gas firing, the burner must be fired at slightly substoichiometric (air deficient) air conditions. This is necessary because any excess air will cause catalyst deactivation and may result in sulphur fires that can be very damaging to catalyst and equipment.

When firing at near stoichiometric conditions the composition of the fuel gas or natural gas must be known and remain constant. That is where a clear distinction between fuel gas and natural gas exists. Natural gas is normally of fixed and known composition while fuel gas can be made up of almost any mix of constituents, hydrocarbon and non-hydrocarbon, that can be found in a refinery. Furthermore, the only certainty with fuel gas composition is that it most likely will change. Not knowing the exact composition of the fuel gas runs the risk of either firing with excess oxygen, resulting in potential sulphur fires, or firing with significantly deficient oxygen, resulting in soot formation. The effects of a sulphur fire are quite clear. The formation of a significant amount of soot will result in heat exchanger fouling, catalyst damage and the soot will reduce SRU capacity. If the additional pressure drop created by the soot cannot be tolerated, and if the soot cannot be removed on-line, a shutdown will be required to mechanically remove the soot and to clean heat exchanger tubes. The SRU must be designed and operated with known composition natural gas for start-up, shutdown and hot standby operation. During fuel gas operation the flame colour should be field checked systematically. An orange flame colour is indicative of air-deficient operation, a blue flame is oxygen rich and a salmon-pink flame colour is indicative of stoichiometric burn. Whenever fuel gas firing is used intentionally for an extended period, the first condenser outlet should be checked for excess oxygen and CO.

A good indication of the correct (95%) stoichiometry, will produce 0-0.4% oxygen and around 2,000-4,000 ppm CO in the flue gases. The thermal stage is designed to operate with natural gas for start-up, shutdown and hot standby. Natural gas firing requires stoichiometric operation and the resulting flame temperature of 1,650+°C (3,000+°F) can be damaging and thus natural gas firing requires flame moderation. The refractory in the reaction furnace and fired reheaters must be designed for the elevated temperature of the natural gas operation.

Nitrogen

It is paramount for the continuous successful operation of the reaction furnace burner that during normal operation the continuous purge is provided to the following burner nozzles:

- flame scanners;
- sight glasses on the burner and reaction furnace;
- ignitor port;
- reaction furnace temperature measurement;
- idle ports, such as natural gas, on burner (purge rate to be set by vendor).

The purge medium can be instrument air during normal operation and nitrogen after an SRU shutdown. If it is available and there is no negative impact upon the furnace flame temperature and flame stability, nitrogen can be utilised at all times. Each purge connection requires an individual rotameter with proper tagging to allow for continuous system monitoring and troubleshooting.

Instrument air

The SRU is no different to other operating units in that the instrument air must be reliable, properly designed and maintained in order to insure safe and reliable of operation of the SRU. There are certain design and maintenance requirements that are somewhat unique to sulphur recovery units.

The air system for an SRU must have adequate capacity for air-consuming instruments, if applicable, all furnace purge connections. As described in the nitrogen section, it is common to utilise air for the continuous purge of burner nozzles during normal operation. This is acceptable as long as the SRU is in operation, but if the SRU trips, the air must automatically be replaced by an inert medium such as nitrogen (preferred) or steam. The quantity of air required for the purges must be included in the design of the instrument air system and supply headers. Some pilots require large quantities of instrument air which can tax the system severely.

The instrument air should be free of all contaminants such as dirt, oil, water and corrosive gases. It is recommended to utilise instrument air for purging rather than a slipstream of air from the SRU combustion air blower. The combustion air stream is dirty, wet and at a lower operating pressure. This will cause problems with rotameters and, where applicable, burner pilots and ignitors. The air system should be designed and operated with a drying system that must reduce the water dewpoint to a minimum of 6°C (10°F) below the ambient temperature at operating pressure. Wet air has been known to short out some ignitor systems.

Electricity

Normally, the UPS is designed to provide enough battery back-up power to allow an orderly shutdown in the case that the instrument air system is depleted of air. For the SRU it is imperative to back up the tail gas analyser, flame scanners and, where applicable, the tail gas treating unit hydrogen and pH analyser. An SRU designed with steam turbine air blowers will continue to operate without external power, but without the analysers, the operator will be running the plant blind. While operating on battery back-up, it is recommended to field check the unit including the following items:

- main burner sight glasses to verify the flame colour and pattern;
- Draeger tube the tail gas sample to determine "ball park" H_2S/SO_2 ratio;
- quench water pH.

There is no replacement for field checkout! Extended off-ratio operation can lead to severe damage of the quench water system and the amine in the tail gas treating unit. Operator training becomes very important in this type of situation.

Conclusions

In theory, the SRU is a relatively simple process operating unit, but the details in design and operation of the SRU, the upstream AGU and SWS unit, are critical in maintaining very high on-line factors. In comparison to the process side of the SRU, the utility side of the SRU is frequently neglected in both the details of the conceptual design and in the normal day-to-day operation. The utility component and in particular the thermal heat maintenance system is critical to ensure safe and reliable SRU operation.

Based on operating experience, shutdowns in the sulphur complex can be linked directly to the SRU and TGU but more importantly the upstream AGU and upstream SWS. The four typical, high-priority causes of unit failure (causes that fall in both the high probability and high consequence categories) can be categorised in general terms as follows:

- fouling problems;
- instrumentation problems;
- utility problems;
- human or procedural errors.

In summary, the SRU reliability can be directly linked to keeping contaminants out and keeping the SRU hot. While simple in description, the execution in keeping contaminants out and consideration for keeping the SRU hot in the design phase, maintenance program and daily operation will result in reliable SRU operation. ■

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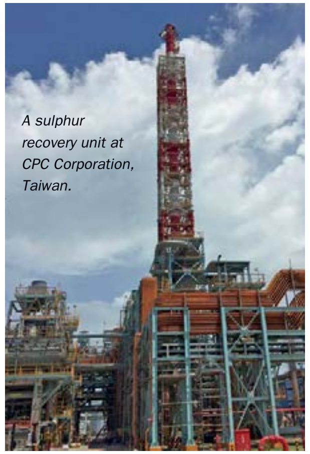

A sulphur recovery unit at CPC Corporation, Taiwan.

CPC refineries improve SRU reliability

Taiwanese refining corporation CPC has installed DynaWave® scrubber technology in sulphur recovery units at two of its refineries to provide a low maintenance, efficient and flexible emission control system that is easy to operate and achieves very high SO_2 removal efficiency.

Refineries around the world are faced with the challenge of meeting increasingly stringent SO_2 emissions regulations from their sulphur recovery units (SRUs), while minimising their capital and operating expenditure. The reliability and efficiency of the SRU and its tail gas treatment process is key to meeting emission targets, minimising maintenance requirements and operator time.

A common solution to improve the reliability and sulphur recovery efficiency has been to install a highly efficient but capital intensive amine-based tail gas treatment unit (TGTU) downstream of the Claus plant, but is this akin to using a sledgehammer to crack a nut? CPC, a large Taiwanese state-owned refining corporation, has chosen a more efficient and cost-effective option, combining a slightly less efficient TGT process with the highly flexible MECS® DynaWave® reverse jet scrubbing technology (licensed by DuPont Clean Technologies). This allows the refinery to remove sulphur efficiently on a small plot space at lower capital expenditure while at the same time achieving high on-stream time.

Meeting emission targets at CPC Ta-Lin refinery

Following the closure of CPC's older Kaohsiung refinery a couple of years ago due to environmental reasons, CPC is now set to increase the capacity of its 300,000 bbl/d Ta-Lin refinery to 350,000 bbl/d. The main products of the Ta-Lin refinery are gasoline and diesel. The refinery operates one two-stage and three three-stage Claus sulphur recovery units with a combined capacity of 780 t/d. In order to meet Taiwanese government air emission regulations at the Ta-Lin refinery, DynaWave® technology was installed at one of the SRUs, to guarantee reliable SO_2 removal from the SRU off gas stream at all times. This system has now been in operation for about three years.

CPC has also chosen to combine a well-known sulphur recovery tail gas technology with the DynaWave® technology for the two-stage, two-train SRU No. 10 to reduce SOx and total suspended particulate (TSP) emissions.

Both trains are equipped with a DynaWave® system, which has two reverse jet stages in the inlet barrel, combined with a packing section inside the vessels. This set-up allows the scrubbers to operate with an extremely high liquid to gas ratio and makes it possible to bypass the upstream main tail gas treatment unit during start-up, shutdown and malfunctioning (SSM) conditions. High-efficiency diffusion bed mist eliminators have also been installed in the vessels to reduce SO_3 emissions.

To meet CPC requirements, DuPont Clean Technologies specifically designed the DynaWave® wet gas scrubbers to reduce SO_2 levels to ≤30 ppmv (dry basis) and SO_3 levels to ≤30 ppmv (wet basis), both values corrected to 6% oxygen. Both of the custom engineered scrubbing systems remove SO_2 and SO_3 from the gas stream based on the specific design inlet conditions.

The DynaWave® technology has allowed CPC to opt for an oxygen-enriched tail gas treatment process, which runs under normal conditions, but also gives them the flexibility to operate the Claus plant without interruptions during maintenance or malfunction of the main tail gas treatment process and still meet SO_2 emission limits.

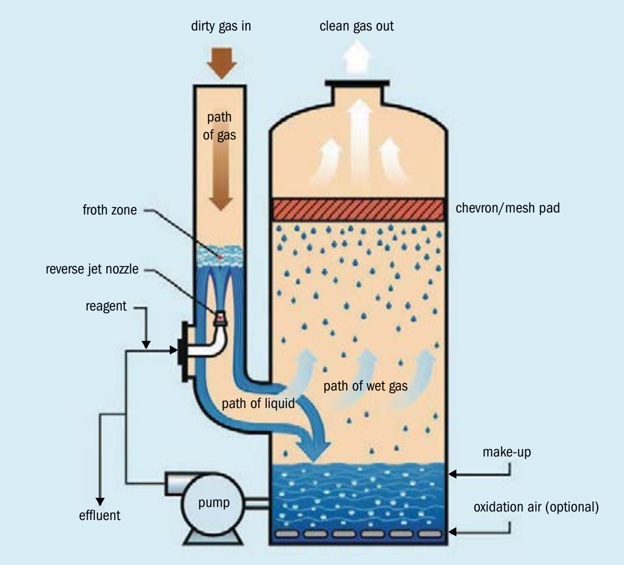
Advantages of new scrubber

Overall, the Ta-Lin refinery noticed a significant difference after the installation of the DynaWave® reverse jet scrubbers in 2014. The sulphurous emissions from SRU no. 10 are now below environmental regulation limits at any given time, 24 hours a day, 365 days a year in both trains. Stack emissions have dropped from 1,000 ppm to levels of below 10 ppm as detected during performance testing.

CPC refinery has also operated the DynaWave® scrubber system in SRU bypass mode several times and says it believes the inlet SO_2 concentration may have been up to approximately 7,000-8,000 ppm. Even in that mode, CPC measured outlet SO_2 gas below 10 ppm.

The refinery estimates that the DynaWave® technology has allowed it to save at least 30% of its overall TIC budget compared to the installation cost of an amine-based TGTU alone. The capital cost of the combined tail gas treatment/DynaWave® process was less than 70% of the estimated capital cost of a similar sized amine-based TGTU process alone would have been, in part because fewer pieces of equipment are required.

Fig. 1: Basic DynaWave® scrubbing system



Source: MECS

Solving environmental issues at Taoyuan refinery

In July 2017, CPC's Taoyuan refinery started up a new DynaWave® wet gas scrubbing system to comply with stricter SO_2 emission regulations from Claus tail gases. This CPC refinery in Taoyuan began operating in 1976 and has a capacity of 200,000 bbl/d. Up to a few months ago, the refinery used to require seven to eight days after turnaround of the SRUs at the refinery before acid gas could be fed to the units and commence normal operation. As a result, off-gas from the catalyst would be released directly to the stack and into the air, causing environmental issues. CPC researched different solutions to resolve these issues, and eventually selected a DynaWave® scrubber for this site.

"CPC chose the DynaWave® scrubber for the high reliability of its outlet gas emissions when inlet gas SO_2 concentration varies," explains William Lam, Senior Business Development Manager, Taiwan and Japan, "This means, there is no need to adjust DynaWave® equipment such as valves or pumps in order to meet strict emission targets. The SO_2 removal efficiency of DynaWave® turns an average of 10,000 ppmv SO_2 at the inlet into a guaranteed outlet of less than 50 ppmv SO_2." At start-up, this summer, CPC technical teams measured only 10 ppmv SO_2 at the stack outlet.

"The tail gas of two two-stage Claus units (SRU2 and SRU3) at the Taoyuan refinery are treated directly in one single DynaWave® scrubber with two reverse jet stages," says Mr Lam. The SRUs have a capacity of 100 t/d (SRU2) and 200 t/d (SRU3), respectively.


PHOTO: MECS

Fig. 2: A DynaWave® reverse jet nozzle after one year of continuous operation.

DynaWave® technical performance

The DynaWave® reverse jet scrubbing system is illustrated in Fig. 1. It is a unique open bore, reverse jet scrubber that uses froth zone technology to achieve desulphurisation in a wet gas environment. For SRU applications, the DynaWave® system is installed after the incinerator to treat the SO_2 before the outlet gas leaves through the stack.

The heart of this system is the reverse jet nozzle, a gas-to-liquid contactor that creates a zone of intense mixing. The feed gas enters the top of a vertical duct and collides with the scrubbing liquid that is injected upward through a large bore injector or reverse jet nozzle.

The reverse jet nozzle is a very large bore, open throat nozzle, fabricated of silicon carbide for corrosion and temperature resistance (see Fig. 2) that creates the full cone liquid flow essential to producing a froth zone. The froth zone, a standing wave of highly turbulent flow, is produced at the point where the liquid is reversed by the gas. This froth zone creates a very high rate of liquid surface renewal and efficiently quenches the gas to the adiabatic saturation temperature. At the same time, it converts all the SO_3 present to acid (H_2SO_4) mist and absorbs the SO_2.

The DynaWave® reverse jet scrubber can be designed to quench hot gases up to 1,200°C. In addition to quenching and acid gas absorption, it can also efficiently remove particulate. This feature provides extra reliability in case elemental sulphur particulates enter the system.

CPC has installed several DynaWave® scrubbers over the last ten years to treat different refinery off-gas streams and is so convinced of its benefits that the company is planning on installing DynaWave® scrubber technology at the next available opportunity for other SRU plants in the company's refining complexes. ■

Acknowledgement

The authors are grateful to Mr. Jinn-Kuen Lu, head of the technical service subsection and Mr. Wei-Chen Ke, SRU no. 10 Superintendent at the Ta-Lin refinery of CPC Corporation, Taiwan for their support in the preparation of this case study.

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Meeting capex, opex and emissions challenges

To help customers address increasingly stringent capital expenditure (capex), operational expenditure (opex), and emissions challenges in a competitive marketplace, MECS continues to engineer creative and cost-efficient solutions to maximise heat recovery in sulphuric acid plants.

MECS has been designing and improving sulphuric acid plants and related processes since 1917. Technologies such as MECS's Heat Recovery System (HRS™) allow customers to gain more value from their plant by recovering heat from the formation of acid and transforming that energy into intermediate-pressure steam. As emissions requirements become increasingly strict and capex becomes tougher to control, companies in the sulphuric acid industry want heat recovery solutions that offer them both reliability and value. This can be difficult to achieve, especially with regards to maximising heat recovery in a plant while minimising capital cost.

SteaMax™ HRS™

Table 1: **Economic comparison of HRS™, HRS™ steam injection and SteaMax™ HRS™**

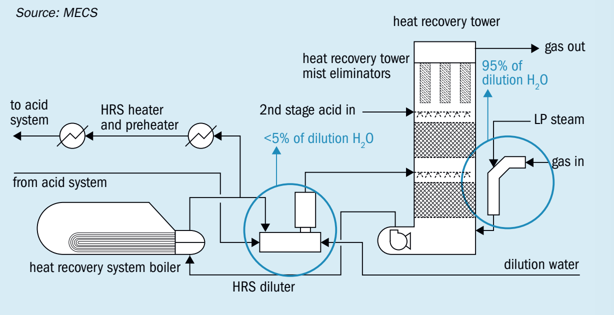
	Design export steam (kg/h)	Design export steam (t/t)	Net present value (US$)
No steam injection	47,000	0.47	11 million
Conventional steam injection	52,800	0.53	14 million
SteaMax™ HRS™	63,800	0.64	18 million

The values in the table above assume a 2,400 t/d sulphur burning plant with a 12% cost of capital and a steam value of $15/t. These values also assume that the HRS steam is used as process heat.

Source: MECS

Fig. 1: **SteaMax™**

Source: MECS



MECS has designed numerous HRS™ installations around the world. The idea behind HRS™ is that the heat generated by the formation and dilution of sulphuric acid, which is normally lost to cooling water in conventional plants, can be recovered as intermediate-pressure steam. Gas enters the HRS™ system in the heat recovery tower, where is it is contacted in two packed beds by strong acid. The resulting acid leaves the heat recovery tower, and the heat of formation of the newly-formed sulphuric acid, as well as the heat of dilution from the HRS diluter, is captured in the HRS boiler as the acid is cooled. Some acid leaving the HRS boiler will crossflow to the drying tower acid system for concentration control, but not before that acid is cooled in the HRS heater and HRS preheater, which transfer heat from the HRS acid to HRS boiler feedwater and treated water feeding the deaerator, respectively.

In order to maximise the amount of heat generated and recovered, steam injection is used in the HRS™. A portion of the required dilution water is added as low-pressure steam in a chamber upstream of the heat recovery tower, thus providing the added benefit of higher enthalpy as compared to a liquid water dilution stream. The capture of latent heat from condensation that results from steam injection creates an additional boost in the steam production in the HRS™.

To further maximise this benefit, MECS designed and patented an improvement to steam injection called SteaMax™, in which nearly all the required dilution water is added through steam injection. A typical sketch of a SteaMax™ HRS™ system is shown in Fig. 1.

In a SteaMax™ HRS™ design, the heat recovery from steam injection is maximised since very little liquid water is used for acid dilution. In fact, SteaMax™ can yield up to 30% or more in additional intermediate pressure steam production as compared to a traditional HRS™. As shown in the case illustrated in Table 1, the increase in steam export can translate directly to increased profit.

Fig. 2: **SolvR®**

Source: MECS

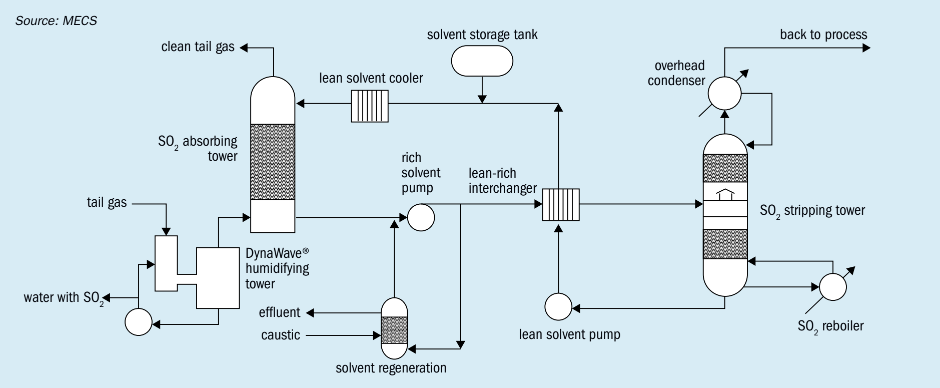
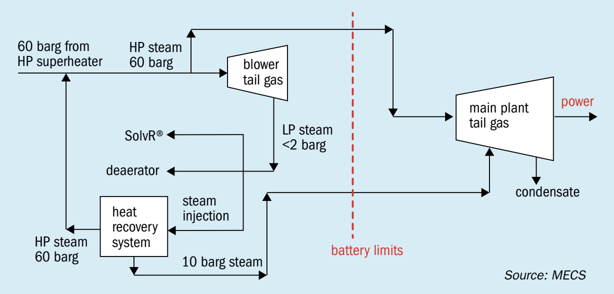


Fig. 3: **MAX3™ steam export and utility integration**



Source: MECS

SolvR®

In 2014, MECS developed a regenerative process that absorbs SO_2 from a waste gas stream and returns it as a nearly pure, saturated SO_2 gas while achieving ultra-low emissions. Called SolvR®, this technology is designed so that the waste gas is first quenched in a DynaWave® scrubber, and then the gas stream is contacted with solvent in an absorbing column where the SO_2 in the gas is absorbed into the solvent. The clean flue gas will leave the system out of the absorbing column. The absorbed SO_2 is stripped out of the solvent with steam in a stripping column, and the stripped solvent flows back to the top of the absorbing column. Within the process also exists a solvent regeneration loop, in which contaminants (sulphates) in the solvent are purged from the system as a sodium sulphate solution. A typical SolvR® flow scheme is shown in Fig. 2.

One of the major benefits that this technology offers is that it allows for additional heat to be recovered in an acid plant. A single-absorption scheme with SolvR® eliminates the need for a fourth catalyst bed, as the system can achieve much lower emissions than a conventional double-absorption sulphuric acid plant. In addition, switching to a single-absorption process eliminates interpass heat exchangers, and steaming equipment instead can be placed after the converter beds. Doing so allows for the recovery of the heat of reaction of the oxidation of SO_2 either as steam superheat or as boiler feedwater preheating, rather than having that energy lost to the required re-heating of cold gas flowing from an absorption tower back to the converter.

MAX3™

Although the SolvR® process can achieve emissions levels that are significantly lower than conventional sulphuric acid plants, the process itself is a net consumer of energy and requires a low-pressure steam utility to strip SO_2 out of the solvent. In some cases, a customer may not have convenient access to low-pressure steam, bringing added cost to implement such a utility. In addition, SolvR® adds an extra burden to the cooling water requirement of the plant. MECS, however, has engineered a new sulphuric acid plant flow scheme that both significantly mitigates the utility requirements of SolvR® while maximising high-pressure steam export and minimising capital cost.

The new sulphuric acid plant flow scheme, MAX3™, combines a steam injection HRS™ system and a single-absorption sulphuric acid plant with SolvR® tail gas treatment. Although this configuration offers many benefits, such as ultra-low emissions and increased heat recovery, it also offers a unique, breakthrough benefit in that all the low-pressure steam produced from the sulphuric acid plant main blower turbine can be either upgraded to higher-grade steam or used within the plant. Thus, a low-quality

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Table 2: **Steam export and utilities for different sulphuric acid plant flow schemes**

	Conventional double absorption	**Double absorption with HRS™**	**MAX3™ with steam injection**
Total export steam, kg/h	176,000	215,000	205,000
HP steam export (60 barg, 500°C), kg/h	132,000	132,000	179,000
IP steam export (5 barg, saturated), kg/h	0	67,000	26,000
LP steam export (2 barg, saturated), kg/h	44,000	16,000	0
SO_2 emissions, ppmv	400	400	30
Cooling water, m³/h	6,500	3,500	2,700
Power use, kW	2,400	2,400	2,300
Effluent (1% Na_2SO_4), m³/h	0	0	15
Solvent regeneration, $/year	0	0	575,000

Source: MECS

Table 3: **MAX3™ no steam injection vs SteaMax™**

	MAX3™ without steam injection	**MAX3™ with SteaMax™**
Total export steam, kg/h	153,500	151,800
HP steam export (60 barg, 500°C), kg/h	91,000	101,300
IP steam export (7 barg, 240°C), kg/h	50,500	50,500
LP steam export (2 barg, 230°C), kg/h	12,000	0
Cooling water, m³/h	1,450	1,450
Power use, kW	1,800	1,650

Source: MECS

steam export is minimised or eliminated, and the plant sees increased production in its high-quality steam exports. Fig. 3 depicts the integration of the unit operations in MAX3™ to maximise low-pressure steam usage. Table 2 contrasts MAX3™ with other sulphuric acid plant flow schemes with respect to exports and utilities.

As seen in Table 2, MAX3™ can provide a significant increase in high-pressure steam export while simultaneously putting to use all low-pressure steam generated and eliminating any low-pressure steam export. It can also be observed that this design achieves lower emissions by more than a full order of magnitude compared to the double absorption configurations. If the emissions level were to be raised, the steam export from the MAX3™ case would increase further. Although the system has an additional effluent stream in the form of a sodium sulphate solution, it decreases the required cooling water flow rate throughout the plant by a substantial margin, even compared to the conventional HRS™ configuration.

Adding SteaMax™ to a MAX3™ design unlocks the maximum potential for energy recovery in a sulphuric acid plant. All of the low-pressure steam from the blower turbine is consumed by steam injection, SolvR® usage, and deaerator usage, resulting in no net export of low-pressure steam from the plant battery limits. Instead, the steam export from the HRS™ system is maximised. A case study of a 2,300 t/d MAX3™ plant was conducted to analyse the benefits of SteaMax™ compared to the same MAX3™ configuration without any steam injection. The results are listed in Table 3.

As highlighted in the table, SteaMax™ allows for approximately a 10% increase in high-pressure steam export, while simultaneously eliminating the low-pressure steam export when contrasted to a similar design without steam injection.

MECS sold its first MAX3™ plant in 2015, followed by a second MAX3™ project signing in 2016. Both projects are currently in the detail engineering phase and are projected to start-up in 2019.

Customisation

It is possible to customise the MAX3™ configurations to allow sulphuric acid producers to get the most value from their sulphuric acid plant while meeting all necessary regulatory requirements and encompassing any specific requests. Thanks to its single-absorption contact section with SolvR® regenerative scrubbing, MAX3™ provides opportunities to engineer solutions that meet individual requirements. This flexibility is something not available in conventional double-absorption plants, as gas reheating and other requirements significantly limit the amount of modifications that can be made to the process.

One example of this customisation involves adjusting steam production rates with respect to high-pressure steam from the plant waste heat boiler(s) and intermediate-pressure steam from the HRS Boiler. Not only is it possible to engineer MAX3™ to produce as much high-pressure steam as possible, but it can also accommodate maximising intermediate-pressure steam instead if desired. To accomplish this goal, a superheater is removed after a converter pass and an intermediate-pressure boiler put in its place. Moreover, economiser duty from the high-pressure steam system is shifted to the intermediate-pressure system by adjusting the arrangement and number of economisers in the overall steam system. Note that this kind of customisation allows for any balance of steam production within the range of maximising high-pressure steam production to maximising intermediate-pressure steam production. Compared to a double-absorption plant, the movement and addition of steaming equipment can be done without the restraints caused by gas heating and reheating requirements around the converter.

Additional customisation can be implemented including the recovery of condensation duty from the SO_2 gas condenser in the SolvR® unit. For some extra capital cost, two condensers are used to cool the saturated SO_2 gas leaving the stripping column. The first condenser is cooled with water circulating in the steam system, while the second condenser acts as a trim cooler to bring the SO_2 gas down to the required temperature by using cooling water. Not only is more heat recovered this way, but also much less cooling water is required in the SolvR® system, as the SO_2 condenser encompasses most of the cooling water use. ■

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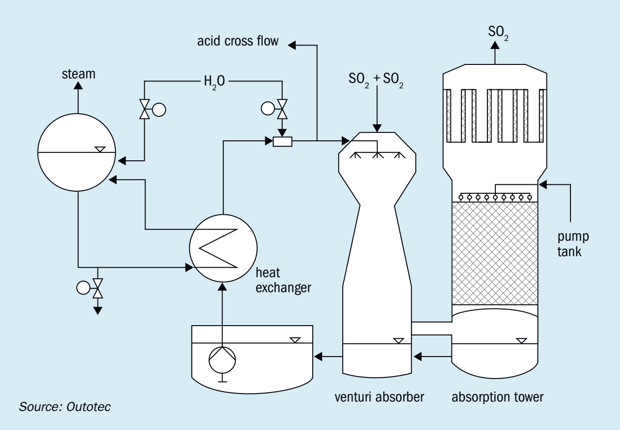
Enhanced HEROS™ for better safety

Outotec has introduced an improved, safe and robust HEROS™ concept, which will enhance the acceptance and reliability of heat recovery systems in the industry. **Stefan Brauener** of Outotec describes a reference case in a metallurgical sulphuric acid plant where it has demonstrated its reliability over the past three years under various operating scenarios, i.e. gas flow and SO_2 fluctuations induced by the upstream smelter operation.

Outotec's heat recovery system, known as HEROS™, was first introduced to the industry in 1989. It was developed with particular emphasis on ease of operation and high safety standards. The key element of the system is a venturi absorber with a dedicated acid circulation system that is installed upstream of the intermediate absorption tower (see Fig. 1). Heat generated in this system is transformed into low-pressure steam in a specially designed boiler. The system can be easily retrofitted in existing sulphuric acid plants as it is designed to permit the shutdown of HEROS™ whilst the intermediate absorption tower remains in full operation. Additional steam production of up to 0.46 tonnes of low-pressure steam per tonne of sulphuric acid is achievable, depending on the plant configuration. Thus, a large percentage of the "low-level" heat is transferred into valuable steam, whilst the cooling water consumption is reduced by the same degree.

In the years since the initial installation, the concept has been further refined in order to further increase efficiency and safety, culminating in recent installations in metallurgical plants in Turkey and Asia, as well as in sulphur burning plants in Egypt.

Fig. 1: **Outotec HEROS™ configuration**



Source: Outotec

Reference case for metallurgical acid plants

Inclusion of energy recovery in metallurgical sulphuric acid plant designs played only a minor role in the past. Most of the few existing energy recovery applications in metallurgical acid plants use low level heat integration where hot air is utilised or hot water is produced. Apart from the recent projects mentioned, which enable production of high pressure steam in metallurgical plants, low level energy recuperation is targeted today.

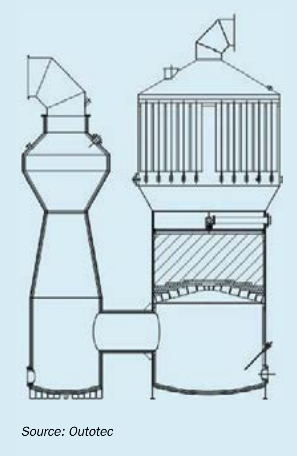
A specific retrofit project and the operational experiences gained from an enhanced Outotec HEROS™ is described. It was ordered by a customer with a pioneering vision and was integrated as a retrofit solution in an existing modern metallurgical sulphuric acid plant complex with challenging space for installation. In continuous operation since early 2014, the installed HEROS™ includes a venturi tower, fully clad with acid-resistant brick lining as well as different levels of process and automation control. This process philosophy was pursued to meet the customer's requirement for continuous operation of the acid plant without disturbing the metallurgical production process, while utilising the majority of the excess heat from the intermediate absorption to produce low-pressure steam for internal industrial demands.

Acid section modification

The existing inter absorption system consisted of a conventional packed bed absorption tower suitable to be used for the envisaged Outotec HEROS™. The inter absorption acid circuit including pump tank, pump, acid cooler, acid piping and instrumentation were also reused.

In principal, if a heat recovery system is to be used in an acid plant, the intermediate absorption consists of two stages, namely a venturi co-current absorber and the downstream conventional absorption system based on a packed tower design (Fig. 2).

Fig. 2: **Venturi and intermediate absorption tower setup**



Source: Outotec

The retrofit HEROS™ is an independently operable acid circulation system using "normal" sulphuric acid with a concentration of 98.5-99.5% H_2SO_4. On account of the absorption of SO_3, and its reaction with water introduced in the venturi, the acid temperature rises. A large part of the SO_3 contained in the process gas is absorbed in the venturi section, which means that the sulphuric acid concentration has to be monitored and controlled in the venturi circuit. The hot acid flows by gravity into a pump tank, from where it is pumped using a vertical pump through the evaporator and then again into the venturi (Fig. 1).

When the HEROS™ is out of operation, the gas passes through the venturi absorber operated without irrigation, hence acting as a 'duct', while the whole SO_3 is absorbed in the conventional absorption tower. For that reason, a much higher acid irrigation rate is required and realised by means of a patented, dual operation Outotec FiDi™ system (acid film distribution, refer to Fig. 3), a combined system with two different acid headers (refer to Fig. 4).

During HEROS™ operation, a smaller acid stream from the drying and final absorption tower is fed with flow rate control to the "smaller" FiDi™ sub-system only. If the HEROS™ is out of operation, the HEROS™ acid pump will be shut off and the acid circuit to the venturi will be out of operation. Therefore the related acid pump will be started and feed acid through the "larger" sub-system of the FiDi™ system, complementing the flow from the "smaller" FiDi™ sub-system, which remains in operation during these periods.

As mentioned earlier, the Outotec heat recovery system can be taken out of operation while the acid plant continues normal production. The process technology has been developed in such a way to ensure a smooth transition between the HEROS™ operation and the conventional inter-absorber operation. This is a significant improvement during start-up of the sulphuric acid plant. It is possible to first stabilise the operation in the conventional inter absorber mode and then slowly "activate" the Outotec HEROS™. This is also valid vice versa, i.e. it facilitates a controlled plant shut down. This feature also makes it possible to commission instruments of the Outotec HEROS™ independently from the sulphuric acid plant and was highly valued by the customer.

Nature of heat recovery systems

Any heat recovery process for low-pressure steam production needs to operate the absorption plant with sulphuric acid at very high temperatures, typically 200 to 220°C. This is thermodynamically required when producing saturated low-pressure steam of e.g. 10 bar. Concentrated acid at 200°C or higher can be extremely corrosive unless a very strictly defined window of operation is adhered to, with respect to acid concentration and temperature. A few suitable stainless steel materials of construction have been identified, but all have a window of operation, dependent on the different material characteristics. Although the tolerable windows are well defined, there will always be upset situations/process excursions in an industrial sulphuric acid plant, which can push the operating parameters outside the tolerable window. This in turn leads to immediate and potentially catastrophic corrosion of the equipment (piping, heat exchangers, coolers, pumps, vessels). Despite all efforts, including extensive instrumentation, such failure of process control cannot be entirely avoided. Beside the corrosion based damage of the equipment, a more significant obstacle recently has become the evolution of hydrogen gas as a result of corrosion and

Fig. 3: **FiDi™ acid distribution system**

Source: Outotec

Fig. 4: **Dual operation FiDi™ system installed**

PHOTO: OUTOTEC

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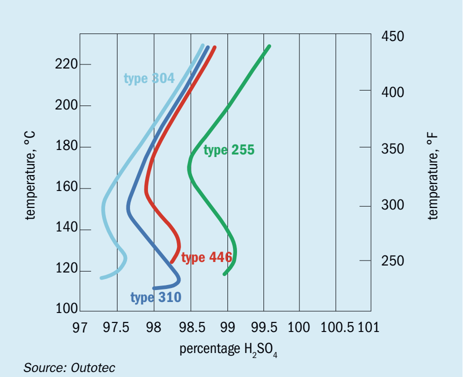
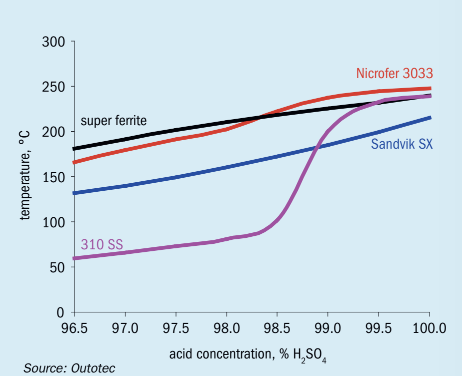
Fig. 5: **Corrosion chart for various stainless steels**



Source: Outotec

Fig. 6: **Iso-corrosion of high alloy material (0.1 mm/y)**



Source: Outotec

the subsequent potential of explosions in sulphuric acid plants.

In the worst case of such an event the complete acid plant must be shut down and cannot continue operation whilst the heat recovery system is off-line. This effect can be dramatic, as the unavailability of the sulphuric acid plant would seriously affect the metallurgical operation and lead to shut down of the upstream smelter. Thus, the security of plant availability and the safety for plant and personnel is a major demand.

While the industry has largely focussed on the prevention of such events, it must be acknowledged that it cannot be entirely avoided and hence the mitigation of the effects, e.g. damage, has become a major issue of concern.

Sulphuric acid at around 200°C can be very corrosive in case the correct concentration is not maintained, e.g. with a tiny leakage of water to the sulphuric acid. Note that the water (steam) pressure is higher than the acid pressure in any heat recovery system in use today. Thus, any leakage will predominantly push water to the acid side and such leakages are extremely difficult to detect or determine. In conventional acid plants, the pressures are such that acid always penetrates into the water side, which can easily be monitored by pH or conductivity. This is not the case in heat recovery systems, hence the serious potential of catastrophic corrosion. Fig. 5 and Fig. 6 illustrate the limitations of the parameters, acid concentration and temperature. The greater the corrosion resistance, the better the material is suited for this purpose. However increased corrosion resistance is directly related to the specific cost of materials of construction.

The fact that the acid plant should not be shut down in case the heat recovery system is taken out of operation, deliberately or forced, is a key element of the design basis. The core plant must be able to continue operation to produce sulphuric acid for the downstream process, e.g. phosphate rock digestion, including HP steam. In case of a metallurgical plant, the upstream metal production would not tolerate a shutdown of the acid plant either. This is a fundamental demand, which Outotec's design fully incorporates.

It was always recognised that the window of operation is crucial and the system can fail despite all instrumentation and control precautions. Acknowledging this, the design must ensure that plant damage can be mitigated.

Wherever possible, Outotec has therefore aimed to use conventional proven materials, i.e. carbon steel with brick lining. This material of construction is "forgiving" in case of accidently operating outside the corrosion limit. Thus, the venturi absorber, the intermediate absorber and the pump tanks all follow the same design (Fig. 2). The only stainless material, which is exposed to the hot acid, is used for pumps, piping and the HEROS™ acid cooler, where there is no other choice. Outotec's material of choice is alloy 3033 rather than type 310 stainless steel used by other technologies. Alloy 3033 offers significantly higher corrosion resistance, and also a wider range of acid concentration before corrosion becomes a serious issue (0.1 mm/year corrosion rate at 200°C between 98.0 and 99.7 wt-% H_2SO_4 for alloy 3033 compared to 99.0 and 99.7 wt-% H_2SO_4 for type 310. On first sight this does not look to be a large difference, however in terms of corrosion using alloy 3033 practically doubles the size of the tolerable window.

In recent years, a number of heat recovery units have experienced hydrogen explosions. The formation of hydrogen as a result of metal corrosion e.g. caused by leakages in acid coolers at conventional plants is not unusual in the sulphuric acid industry. In such a case, cooling water and concentrated acid form a "weak acid" which is extremely corrosive. The amount of hydrogen is dependent on the "weak acid" concentration, the time of exposure and the volume/surface of metallic material exposed to this acid. The hydrogen typically accumulates at the top of the tower and can cause explosions e.g. ignited by static electricity. A number of such events have occurred during the last decade and the resulting damage to the equipment has been significant.

The risk at heat recovery plants is much more pronounced, a) because of the narrow "window" and b) due to the large metallic surface exposed, depending on technology used. Although, so far no fatalities have been reported, the damage at pure metallic heat recovery plants are more severe in such cases.

Boiler

A further improvement has been developed by Outotec by introducing a new design concept on the water side. The Outotec HEROS™ acid cooler design has been converted to a forced circulation water system. Instead of the conventional "reboiler" type, Outotec uses a much smaller shell-and-tube tube type vessel as the boiler. As a result, the amount of water in the system is much less and hence it is easier and faster to separate/drain the water from the system in case of a leakage, thus minimising the exposure time. In a forced or controlled circulation, exchange of water between boiler and drum takes place by means of a pump. This not only reduces the amount of water in direct contact with the hot sulphuric acid but also ensures a uniform temperature distribution in the heat exchanger. Due to the pump and careful design of the water distribution/steam separation piping, intense water circulation is obtained immediately upon start-up. Since all the water is brought quickly into circulation there are no differential temperatures within the boiler that restrict the start-up rate. The higher temperature difference between the fluids allows for smaller heat exchange areas and smaller vessels. There are no constraints regarding design or arrangement of the heat exchanger.

Left: Installed Outotec HEROS™ system.

Loss prevention

It is absolutely essential to separate hot acid and boiler feed water as safe and as fast as possible if a leakage occurs. Therefore sophisticated control technology is also part of the process, enabling early detection of leakages or operational excursions and thus mitigate the damage to equipment and risk to personnel. Experience has demonstrated that reliance on mechanical devices such as emergency drain pumps etc. is rather critical. As a consequence the HEROS™ operates with a drainage device that has never failed so far, namely gravity.

The low-pressure steam boiler is arranged above the hot acid pump tank. Once the acid pump is switched off, the acid drains automatically back into the pump tank. The normal water circulation circuit is isolated from the boiler by valves; steam and water are safely discharged via emergency drain valves.

In the unlikely event of a failure of the low-pressure steam boiler the plant is still capable to run at 100% capacity, which prevents a cold shutdown of the complete sulphuric acid plant with all the known negative impacts on plant lifetime and overall availability.

Acid and water/steam are separated and completely discharged within a few minutes upon leak detection. The emergency shutdown is fully automatic and does not rely on manual intervention of field operators. ■

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Steam or water?

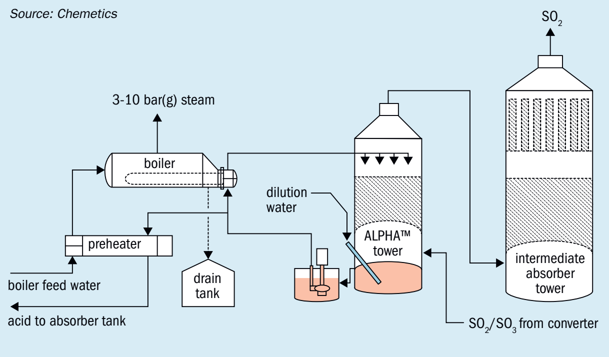
Chemetics provides a number of solutions to extract more of the energy released from the production of sulphuric acid. **R. Dijkstra** of Chemetics gives an overview of these process systems and how each is designed as an independent system from the main process.

Extracting more of the energy released during the production of sulphuric acid is increasingly important to create additional revenue for plant operators. Chemetics has developed a family of process add-on systems that recover additional energy without causing a reduction in plant availability. Marketed as Chemetics Energy Solutions (CES), they provide options for production of low pressure steam, preheating boiler feed water upstream of the deaerator and for the production of hot water. The benefits of producing low pressure steam are relatively well known within the sulphuric acid industry. However, a very interesting application for using hot water is the production of desalinated sea water at locations where fresh water is not readily available.

CES-ALPHA

The Chemetics acid low pressure heat from absorption (ALPHA™) system is used to produce valuable steam from the energy released during the absorption of SO_3 into the strong acid in the absorber tower. Steam is produced at pressures up to 10 barg.

Fig. 1: **Schematic flow diagram of the Chemetics CES-ALPHA™ system**



Source: Chemetics

Chemetics has developed the ALPHA™ system with focus on two main areas:

- Safety – Due to the high operating temperatures the operation of the ALPHA™ system must be tightly controlled to prevent excessive corrosion and possible operator exposure.
- Availability – The ALPHA™ system must not reduce the availability of the sulphuric acid production of the plant as the cost of lost production very quickly exceeds the value of the additional low pressure steam produced.

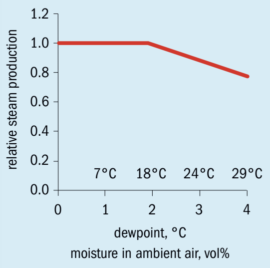
Chemetics has approached these requirements by designing the ALPHA™ system as a true add-on system with a separate hot absorption tower as shown in Fig. 1. This allows the acid plant to remain fully operational during times when the system is not in use. One of the main benefits of this design is that the system can be stopped or started independently of the rest of the sulphuric acid plant allowing the operators to focus on getting the plant to stable operation first before starting the ALPHA™ system.

In order to safely contain the hot sulphuric acid during upset conditions the tower and pump tank are made using brick lined construction. The brick lining provides resistance to hot acid at any concentration allowing safe storage of hot acid at all times. If the control system determines that the operation of the ALPHA™ system is outside the established safe range, the pump is stopped, and all acid drains by gravity into the pump tank while the process gas either continues to flow through the tower or is automatically diverted to the intermediate absorption tower. The system can stay in this state until the issue is resolved without causing corrosion of the metallic boiler and piping systems. In addition, because the main acid plant can continue to operate during an upset in the ALPHA™ system the overall impact on sulphuric acid and HP steam production is negligible.

The ALPHA™ system can be designed to produce up to 10 barg steam. At this pressure it is not practical to maintain the acid at a higher pressure than the water/steam and, in the event of a leak in the boiler, water would leak into the acid circuit resulting in dilution of the acid. If the acid circulation is stopped the water leak would grow rapidly due to weak acid formation and a weak acid layer would form on top of the acid in the pump tank. Once the acid concentration drops below ~98 wt-%, corrosion of any metallic parts becomes rapid and catastrophic failure becomes possible. To prevent this scenario, the ALPHA™ system includes an automated gravity drain system to rapidly separate the pressurised water in the boiler from the hot sulphuric acid in case of a suspected leak or unsafe situation. Immediately separating these streams prevents (further) water ingress into the acid and allows the acid circulation to be stopped before the metallic components are damaged.

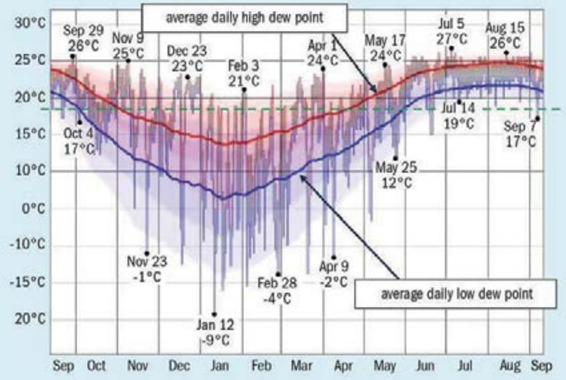
Besides choosing the correct design features for the plant to guarantee safe and reliable operation it is also important to recognise that the amount of steam that can be recovered is dependent on the moisture contained in the ambient air. In order to maintain water balance in the cold absorber circuit, which includes the dry tower and final tower, the maximum amount (in kmol) of moisture in the ambient air cannot exceed the amount (in kmol) of SO_3 absorbed in the cold absorption circuit. If this threshold is exceeded then water has to be transferred from the cold circuit to the hot circuit in the form of crossflow acid. This acid provides a source of cooling in the hot absorber circuit that reduces the amount of energy available for steam generation (see Fig. 2).

Fig. 2: **Influence of atmospheric moisture on steam production**



Source: Chemetics

Fig. 3: **Daily dew point temperature in Tampa, Florida**



Source: www.weatherspark.com

The threshold moisture content in the ambient air is dependent on the following parameters:

- product acid concentration;
- SO_2 conversion achieved before intermediate absorption;
- SO_3 absorption efficiency in the hot absorption system.

For most plants the threshold value is calculated to be between 1.8 to 2.1 vol-% water in the ambient air. This is equivalent to a wet bulb temperature of 16 to 19°C. If the local weather conditions result in a higher wet bulb temperature then the steam production that can be achieved is reduced as can be seen in the chart above. It should be noted that the slope of the line past the breakpoint depends on the design of the system and varies significantly between technology suppliers. The entire system also needs to be designed to cope with the atmospheric conditions that would cause the maximum wet bulb or dew point temperature. In some cases this will increase the cost of the plant.

Whether this issue is something to worry about depends on the location of the plant. For example, if the plant in question is located in Antofagasta in Chile where the dew point never climbs above 19°C there is little cause to worry about reduced steam production due to atmospheric conditions. On the other hand, if the plant is located in Saudi Arabia, India or Florida where the maximum dew point is much higher (up to 33°C in Yanbu, Saudi Arabia), it is likely the plant will experience many hours per day where the steam production is less than the design value, simply due to your ambient conditions. Using climatic data it is possible to calculate exactly how much steam production is impacted, but it can also be easily demonstrated using a graph of the historical dew point temperatures. Fig. 3 shows this graph for Tampa, Florida. Climatic data is generally readily available for any major airport.

The horizontal dotted green line is at 18°C or 2.0 vol% water in ambient air. The solid red and blue lines are daytime and night time average dew point temperatures. Using this method it is easy to determine that there are four months (July to October) where the steam production will be below design the entire day and up to 20% less steam can be expected during those months. Furthermore there are several other months where maximum steam production is not reached during at least part of the day. Clearly this can have a considerable effect on the overall payback time of the entire system and needs to be considered.

CES-HWS

The CES-HWS™ (Hot Water System) is offered to produce hot water from the acid in the absorber circuits. For this process the anodically protected acid coolers in the absorption circuit are specially designed to allow significantly higher water side temperatures. As the inventor and the world's leading fabricator of anodically protected stainless steel acid coolers Chemetics has the experience to design coolers that can produce hot water at temperatures up to 95°C while still maintaining effective passivation of the metallic surfaces. If required, temperatures up to approx. 105 to 110°C can be reached using SARAMET® coolers instead. The upper temperature limit is determined first by the absorber tower design as reduced acid circulation (to achieve higher exit temperatures) could result in SO_3 slippage if the tower design is not properly adjusted and secondly by the need to maintain a reasonable temperature gradient in the acid cooler to keep the required heat transfer area reasonable.

The amount of energy that can be economically recovered depends on the plant configuration. If a single pump tank provides acid to all towers then all the absorption energy can be recovered. If multiple pump tanks are used, then it is typically only economically justified to recover the energy from the intermediate tower.

In order to benefit from hot water production it is necessary to have a user within reasonable distance that can use the hot

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Fig. 4: **Integration of sulphuric acid plant with MED unit**

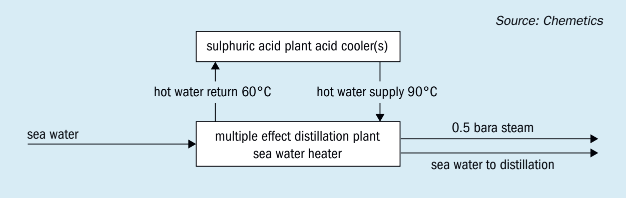
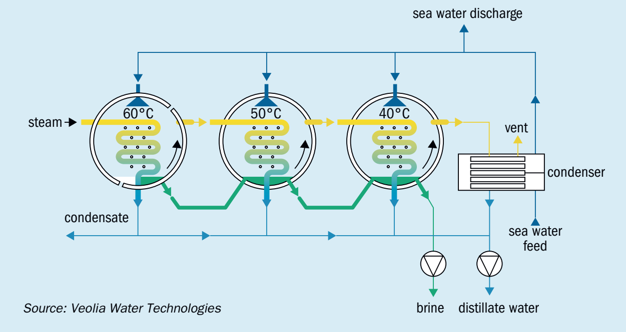


Fig. 5: **Typical 3-stage MED system**



Source: Veolia Water Technologies

water (e.g. for process heating). It is equally important that this user can cool the water to approximately 60°C before it is returned to the acid plant. This temperature is important as the absorber acid has to be cooled to 75°C or less before entering the acid towers. If the hot water user is not able to utilise all the energy or if there are periods when the hot water user is not available to use the energy then trim coolers using cooling water, sea water or air should be installed to allow the acid plant to operate normally.

CES-DSW

The CES-DSW™ or Desalinated Sea Water system is a further evolution of the hot water system. Similar to the previously described system, hot water is generated in the acid plant. In this case, however, the hot water is used in a closed loop to produce desalinated water from sea water or brackish water using a multiple effect distillation (MED) system. The hot water generated at 90 to 95°C flows from the acid plant to the MED unit where it is used in the sea water heaters to create low pressure (0.5 bara) flash steam (see Fig. 4). This flash steam in turn is the energy source for the multiple effect distillation itself, ensuring that the circulating hot water does not have a direct path to the produced desalinated water.

As the name implies the MED unit uses multiple evaporation stages. In the first stage part of the seawater is evaporated using the flash steam that is generated in the sea water heaters. The steam is condensed and forms the desalinated water. The vapour generated in the first stage is used in the next stage operating at slightly lower pressure (Fig. 5). The entire system is operated under vacuum to ensure temperatures are low which eliminates scaling and corrosion of the heat transfer surfaces in contact with the sea water.

Depending on the efficiency of the MED unit up to 10 kg of desalinated water can be produced from each kg of steam entering the unit.

The combination of a sulphuric acid plant together with a multiple desalination unit is a very economical way to produce desalinated water in areas where fresh water is not readily available. Compared to sea water reverse osmosis (SWRO) the multiple effect distillation provides better quality water (lower TDS), has fewer operational issues and lower production cost. As a further benefit, when combined with an acid plant, the sea water flow required for the desalination system and the sea water flow that is required for acid cooling while the MED system is not operational are essentially the same. This means that a single sea water supply can be used which can be directed to where it is needed.

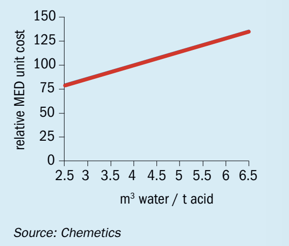
Normally all sea water flow will flow to the MED unit when it is operating at full capacity. If the demand for desalinated water is reduced then part of the sea water would instead flow to the trim coolers in the hot water loop. Having a single sea water supply that is used for cooling or desalination reduces capital cost and simplifies operation.

As mentioned earlier, the efficiency of the MED unit determines the amount of desalinated water produced.

For the combination with an acid plant it is beneficial to express the production of desalinated water as a function of the acid plant production. Chemetics has determined that between 2.5 and 6.5 m³ of desalinated water can be produced for every tonne of acid production. For example, a 3,000 t/d acid plant provides enough energy to produce 7,500 to 18,000 m³ of water per day. It is clear that higher efficiency in the MED units increases the price of the unit, but this increase is relatively modest and is almost linear as can be seen in Fig. 6. This means that only a small incremental investment is required to provide additional desalination capacity. This extra capacity can be used if future demand for desalinated water is expected to increase or can be delivered to local communities as drinking water.

Operation of the MED system is very easy and requires minimal operator attention. Chemetics installed a CES-DSW™ system in Australia in 2004. The performance of this system has exceeded expectations during its 10+ year life and continues to produce high quality desalinated water. ■

Fig. 6: **Relative cost of MED system 4 m³/t, production = 100**



Source: Chemetics

Safely increasing energy generation

Clark Solutions' SAFEHR® heat recovery technology is a new approach to sulphuric acid production which addresses issues and concerns with regard to corrosion, shutdown and hydrogen explosions to make heat recovery safer than conventional operation. **Nelson Clark** describes the SAFEHR® technology, benefits and uses to help the acid plant operator recover energy efficiently and safely.

Sulphuric acid plants are energy producers. Sulphur burning and spent acid recovery plants burn sulphur or fuel to produce SO_2 gases while generating heat. The reaction of oxidation of SO_2 into SO_3 is also exothermic and produces heat. Finally, both moisture and SO_3 absorption into the strong acid generates heat along towers packings.

The major exothermic reactions on which heat is generated in a typical plant are:

Sulphur combustion: $S + O_2 \rightarrow SO_2$
SO_2 oxidation: $SO_2 + ½O_2 \rightarrow SO_3$
SO_3 absorption: $SO_3 + H_2O \rightarrow H_2SO_4$

In a typical sulphur burning plant heat is generated in many process units. Table 1 shows the heat generated at different stages in a typical 1,000 t/d plant, operating at 11.5% SO_2 concentration.

Standard heat recovery technology uses sources 1 to 5 to generate energy by typically producing superheated high pressure steam, up to 63 bar and 480°C. The energy from sources 6 to 8 is usually rejected to the atmosphere via cooling water towers.

Table 2 shows the heat recovery on a standard high efficiency sulphur burning plant.

Table 1: **Heat generation in a 1,000 t/d 3+1 double absorption sulphur burning plant**

Source	Equipment	Generated heat (MW)	Temperature level (°C)
1	Sulphur furnace	33.8	1125
2	Catalytic bed 1	6.9	625
3	Catalytic bed 2	2.9	530
4	Catalytic bed 3	1.1	460
5	Catalytic bed 4	0.6	433
6	Drying tower	1.7	85
7	Interpass absorption tower	14.8	110
8	Final absorption tower	4.3	90
	Total heat generation	66.1	

Source: Clark Solutions

Table 2: **Heat recovery on a standard, high efficiency, sulphur burning plant**

Sources	Equipment	Recovered heat (MW)	Temperature level (°C)
1, 2	Waste heat boiler	33.8	425
2, 3	Superheater	6.9	440
3, 4	Economiser	2.9	180
4, 5	Economiser	1.1	160
	Total heat generation	45.3	

Source: Clark Solutions

The fraction of heat recovered is converted into high pressure steam which, in turn, is used to generate electrical power and/or used for other heating purposes such as phosphoric acid evaporation, etc.

This was the standard for heat recovery in sulphuric acid plants until the early 1980s. As a general rule, a very efficient double absorption sulphur burning acid plant would recover no more than 65% of the total heat generated at the plant.

With the advent of heat recovery processes to recover heat from the interpass absorption step from the reaction

$$SO_3 + H_2O \rightarrow H_2SO_4$$

the total heat recovery from sulphuric acid plants rose from 65% to 90%.

The success and quick investment recovery obtained with heat recovery at the interpass towers has on a few occasions been followed by corrosion, shutdown and explosion concerns.

In the few cases where boiling water leaked into the strong hot acid, the effect was very harmful for the operation. The water-acid reaction at high temperatures

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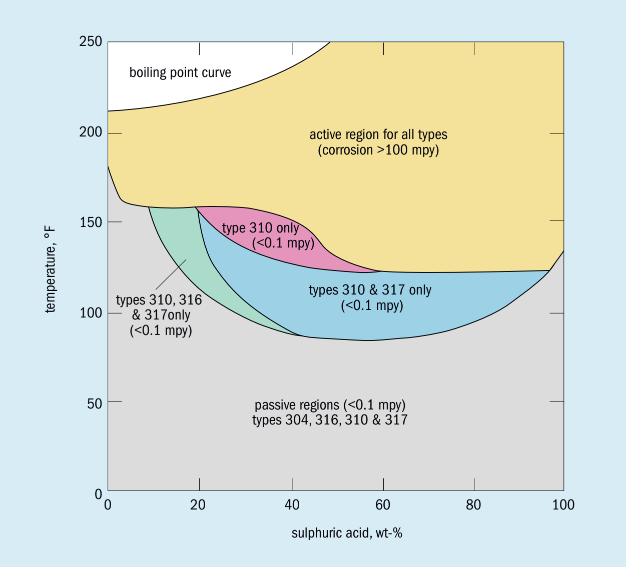
Fig. 1: **Isocorrosion curve for sulphuric acid**



is very exothermic and very quick; as the reaction takes place acid dilutes and heats up and, particularly at the leak location, gets more corrosive, accelerating the corrosion process.

The failure of the heat recovery boiler can be catastrophic; in addition to the failure itself, as a general rule, the acid plant and consequently the entire complex is required to shut down, making failure costs escalate.

Sometimes, downtime is much more critical than the costs of damaged equipment; some plants, to avoid the unexpected shutdown, have built tower independent heat recovery towers and heat recovery systems to protect against such a failure.

The failure of a boiler or of the acid cooler is still a critical problem that can potentially shut the plant down in case of hydrogen explosions.

The hydrogen generation issue

Corrosion of iron by sulphuric acid generates hydrogen according to the following:

$$H_2SO_4 + Fe \rightarrow FeSO_4 + H_{2(g)}$$

The rate of hydrogen formation increases alongside acid operating temperatures.

Hydrogen can damage equipment by several mechanisms, such as solid solution hardening and hydrogen embrittlement, blistering and others. It can also accumulate at high points in the plant and ignite, causing explosions.

The recent literature registers several hydrogen explosion events, in the five continents. All of them were followed by enormous damage to equipment, property and in some cases people.

In normal operation, within the standard <1 mil/year corrosion rates, the generation of hydrogen is minimal (see Fig. 1). As strong acid dilutes, its corrosiveness increases and hydrogen generation rises accordingly.

So, in order to definitively avoid hydrogen formation and its deleterious consequences, while not losing the benefits of heat recovery, it is important to avoid the formation of weak acid.

With this concept in mind, Clark Solutions has developed and patented SAFEHR® Heat Recovery Technology.

The SAFEHR® concept

The concept behind SAFEHR® technology is the use of a family of proprietary inert fluids, CS fluids, to work as intermediate media between the hot acid and boiler feed water.

The CS fluid products present a series of properties that make them unique for working as intermediate media in such systems:

- Inert to acid and water: the fluid is totally inert to acid (in any concentrations) and water.
- Non-corrosive: they can be used with virtually any materials without any corrosion risk, being compatible with strong acids, water, organics fluids among others.
- Non-toxic: the fluid is FDA approved and its handling and storage requires no special measures.
- Non-flammable: it with not catch fire, even if an ignition source is put in contact with hot fluid.
- Non-oxidant: oxygen or atmospheric air will not oxidise the fluids, so they can be used and store in non-blanketed environments.
- High boiling points: boiling points will vary between 200°C and 300°C, depending on the fluid and application selected.
- Density in-between water and acid: fluid densities at operating temperatures will be between 1,3 g/cm³ and 1,5 g/cm³, in between that of liquid water, 880-980 g/cm³, and strong acid, 1,6 -1,8 g/cm³, keeping the phases separated even in leakage situations.
- Low vapour pressures: usually less than 20 mm w.c. what will minimise losses by evaporation.
- Odour: fluid is odourless and requires no mask or other respiratory devices while being handled.

Basically the SAFEHR® system is a closed loop, where hot acid is cooled by the CS fluid, which in turn heats the boiler feed water:

Fig. 2 shows the SAFEHR® closed loop for high temperature conditions.

The CS fluid is a polymeric fluid, inert and immiscible to both water and sulphuric acid.

The CS fluid system is maintained at a pressure below the acid and water systems so in the event of a leak, the leaking fluid follows into the CS fluid circuit, which will allow the leak to be identified.

The interfacial tension and density differences between the fluids make a liquid liquid coalescer an excellent storage tank. Acid will settle at the bottom of the coalescer and water will stay at its top, so, even in the improbable case that both fluids would leak, there would still be no contact between them. The coalescer/settling tank is designed to easily segregate the fluids. Conductivity and level control guarantee that a leak is quickly identified.

Fig. 3 shows corrosion promoted by sulphuric acid with water contact (left) and CS 270 fluid contact (right).

SAFEHR® applications

Hydrogen explosions are not limited to conventional heat recovery plants. In Brasil, in the last ten years, three acid plants have registered hydrogen explosions. Two of these were acid cooler leak related. None of them produced personnel injuries but all of them caused major equipment and loss of production costs.

Conventional plants

SAFEHR® as a concept can be used in existing plants, as an intermediate cycle in the acid cooling circuit (see Fig. 4).

In this case, the strong acid system will be protected from leaks, even in upset conditions.

The strong acid cooler can be either a shell-and-tube unit or a plate unit; this last one will requires smaller coolant fluid loads. The water heater will be a plate unit built in 304/316 stainless steel as there is no corrosion risk on this side of the process.

The water side of the strong acid cooler will be protected and free from corrosion or incrustation as it will be only in contact with the CS fluid, inert and thermally stable. In such a case, the purpose of SAFEHR® is to add reliability to the acid cooling system(s) and eliminate the hydrogen explosion risk.

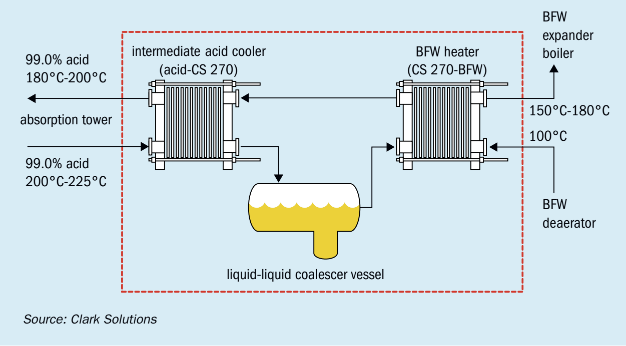
Existing heat recovery systems

An existing heat recovery system can benefit from a skid mounted SAFEHR® system as a replacement to the strong acid to boiler feed water exchanger.

This will aggregate safety to the process and allow for the boiler to be constructed of less expensive materials.

While a boiler feed water leak will flow to the acid system in a conventional system, requiring the shut-down of the whole acid plant or the heat recovery unit, in a SAFEHR® unit the leak will flow into the SAFEHR® skid, with no contact between fluids, allowing the operator to plan the maintenance in advance.

Fig. 2: **SAFEHR® closed loop for high temperature conditions**

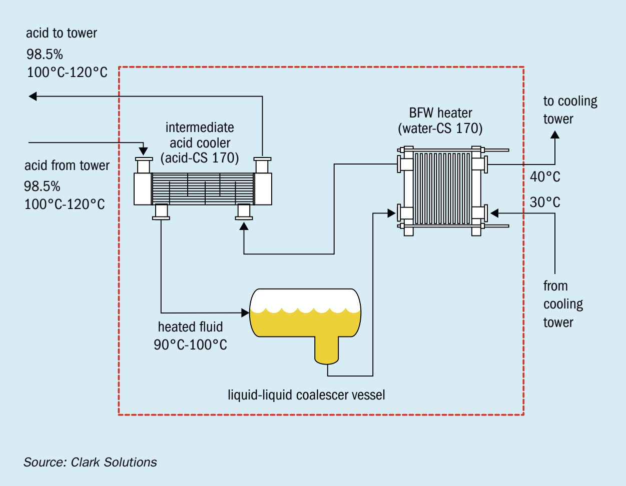


Source: Clark Solutions

Fig. 3: **Corrosion promoted by H_2SO_4 with (L) water and (R) CS 270 fluid contact**

PHOTO: CLARK SOLUTIONS

Fig. 4: **SAFEHR® closed loop for conventional operating conditions**



Source: Clark Solutions

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Fig. 5: **SAFEHR® schematic**

Source: Clark Solutions

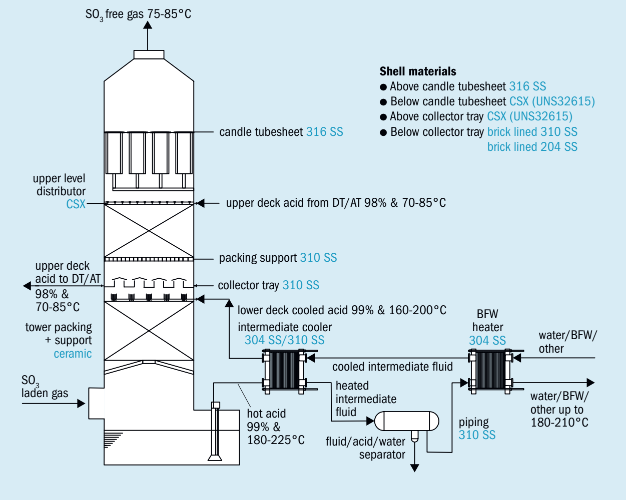
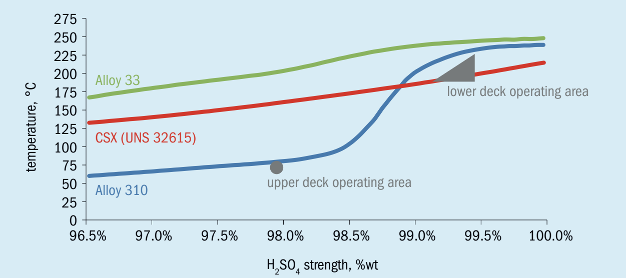


Fig. 6: **SAFEHR® operating envelope**



Source: Clark Solutions

Complete system

SAFEHR® can also be implemented as a complete system (see Fig. 5). In this case Clark Solutions chose to design the system using 99.0-99.5% sulphuric acid as an absorbing media as this will allow the use of less expensive 310S stainless steel materials. Nothing, however, prevents the system from being built for 98.0-98.5% acid and using Alloy 33 or CSX stainless steel (UNS32615).

The complete system is basically composed of a two-stage absorbing tower with integrated pump booth, an acid pump and the SAFEHR® system.

The SO_3 admitted to the bottom of the tower is absorbed in the lower packing deck, where the reaction heats the acid to 220-225°C. The gases leaving this stage pass through a collector tray where they get remixed before it reaches the upper packing deck.

The hot concentrated acid from the bottom of the tower is pumped from the pump booth by a vertical centrifugal pump into the intermediate cooler where it exchanges heat with the CS fluid. The fluid is circulating in an enclosed system and heats boiler feed water or other fluids in this circuit.

The collector tray brings a substantial benefit to the energy recovery as it avoids cool acid mixing with the bottom section acid, cooling it down and reducing the bottom temperature.

At the top of the upper deck, cold acid is irrigated in order to condense mist and absorb any non-absorbed SO_3 traces from the lower deck. This guarantees maximum absorption and minimal acid mist carryover.

Once the upper level acid, from the drying tower or the final tower depending on plant arrangement, reaches the top of the collector tray, it is collected and re-routed by gravity back to the tower from which it came.

The upper deck as well as the piping system to it, can be designed for full absorption of SO_3, allowing the tower to operate with or without the intermediate loop.

The gases, free of SO_3, flow through candle mist eliminators where the fine acid mist is captured and the gas flows to the process or to the stack/scrubber in single absorption systems.

The intermediate cooling system

The intermediate cooling system can be supplied as separate skid for an existing plant or as part of a new heat recovery system.

It is composed of an acid-fluid heat exchanger, a liquid-liquid coalescer, pump, fluid-water heat exchanger and a buffer vessel.

The acid-fluid heat exchanger can be a plate exchanger, a shell-and-tube exchanger or an Alfa-Laval Compabloc fully welded exchanger. The choice of exchanger depends on the acid temperature and water pressure levels in the system.

The pressures are controlled so that the fluid circuit operates at the lowest pressure condition. In the case of eventual leaks, the pressure difference forces liquids into the intermediate loop. Acid leaks will reach the coalescer, while water leaks will circulate to the buffer or coalescer vessel. Acid leaks will be detected at the bottom of the coalescer by conductivity while water leaks will be indicated by a liquid level increase in the system.

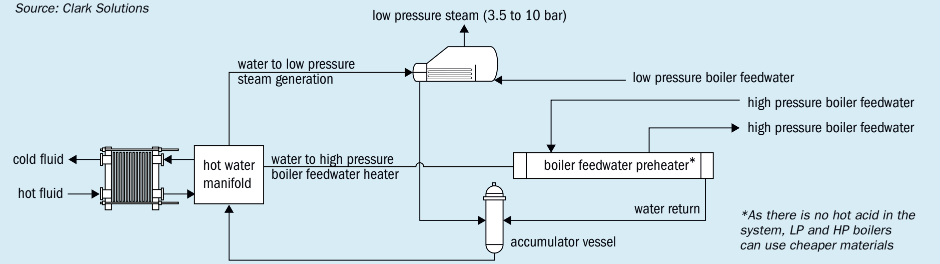
Acid leaks will not accelerate as there is no heat of dilution or weak acid formed at the leak area, thereby conditioning the localised corrosion process to evolve slowly, giving time for a planned shutdown.

Materials of construction

SAFEHR® is designed to be safe and last for many decades. Materials of construction are chosen accordingly. Fig. 6 shows the SAFEHR® operating envelope.

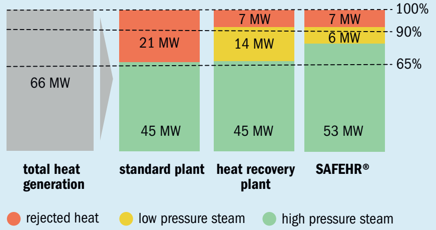
Fig. 7: **Steam system schematic**

Source: Clark Solutions



**As there is no hot acid in the system, LP and HP boilers can use cheaper materials*

Fig. 8: **Heat recovery comparison chart**



Source: Clark Solutions

Table 4: **Steam production on a 1,000 t/d plant with several energy options**

	No heat recovery	**Heat recovery**	**SAFEHR®**
High pressure steam, t/h	54.0	54.0	65.2
(40 bar and 400°C), MW	44.4	44.4	53.6
t/t	1.3	1.3	1.56
Low pressure steam, t/h		20.8	7.6
(10 bar saturated), MW		14.6	5.4
t/t		0.5	0.18

Source: Clark Solutions

The SAFEHR® tower is built of three different material sections.

The bottom section and the pump booth, where the hot strong acid is stored, is brick lined 310S. The 310S stainless itself is extremely resistant to the operating conditions, but, the extra care with brick lining will guarantee the long term reliability and reduce risk of hydrogen generation and presence of nickel and chromium in product acid.

The collection tray is a 310S stainless construction.

From the collection tray and above, up to the candles tube sheet, the construction is SX®. In this region, acid at 80°C will pose no risk to SX. This section could be built using 310S stainless, but as Fig. 6 shows, the operation would approach the 1 mil/year line and per design principle Clark Solutions chose to keep corrosion bellow that limit whenever possible.

Tube sheet, candles housing and outlet duct are built of 316L stainless steel.

Entering the intermediate system, the acid fluid exchanger is a 310S construction (Compabloc) or 310S (tubes and headers) and 304S (shell) in the shell-and-tube case.

The fluid-water heat exchanger can be carbon steel/304/316, plate, spiral or shell and tube exchanger, depending on how heat will be distributed. Important to notice however is that the SAFEHR® boiler can be made of less expensive materials as it will be handling water instead of sulphuric acid.

The liquid-liquid coalescer is a cylindrical, vertical, 3 phase vessel equipped with a 316/310S plate-pack coalescer to keep phases (water/acid/fluid) separated even in the case of a leak.

The main acid pump is CD4MCu while the intermediate circuit fluid pump is a 316 SS centrifugal pump as well as the piping and expansion tank.

Steam system

With SAFEHR® there are no limits as to how to use the recovered heat. For instance, part of the energy could be used to heat high pressure boiler feed water as shown in Fig. 7.

As an example, an acid plant that produces 1,000 t/d without a heat recovery system would produce approximately 54 t/h of 40 bar and 400°C steam.

It if had a conventional heat recovery system, an additional 20 t/h of saturated 10 bar steam could be produced.

With SAFEHR® some of the energy used to produce low pressure steam could actually be shifted into high pressure. For example, if all the available heat could be used to pre-heat boiler feed water at 40 bar from 60°C to 180°C there would be an increase of 20% in the amount of high pressure (see Table 4 and Fig. 8).

SAFEHR® heat, in the form of hot water or steam can be used for other purposes.

Conclusion

SAFEHR® is a new approach to the acid production. While adding a great deal of safety to the process and reducing corrosions risk, this is accomplished without any substantial energy losses. On the contrary, depending on the arrangement the SAFEHR® system it can improve quality of steam, a particularly interesting advantage for plants generating electrical energy. ■

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