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Khursaniyah gas plant in Jubail Industrial City, Saudi Arabia

Photo: Saudi Aramco



The Atlas Copco logo is positioned in the top right corner of the page. It consists of the company name "Atlas Copco" in a white, serif font, centered between two horizontal white bars. The background of the entire page is a photograph of a large industrial chemical or petrochemical plant, featuring a complex network of blue steel structures, silver pipes, and tall distillation columns against a clear blue sky. A large, semi-transparent teal graphic is overlaid on the bottom left, containing technical drawings and blueprints.

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Editor
Chris Cunningham
editor@petroleumtechnology.com

Production Editor
Rachel Storry
production@petroleumtechnology.com

Graphics
Peter Harper
graphics@petroleumtechnology.com

Editorial
tel +44 844 5888 773
fax +44 844 5888 667

Business Development Director
Paul Mason
sales@petroleumtechnology.com

Advertising Sales Office
tel +44 844 5888 771
fax +44 844 5888 662

Managing Director
Richard Watts
richard.watts@emap.com

Circulation
Fran Havard
circulation@petroleumtechnology.com

EMAP, 10th Floor, Southern House,
Wellesley Grove, Croydon CR0 1XG
tel +44 208 253 8695

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To flare or not

What do you do with the gas associated with crude oil production if there is no local processing capacity and no gas gathering network to collect and deliver cleaned-up natural gas? If the value of the gas is attractive enough, you can invest in more processing and build a section of pipeline.

Or you could just vent it to atmosphere, reinject it to produce more oil, or flare it off and have done with it. The argument in favour of flaring (and, let's face it, it is the only argument in its favour) is that its chief release is carbon dioxide. Venting means a release of methane which is generally reckoned to be a much more serious contributor to climate change.

So flaring is the simple option for oil producers, provided there are no moves to force them to clean up and monetise their sideline in gas production. It is a global practice and most regions have local permitting bodies to give the go-ahead or otherwise to applications to burn off gas production. In several producing nations, steps are afoot to reduce flaring as much as possible. Nigeria, for instance, was recently horrified to note that flaring operations by its oil industry were losing one billion dollars worth of revenue. However, the centre of attention in the debate about gas flaring, like news in general about oil exploration and production, is in US tight oil operations.

One operator in the Texas Permian, ExxonMobil, has made a stand about one aspect of its environmental performance. It has devised what it calls a model framework for methane regulations in the US oil industry with the aim of developing "enhanced rules to reduce emissions in all phases of production". The company says that it has been applying the principles of its framework to oil and natural gas operations for several years, resulting in improvements that demonstrate what is practicable and achievable. The model framework is based on a voluntary methane reduction programme, which involves replacement of leaky components at production sites, as well as improvements to technology, data gathering, and research. ExxonMobil says that it has reduced methane emissions from its tight oil operations by 20% in four years with the aim of 15% reductions across the company. In other words, the intention is to reduce gas leaks, but the contained gas can still be flared.

The outlook for objectors to flaring in Texas is not promising. The state has elected regulators to oversee its oil and gas industry and they are reportedly highly defensive about local flaring activities, comparing them as favourably as possible to other oil-producing regions at home and abroad. In recent years, Texas has not turned down any applications for flaring permits during the rush to develop Permian oil resources.

Operators in the Permian say that they are striving to reduce flaring and some are taking strides to do so. However, the incentives to eliminate flaring in Texas and elsewhere are fiscally limited. The tight oil bonanza is, in the general scheme of petroleum production, a short-lived operation. If in five years' time the industry is winding down, as seems likely, a flare-free operation would leave behind the expensive carcasses of redundant gas processing and gas gathering hardware.

CHRIS CUNNINGHAM

The ExxonMobil logo is positioned in the top right corner. It features the word "ExxonMobil" in a white, sans-serif font, with the "X" in "Exxon" and "Mobil" having a distinctive slanted design. The background of the entire advertisement is a dark, almost black space filled with a complex, glowing molecular structure. This structure consists of a central cluster of red and white spheres connected by thin lines, representing a catalyst particle. From this central point, a large, translucent, multi-colored wave (shades of purple, blue, and green) extends upwards and outwards, resembling a sound wave or a field of energy. The overall aesthetic is scientific and futuristic.

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Q Is SO₂ breakthrough in our tail gas treating unit (TGTU) a result of poor excess air control?

A Mark Edling, Technical Services Engineer & Gas Treating Specialist, Shell Catalysts & Technologies, Mark.Edling@shell.com and Hans Wijnbelt, Global Manager Tail Gas Catalyst, Shell Catalysts & Technologies, Hans.Wijnbelt@shell.com

The response to this question makes the following assumptions:

- The TGTU uses an inline burner to heat the tail gas to the required inlet temperature
- The loading of the reactor was done correctly and there is no bypassing
- The catalyst was activated correctly
- At start-up, the catalyst was fully meeting expected performance and there was no indication of SO₂ breakthrough
- Performance issues started to appear after a certain time of operation with no indication of a clear operational error or extreme temperature excursions

Tail gas catalyst operates in the temperature window of roughly 430-600°F (220-315°C) depending on the catalyst type and process conditions. The burner gas rate controls the reactor inlet temperature, which should be high enough to achieve the desired conversion of the sulphur species in the tail gas. The air: gas ratio of the burner should be low enough to provide some reducing gases (CO and H₂) with virtually no O₂ slip, but not

so low that soot is generated. For a TGTU with an inline burner, there is always the potential risk that, in the course of time, the air control shifts.

What happens if the ratio control shifts toward excess air?

If the actual air: gas ratio is higher than it should be, the burner will generate less reducing gas. In most cases, there is adequate H₂ generated in the SRU reaction furnace for all the tail gas reactions, and therefore the tail gas reactor is not strictly dependent on the reducing gases generated by the inline burner. However, this is not always the case. If the actual air: gas ratio shifts high, the burner will generate less CO/H₂ and there may be insufficient excess hydrogen for the hydrogenation of SX and SO₂. In this case, the reactor would start slipping SO₂. Typically, this is not observed, or if it is the slipping occurs intermittently with normal unit swings. The quench overhead hydrogen concentration should be regularly monitored to ensure excess hydrogen is always present.

There are also longer term consequences of a high air: gas ratio. If the actual ratio drifts high, a dramatic loss of catalyst activity that quickly results in SO₂ breakthrough will not be observed.¹ Generally, excess air is a slow killer of TGTU catalyst and only progresses to the point of SO₂ breakthrough when the unit is not properly monitored.

Proper monitoring of the in-bed temperatures of

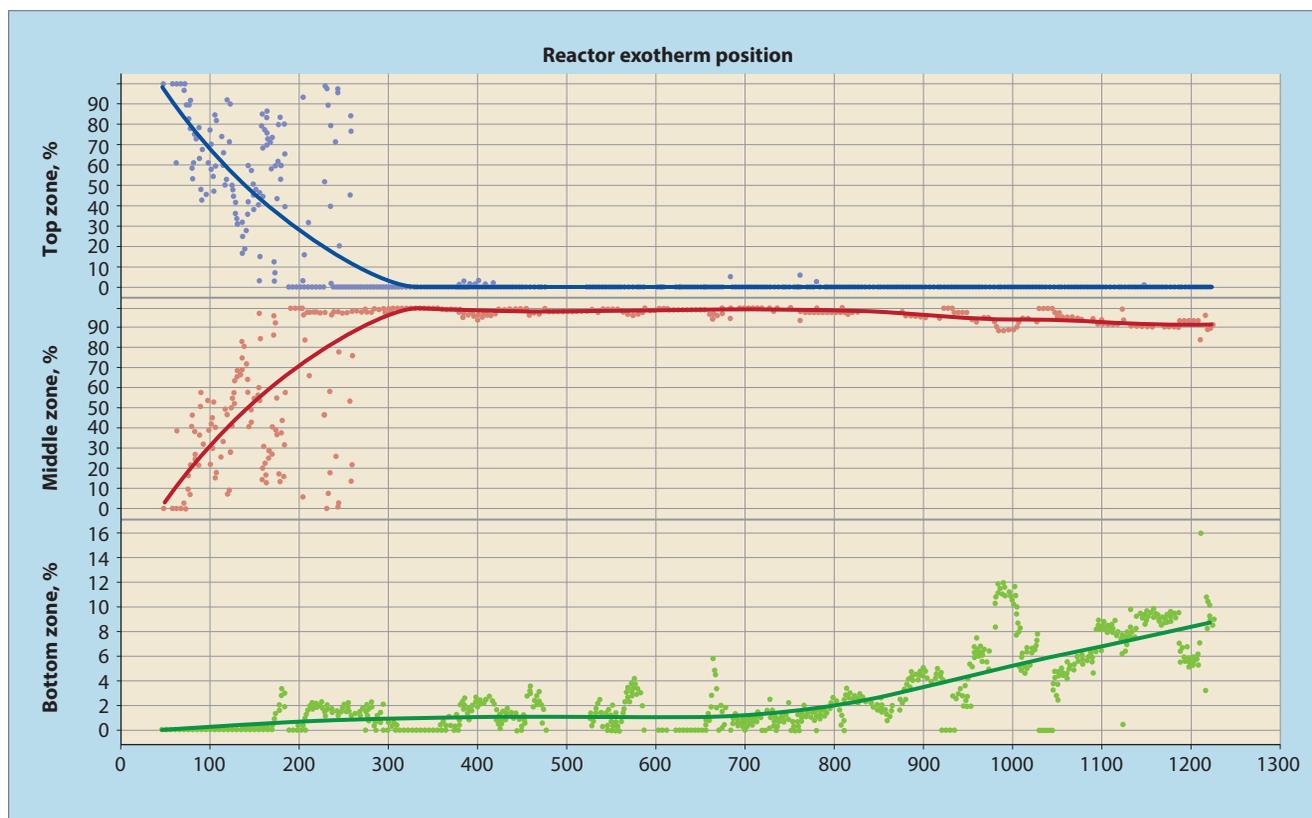


Figure 1 Impact of air intrusion on tail gas catalyst bed

the reactor is the primary way to determine if oxygen is slipping into the reactor. If oxygen is present, the tail gas reactor profile will indicate slow but definitive deactivation. If the oxygen slip component flow rate is steady, the deactivation profile will be linear. Depending on the amount of slip, the deactivation normally takes months or years of operation before the catalyst is poisoned to the point of allowing SO₂ breakthrough.

Monitoring the bed temperatures will show the deactivation starting at the top of the bed if and when oxygen begins slipping into the reactor. An example is shown in **Figure 1**.

Figure 1 shows what percentage of the total exotherm is in the top, the middle, and the bottom zones of the reactor. In approximately 200 days of operation, the exotherm in the top bed of the reactor (blue line) had disappeared. The catalyst above the top row of thermocouples is completely deactivated.

At the same time this deactivation was occurring, the percentage of the exotherm in the middle zone of the reactor (red line) started to rise. This indicates that the exothermic conversion reactions moved to the middle zone where SO₂ (and other sulphur species) are con-

Every time the unit is down for maintenance work, the physical components of the meter should be inspected and the meters should be recalibrated

verted to H₂S. Such a rapid top-down deactivation as seen in the top zone of the bed is almost always due to oxygen ingress. In this case, the oxygen slip from the burner was in the order of 5000 ppm.

In the case of lower-level oxygen slip (ex 100 vppm O₂), the deactivation caused by the air will not be as extreme as in the first 200 days in the example above. However, in the example above, low level oxygen slip started again around Day 800, resulting in a steady but much slower deactivation trend. Activity in the middle of the bed (red line) shifts to the bottom zone (green line – note the different scale on this section of the plot). Despite the relatively slow nature of this sort of deactivation, oxygen slip irreversibly degrades tail gas catalyst through surface sulphation.

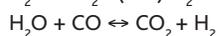
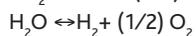
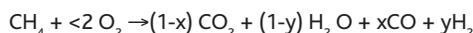
From **Figure 1**, it is clear that oxygen was slipping into the reactor, causing the deactivation. Calibration of the air and gas meters on the inline burner was required to correct the issue. For this specific case using Shell C&T 834 tail gas catalyst, it should be noted that even with a third of the catalyst being destroyed, the Shell catalyst was still able to meet the required performance without SO₂ slip.

It is important to select a robust, high-activity catalyst to give some contingency for events like this, but the best solutions are prevention and early recognition.

Air and gas flow meters on the TGTU inline burner tend not to get calibrated routinely because the indication and the control system appear to be fine. But the calibration can slip over time, and since the system controls to a ratio (inherently non-linear), a small error in the calibration can have a large impact on the catalyst. Therefore, in addition to regular monitoring, meter calibration should be part of the planned maintenance on the unit. Every time the unit is down for maintenance work, the physical components of the meter should be inspected and the meters should be recalibrated.

What happens if the ratio control shifts towards insufficient air?

Consider the following equations that partially describe the sub-stoichiometric combustion of methane with oxygen:



While combustion is often considered irreversible, there are equilibrium reactions that become significant in the tail gas burner application. As the oxygen level is reduced, these equilibrium reactions shift to accommodate the lower oxygen availability. However, eventually the combustion becomes so oxygen starved that formation of solid carbon and hydrogen becomes favourable. Solid carbon is formed as soot, a fine powder.

Soot is well known to tail gas unit operators because it can quickly cause significant pressure drop (dP) across the tail gas reactor. What is less known is that soot also deactivates the catalyst by reducing the accessibility of the active sites. This deactivation can eventually lead to slip of SO₂ and other sulphur species present. As with O₂ slip intrusion, deactivation via sooting can be a slow process where the effect is noticed only after some time. Generally, the dP increase associated with sooting will occur before SO₂ breakthrough is observed, but this is not always the case. With very low levels of sooting over a catalyst with high fouling tolerance, the rate of deactivation can exceed the rate of dP build.

Once again, plant monitoring is critical. Monitoring the bed temperature profile should identify any sort of deactivation, and if sooting is occurring, monitoring the normalised reactor dP should help identify it before it becomes severely limiting. Even if the reactor does not have dedicated dP measurement, any upstream pressure indication can be monitored and normalised to flow rate. If the pressure inexplicably begins increasing, this should trigger troubleshooting activities.

Is SO₂ breakthrough in our TGTU a result of poor excess air control?

Experiencing SO₂ breakthrough as a result of poor excess air control can and does happen. It can be a short term, reversible issue resulting from insufficient reduc-



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ing gas available for the hydrogenation of the sulphur species, or it can be a long term irreversible issue resulting from catalyst deactivation due to poor air: gas control. Routine meter calibrations and a proper ratio setpoint can help prevent catalyst deactivation, and in all cases, regular monitoring should easily identify these problems long before they cause breakthrough or even significantly limit cycle life.

Q Can you suggest ways to reduce CO₂ emissions from our FCC regenerator?

A Manoj Katakdaunde, Catalytic Cracking Engineer, Shell Global Solutions US, Manoj.Katakdaunde@shell.com, Robert Ludolph, Principal Catalytic Cracking Engineer, Shell Global Solutions US, Robert.Ludolph@shell.com, and Laurent Thomas, Gas Processing Licensing Manager, Shell Canada, Laurent.Thomas@shell.com

There are essentially three pathways to reducing the CO₂ emissions of an FCC unit:

- Through modification of the FCC unit operational parameters
- Through modification of FCC unit hardware (followed by operational modification)
- Through capture of CO₂ from the FCC unit off-gas

Operational parameters

An FCC unit is usually operated to a target conversion based on margin. CO₂ reduction is not the typical main driver because changing the FCC unit operation for CO₂ reduction can drive the operation into a less profitable area. If CO₂ emissions reduction is pursued, care must be taken when modifying the FCC unit operation to ensure that one is not just pushing the CO₂ emissions to another part of the refinery, and thereby causing a nil overall CO₂ reduction. Most of the operational or technological handles to reduce CO₂ emissions will come with margin loss or capital investment and may not be economically feasible for an operating refinery. Other means for justification (environmental regulations, carbon credits, unit flexibility, and so on) would need to be in play when setting the future direction of the FCC unit.

There are a variety of potential options to reduce CO₂ emissions:

Option 1

Increase feed preheat to reduce coke burned in the regenerator. The operator will need to reformulate the catalyst for better coke selectivity to make up for the lost conversion. If there is no feed furnace, CO₂ reductions are absolutely reduced by the amount of coke burn reduction, but there may not be much room for coke reduction if the feed preheat exchangers are close to the pinch point. With a feed furnace, there is more flexibility to reduce regenerator coke burn, but total CO₂ reductions are less since the furnace will fire more and produce more CO₂. (The total CO₂ will still be lower since natural gas is less carbon intensive than coke.)

Option 2

Reduce throughput, which will reduce CO₂ since coke burn is reduced.

Option 3

If in partial burn mode, operate to a lower flue gas CO target which will lower coke yield. (This will require flexibility in the air blower without constraint on the capacity.)

Option 4

Use CO promoter, which not only will assist in managing afterburn, but will optimise coke burn in the catalyst bed versus the flue gas and, hence, burn less coke.

Option 5

Go to full burn in the regenerator, which will require a catalyst reformulation, and likely capital project(s) for air blower capacity and possibly conversion of the CO boiler to a flue gas cooler. If there is too much HP steam, CO₂ will be reduced in the full burn option by the elimination of the fuel burned in the CO boiler. If there is not enough HP steam, CO₂ emissions may just be pushed to a steam boiler in another part of the refinery, causing a nil overall CO₂ reduction.

Option 6

Switch the feed source to a higher quality and cleaner feed (lower feed carbon content and/or metals), while maintaining the same conversion. This will directionally reduce the coke burned in the regenerator. To main-

If CO₂ emissions reduction is pursued, care must be taken when modifying the FCC unit operation to ensure that one is not just pushing the CO₂ emissions to another part of the refinery

tain conversion with the new feed, it will be necessary to adjust the fresh catalyst addition rate, and possibly the catalyst reformulation. This will also typically involve a capital project to change the feed source or a catalyst change in the upstream cat feed hydrotreater to improve the feed treating. Without an upstream hydrotreater, capital expenditure will be needed to change the source of feed or to buy a different type of feed from the outside market. (Cleaner purchased feeds directionally cost more in the open market.) With a cat feed hydrotreater, a change in the type of catalyst will be needed to improve the feed hydrotreating, resulting in a better feed quality to the FCC unit.

Option 7

If the regenerator operation is flexible (unconstrained), remove recycles and/or steam/sour water injection to



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the riser, if such streams exist. Catalyst reformulation will be necessary to regain any penalty on conversion from dropping sour water or recycles.

Option 8

Reduce the riser temperature to burn less coke in the regenerator. Again, any penalty on conversion will have to be overcome through catalyst reformulation options (like higher activity, better coke selectivity, and so on).

Hardware upgrade

Other than the operating options above, there are technology options to reduce delta coke (reduce coke yield at same conversion), followed by an operational change to maintain conversion. Potential hardware upgrade options will require capital investment and a turnaround to execute the project. The following hardware changes are possible to reduce coke make:

Option 1

Upgrade feed nozzles to reduce unvaporised feed lay-down on the catalyst.

Option 2

Install close-coupled reactor cyclones to lower spent catalyst coke.

Option 3

Add improved stripper internals to lower spent catalyst coke.

Option 4

Improve catalyst/air contacting in the regenerator to stabilise lower flue gas CO operation in partial burn, by reducing afterburn and optimising coke burn in the catalyst bed versus the flue gas. Installing a new air grid (for good air distribution) and/or a new spent catalyst distributor (for good catalyst distribution) can be explored to improve the contacting between the air and catalyst.

Option 5

Install a flue gas expander to generate power from the flue gases; this would need a third stage separator to remove abrasive particulates and protect the expander blades from erosion and vibration. Some steam generation is lost but the power generation is much greater.

CO₂ capture

CO₂ emissions can also be drastically reduced, without modification of the FCC unit operating parameters or hardware, by addition of a carbon capture system at the tail end of the FCC unit, to capture CO₂ from the FCC unit regenerator off-gas.

The technologies proven at commercial scale are amine based capture systems. Such systems are very similar to the amine systems already used in refineries for acid gas (H₂S) removal and in natural gas treating operations, but they use a solvent that is tailored to capture of CO₂ from low pressure gases containing oxygen. They commonly achieve capture efficiencies of 90-95%,

and up to 99%. Since the FCC unit is usually one of the main CO₂ emitters in a refinery, this can help significantly to reduce the refinery carbon footprint.

Specific challenges for FCC applications are:

Utilisation or sequestration of the captured CO₂

The captured CO₂, regenerated as a pure, water-saturated CO₂ stream, needs to be used or sequestered.

It can be sold to CO₂ consumers if they are present in the area or if a pipeline infrastructure allows delivering the CO₂ to them. However, the demand from most industrial consumers, such as greenhouses, is often less than the amount captured from an FCC. EOR applications, on the other hand, typically consume large amounts of CO₂ (several thousand tons per day).

The alternative is sequestration of the captured CO₂. The CO₂ is then typically compressed and transported by pipeline to a sequestration site – often a depleted oil/gas field and also often offshore due to community concerns over injection of CO₂. In this case, synergies with other carbon capture and sequestration (CCS) projects in the same area allow sharing the transport and sequestration facilities, thus improving the economics of each project, hence the development of so-called CCS ‘clusters’.

Gas pre-cleaning

Before it is treated in the CO₂ absorber, the FCC gas needs to be cooled (to about 30-60°C) and cleaned of contaminants to which the CO₂ capture system is sensitive: catalyst fines, SO_x and NO₂.

This will typically involve gas cleaning solutions already used in FCC applications, such as SCR, fourth stage separator, wet gas scrubbers, or wet electrostatic precipitators.

Additional pressure drop on the flue gas path

The gas cooling, pre-cleaning and CO₂ absorption chain will add a few kPa pressure drop on the flue gas path. In most CO₂ capture applications, this is dealt with by adding a booster fan; however, in FCC applications, this may not be the preferred option because of the impact on overall reliability/availability.

The other option is to accommodate the resulting back pressure in the FCC unit system. This can be challenging because of the maximum allowable pressure in the CO boiler, in which case the design of the cooling, pre-cleaning, and absorber may be strongly driven by pressure drop minimisation.

References

1 Major upsets such as large SO₂ spikes from the upstream sulphur plant or percent-level oxygen incursion will result in a very large, very quickly developing exotherm that can destroy the tail gas catalyst in minutes. These events are out of the scope of this question and answer.

2 It is possible to completely soot a tail gas reactor in a few hours, forcing a shutdown. However, this is rarely due simply to instrument drift. Usually this happens when an incorrect setpoint is selected, the gas composition changes significantly, or if the meters are calibrated incorrectly prior to a unit start-up. Sooting can also result from impurities in the gas and make-up hydrogen.

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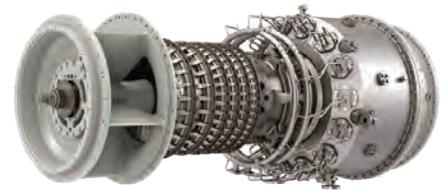
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Contamination in gas compression: causes, effects, and solutions

Identifying and quantifying contaminants including solids, dissolved species, and liquids is essential in the design of a more reliable compression system

DAVID B ENGEL and SCOTT N WILLIAMS
Nexo Solutions

Gas compression systems are a vital yet delicate part of any gas plant. There are many different types of compressors, but all work by imparting energy to the gas and reducing the available volume, thereby increasing pressure. This process creates a drastic change in process conditions for the gas stream, and even small amounts of contamination can create significant challenges in the compression system or downstream. Only a small number of compression systems have the necessary means to adequately remove contaminants in the gas stream, so the need for accurate gas testing and high efficiency separation systems for compressor protection is greater than ever.

Contamination in gas compression

Compressor failures and downstream problems can be and are caused by a variety of mechanisms. Dissolved contaminants in the gaseous phase or in water entrained in the gas can precipitate in the system during compression, leading to fouling and corrosion, reduced throughput, and eventually failure. Suspended solids can cause similar effects. One of the most common and difficult challenges in gas compression however is dealing with lubrication oils and additives injected within the system.

Lubrication oils typically contain a high percentage of a base oil and a low percentage of chemical additives designed for various functions. These additives impart reduced metal-metal friction and wear, viscosity modifications, resistance to corrosion, oxidation, ageing, and traces of contamination among

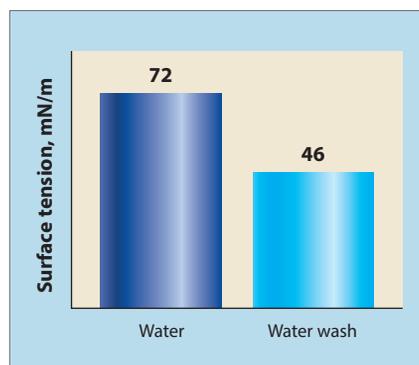


Figure 1 Effect of the surface tension of water when contacted with lubrication oil

others. Most chemical additives in lubrication oil packages have surfactant properties causing a number of downstream problems in processing units. Base oil, usually a heavy hydrocarbon, can also in some cases cause detrimental effects downstream. These are often related to agglomeration with solid particles in the gas stream, forming larger residues and causing deposition and fouling in many gas lines and downstream equipment.

To illustrate this point, Figure 1 shows the change in surface tension of pure water when contacted with lubrication oil. A mixture of 95% water and 5% of a standard lubrication oil is contacted in a small vial and shaken for one minute. Water is then separated and analysed. The decrease in surface tension of pure water changed from 72 mN/m to 46 mN/m. This is a clear indication of the surfactant properties of water-soluble chemical additives present in lubrication oil. The decrease in surface tension leads to an increase in entrained water and dissolved contaminants downstream as separation equipment

loses liquid removal efficiency. Different lubrication oils will have different additive packages and will show somewhat different results. However, lowering of the surface tension in pure water is a consistent observation.

Compression systems are so vital because without the system pressure created by compressors, the process or sometimes the entire plant cannot operate. Compression systems in oil refinery fluid catalytic cracking (FCC) units are often responsible for more than 40% of a refinery's capacity, and failure can even lead to complete refinery shutdowns, causing tens of millions of dollars in lost revenue. Natural gas compressor stations are responsible for the transportation of raw and processed natural gas, and supply the pressure needed for gas plant operations. Adequate compression system protection is thus an extremely important aspect of successful plant operation, as compressor failure and also contamination breakthrough has enormous consequences.

Contamination characterisation

The first step in compressor protection is in understanding the nature of contamination in the stream, and gas testing is a vital piece of any troubleshooting protocol. Feed contamination can play a major role in compression system challenges and is often cited as the main cause of process problems. Plant operators and engineers often overlook the injection of lubrication oils and additives in the compressor itself and neglect to identify that source of contaminant ingress. In cases



Figure 2 Set-up of the GASCO test system for a compressed gas stream

where lube oils and additives are of concern, downstream effects such as foaming and fouling are often observed, and testing of the gas stream at the outlet of the compressor should be performed.

Liquid contamination in gas streams is a complex challenge for a number of process units downstream. This is especially of concern in amine units and glycol units where lubrication oil ingress often causes solvent foaming, severely limiting the processes. The effect is also extended to metering stations, leading to erroneous lower readings. Therefore lubrication oils and chemical additives, in addition to heavy hydrocarbons, water, and other contaminants, must be identified and quantified before any removal solution can be developed. Testing for liquids in gas streams is performed quantitatively using a gas-liquid super coalescer (GASCO) test system (see **Figure 2**). A slip stream of the gas flows across the GASCO test unit where aerosols are

coalesced and liquids are drained from the internal element into a sight glass. These liquids are quantified, sampled, and further analysed for their composition and concentration. Solids are removed from the element media for characterisation purposes only.

Contaminant removal

In any case where feed contamination is present, it is always advisable to locate the source. Oftentimes a capital investment can be avoided by identifying and correcting issues upstream. In gas compression, liquid contamination from injected lube oils and additives is always present, and source removal is not an option, so process protection is a must.

Separation of liquid contaminants in gas streams is usually carried out using demisters (also known as knock-out drums) equipped with a metal coalescing pad element or vane pack installed near or at the outlet of the vessel. Demister systems are typically vertical in orien-

tation, but they are only adequate for removing large diameter contaminant droplet sizes. These separators were originally designed for bulk liquids and slug removal and are not designed for solids separation (usually done by a wet scrubber or a particle filter) with the exception of cyclonic systems that can remove large solid particles and some larger liquid droplets. Only a small number of compression systems have the necessary means to adequately separate the lubrication oil liquids in the gas stream caused by injection at the compressor itself.

As far as contamination in gas streams is concerned, the most prevalent and difficult contaminants to separate are sub-micron liquid aerosols, finely divided liquid droplets with diameters ranging from less than 0.1 micron to a few hundred microns. Droplet sizes below 1.0 micron are the most difficult to remove due to the absence of a specific separation mechanism that yields high removal efficiency. The typical aerosol distribution in gas streams is primarily in the sub-micron range. Larger droplets tend not to be as persistent as they are likely to be separated by gravity but can shatter due to the shear forces surrounding the droplet surface with certain deficient vessel design features. When large droplets shatter, progressively smaller droplets are created until the distribution is stabilised by the balance of energy distribution, gravitational settling, and shear.

Other devices such as mesh pads, vane packs, and cyclones are ineffective because they are not able to capture the small and most penetrating sub-micron aerosols. Vane packs are especially ineffective when dealing with sub-micron liquid aerosols since the small droplets do not have enough momentum to contact the vane surface properly. Interfacial layers in many vane packs and some mesh pads are one cause of inefficiencies and companies have mitigated this by using different designs (double and single pockets). Their efficiencies can be enhanced somewhat for larger liquid droplets, low liquid loadings, and gas velocities within certain

limits. Mesh pads suffer similar inefficiencies and are prone to particle fouling, but their removal rate is somewhat better due to the higher surface area. Today, the technology of choice for high efficiency removal of sub-micron aerosols in gas streams is built around specially formulated microfibre media.

As **Figure 3** shows, about 50 wt% of all liquid contaminants in a gas stream area are smaller than 1 micron (aerosols), and 80 wt% are smaller than 10 microns. Hence, most of the approaches to separating liquid contamination in gas streams using demisters with mesh pads, vane packs, or certain horizontal filter-separators display rather low efficiencies at removing sub-micron aerosols (% weight). The reason for the lack of efficiency is related to the aerosol droplet size distribution, flow configuration inside the separator, and the mechanism of liquid droplet interception. In other words, the separation media is not capable of intercepting and coalescing sub-micron liquid droplets (followed by liquids unloading in order to enable proper high efficiency separation), so aerosol contaminants break out of the system almost intact. The vessel configuration is also critical even if the separation media is appropriate. The internal flow direction and gas routing inside the separator could be a source of significant inefficiencies. Additionally, poor vessel designs can actually shatter liquid aerosols into smaller sizes, adding more difficulty to an already challenging separation process.

The majority of gas separation systems currently installed in refineries and gas plants, as well as existing designs for future projects, are usually not very appropriate for the separation of sub-micron liquid droplets in gas streams. These systems are conventional separation technologies for bulk removal. The efficiency decreases dramatically as particles become smaller than 10 microns in diameter. Mesh pads suffer from flooding when excessive liquids are introduced and the mesh becomes saturated with liquid; this leads to efficiency losses by carry-over. Conventional devices are

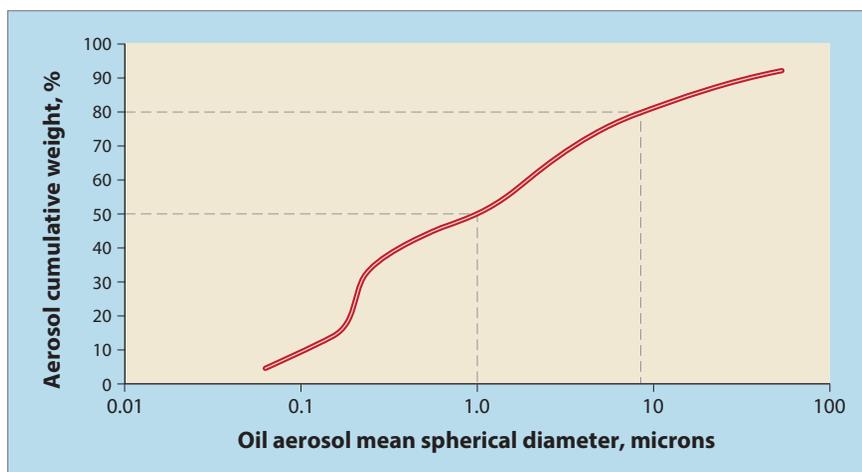


Figure 3 Typical lubrication oil aerosol size distribution at the outlet of a compressed gas stream

also prone to solids fouling by particle deposition at the mesh structure surface, further reducing their efficiency and causing considerable maintenance costs and pad failures. Movement of the mesh pad inside the vessel is somewhat common due to the difficulty of properly anchoring these devices to the vessel interior. Alternative options such as vane packs have better mechanical performance and lower differential pressure but provide inferior separation efficiencies. Even modern developments where improvements are made by the combination of vane packs and mesh pads do not adequately produce the necessary removal efficiency to protect sensitive equipment and processes.

A highly effective separation system for the outlet of compressors is called a 'high efficiency sub-micron coalescer'. Such a system should be equipped with correct instrumentation, valves, and specially formulated microfibre coalescing media. These sub-micron coalescer devices are carefully designed depending on the flow, pressure, temperature, gas composition, and contaminants. They should be installed as closely as possible to the unit or process they are intended to protect. Typically designed high efficiency sub-micron coalescers are capable (in theory) of removing, on average, 99.98%+ of all aerosols with diameters of 0.1-1.0 micron (and larger) as measured in a laboratory setting. In essence, this is the majority of the liquid aerosol contamination in a gas stream.

These devices should be protected

with a suitable particle filter-separator (equipped with the correct separation media) in order to extend the on-line life of the coalescer and to minimise operational costs, as the replacement filter elements for particle separation are much less expensive than coalescing elements. Correctly designed sub-micron coalescer vessels have two stages: the bottom section designed to remove bulk liquids; and an upper high efficiency stage for aerosol removal. On certain occasions, the bottom section can be fitted with a mesh pad or vane pack or designed in such a way as to have cyclonic action. The gas then leaves the bottom chamber flowing into the second stage immediately above via the coalescing element's interior. The gas is then directed across the microfibre coalescing media. The fine aerosols are intercepted, coalesced, and drained from the elements by gravity. Like the lower stage, the upper stage has a liquid removal system comprised of a level control and drain valves. The gas exits from the top of the vessel.

Typical campaign times for gas coalescing elements can vary between six months and two years, depending on the concentration of solids entering the coalescer as well as chemical additive presence among other secondary factors. It is important to point out that many fabricators advertise systems capable of removing sub-micron liquid aerosols. Several however do not correlate these claims and expectations with actual performance. Only

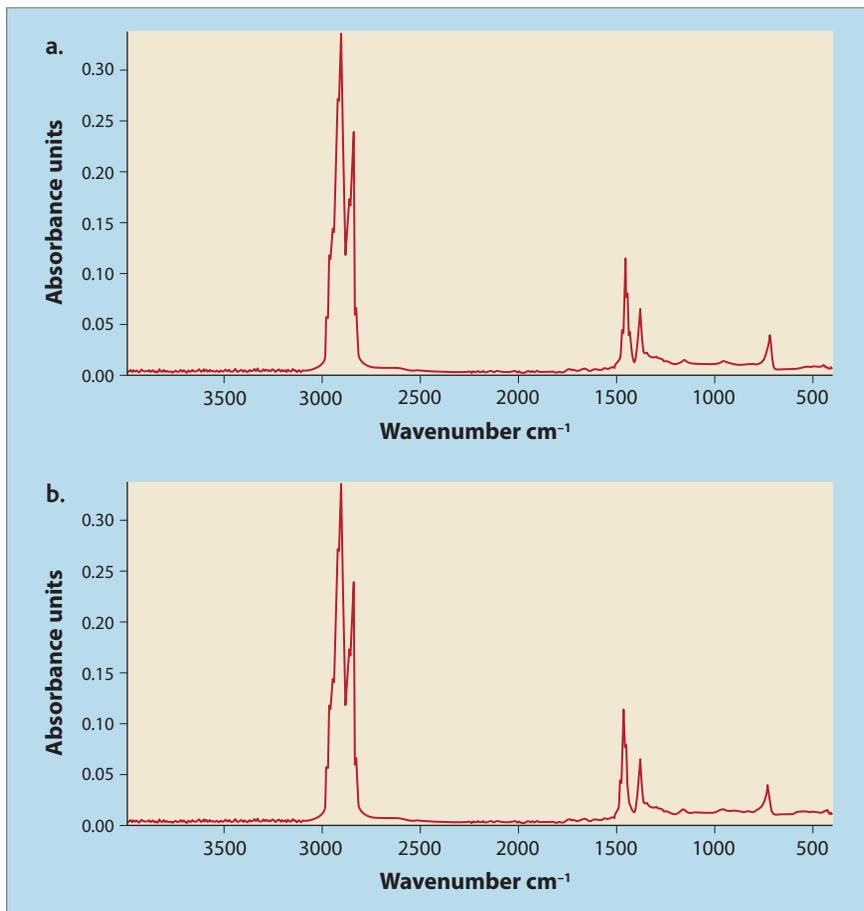


Figure 4 FT-IR spectra of: a) residue from the GASCO test unit and b) sample of lubrication oil

a small number of companies possess the proper technology to supply sub-micron gas-liquid coalescers.

Case study

A South American oil and gas company operates a number of compression stations throughout the region. It is critical to be able to rely on specific standards for compressed gas and compressed gas quality. At these compression stations, the gas is compressed and invariably there is injection of lubrication oils into the gas stream. Testing of the compressed gas was performed to understand the level of contamination in the gas stream and whether the gas coalescing system's design for its removal

was effective. The concentration of lubrication oil present in the form of aerosols and the concentration of lubrication oils penetrating the coalescer equipment was evaluated via testing.

The amount of lubrication oil collected in the GASCO system during testing was not enough to cause visible accumulation in the sight glass at the bottom of the test system. Upon inspection of the test elements, it was however clearly identified that lubrication oil was present in the interior of the element. This can be seen in **Figure 4** as GASCO test element was inspected and had a considerable amount of a viscous residue. This residue was carefully removed and

analysed using Fourier Transform Infrared Spectroscopy (FT-IR). The FT-IR spectrum was a match with the sample of a lubrication oil sample supplied by the compression station facility. The spectra of both materials were consistent with the base oil present in lubricants. Lubrication oils are typically high molecular weight hydrocarbons, mainly composed of carbon and hydrogen atoms. Similarly, the spectrum only shows CH_2 , CH_3 , and C-C vibrations.

As the amount of lubrication oil was not enough to cause accumulation in the test systems, the contaminant was removed from the coalescing element using an organic solvent wash that was compatible with the test element and did not remove any component from its structure (only the lubrication oil was removed). The test element was weighed with the lubrication oil inside and then after the oil was removed. The data for the quantity of lubrication oil separated in each test run and the actual concentration of lubrication oil in the main gas flow is shown in **Table 1**.

From the data acquired by the GASCO test system, it was apparent that the efficiency of the installed coalescer is near 92% (on a mass basis). This efficiency is lower than is normal for a high efficiency sub-micron liquids coalescer. The total amount of oil present in the compressed gas stream was low. This low concentration was achieved by the correct operation and maintenance of the compressors themselves. The correct and periodic maintenance of the compressor parts, seals, and gaskets is critical in order to prevent release of lubrication oils in the form of aerosols. The low efficiency in removing aerosol was caused by a few factors, and further investigation can verify the exact causes. The main possible causes are outlined as follows.

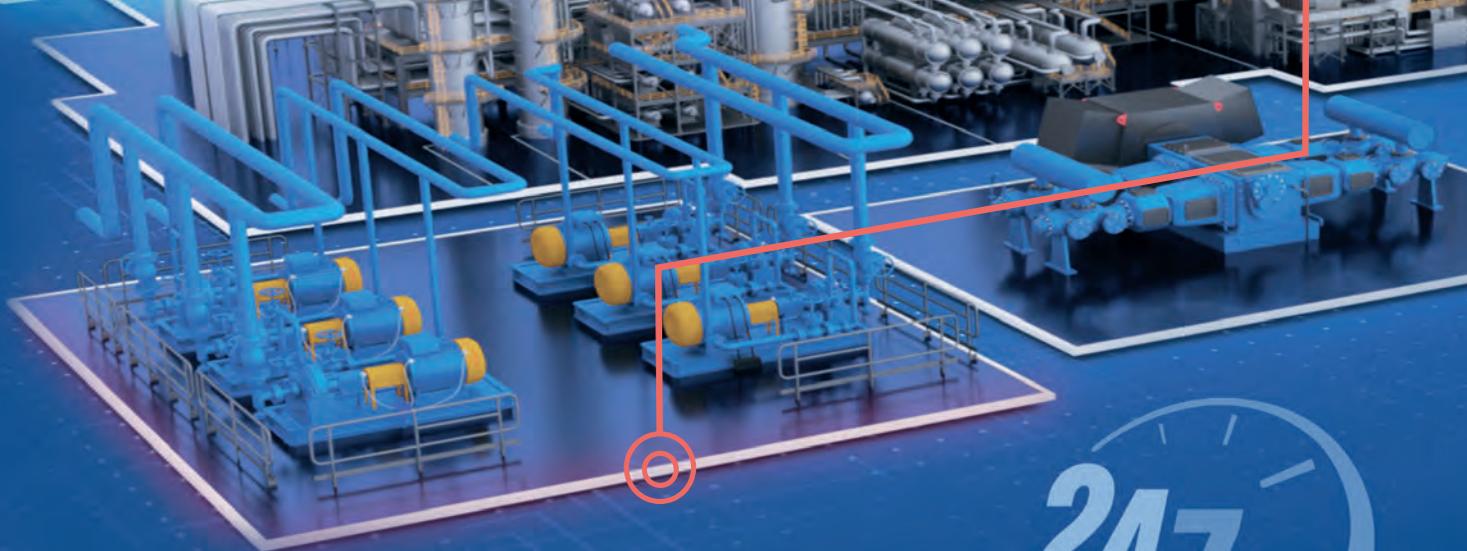
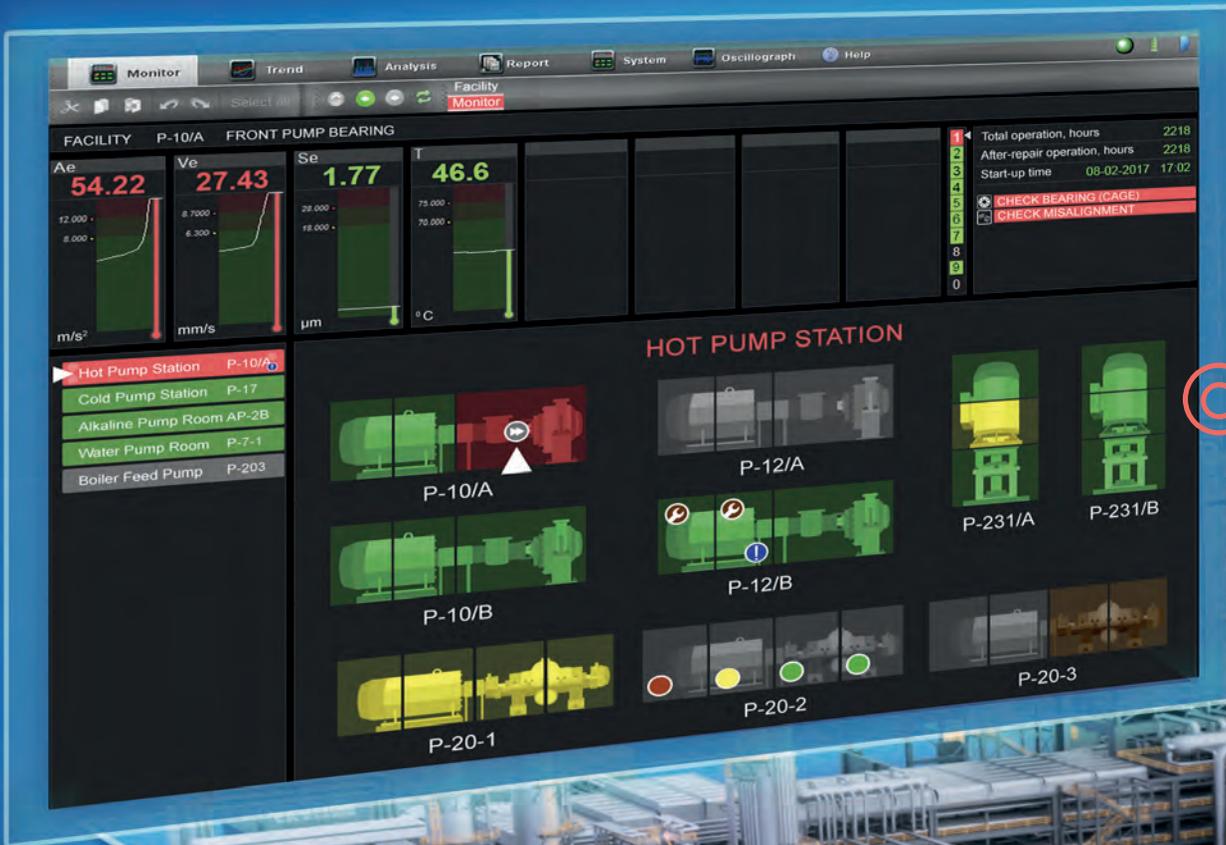
Incorrect vessel design

The process conditions and flow in the vessel were simulated, and the size of the installed vessel was found to be larger than required. One characteristic of the vessel was the positioning of the outlet; it

Concentration of lubrication oil at each test point				
Sample point/parameter	Mass oil recovered inside test element	Test time duration	Lubrication oil concentration	Lubrication oil quantification
Outlet of compressor	4.8 grams	25 hours	0.00598 ppm	5.11 mL
Outlet of coalescer	0.4 grams	22 hours	0.00056 ppm	0.43 mL
Actual coalescer efficiency	91.7%	--	--	--

Table 1

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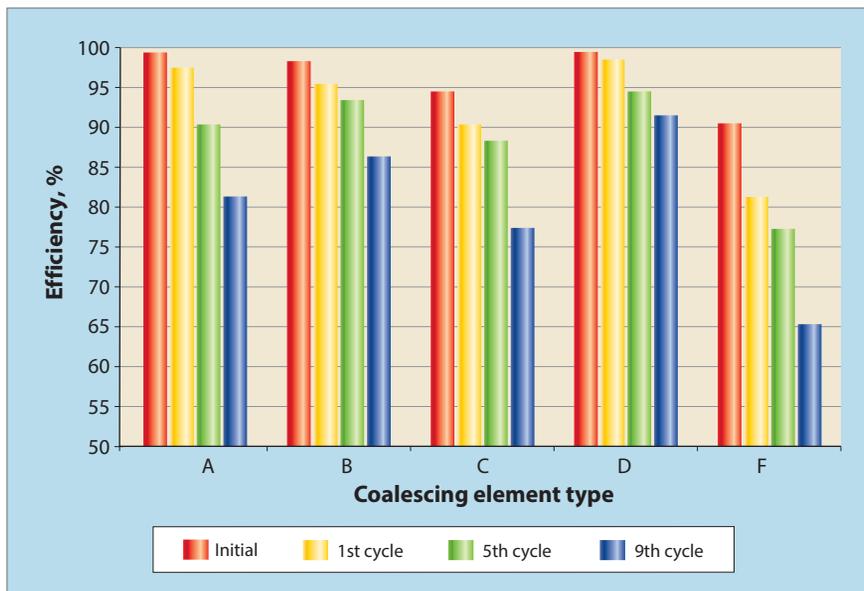


Figure 5 Effect of gas flow interruption on different gas-liquid coalescing elements

was located below the element line using a baffle plate. This arrangement is inefficient as the outlet gas in the vessel needs to change direction many times, causing increased velocity and increased carry-over possibilities. New vessel designs have the outlet a minimum of 10in above the element line with no baffle. This ensures only one gas turn in the vessel prior to the outlet and also reduces localised velocity and carry-over. Baffleless designs also allow for smaller vessel diameters and thus lower cost.

Incorrect maintenance procedures

It is understood that the vessel had been properly maintained periodically. The vessel interior was not inspected. This is important for possible future troubleshooting. One possible area of importance is correctly inspecting the vessel interior for possible depositions in the coalescer support hardware. This can cause bypass if not clear of any residue build-up.

Incorrect coalescing media

One possible approach for enhancing the quality of compressed gas by reducing the concentration of lubrication oil is increasing the removal rates and ensuring that the removal rate is not affected by shutdowns and start-ups of the gas flow. It has been observed that coalescers lose efficiency when the gas flow is interrupted and resumed at a later

time. In **Figure 5** this phenomenon is shown comparatively for some common coalescing elements on the market today. Data was obtained during many field tests over several years. Some coalescer elements actually do not have an adequate initial efficiency for liquids removal. Only two manufacturers showed proper removal, but in all cases the decay in efficiency upon cycling (shutdown and start-up) was considerable.

Ineffective sealing surfaces

The surface section where the coalescing element cartridge engages with the vessel is called 'sealing surface'. This surface requires an effective seal with correct chemical compatibility and design in such a way that any potential liquids bypass is non-existent. Today the industry still utilises flat gaskets. These are prone to bypass and also misalignments. The best avenue for proper sealing surfaces is to use O-ring engagements.

The decay in efficiency at the outlet of compressors in cycling operational modes is related to the interaction of the liquids and other contaminants that remain inside the coalescing element with the various fibrous materials. There is likely to be both chemical degradation of the fibre materials and plugging of small pores responsible for removal of aerosols. Additionally, some viscous liquids might solidify in the coalescing element's interior in such

a way that restarting the flow can cause cracks in the media, leading to by-pass.

From the data in both GASCO tests for aerosol removal and quantification, it was indicated that the compressors were operating correctly with minimal liquids injection into the gas stream. This was primarily due to the age of the equipment (fairly new) and proper maintenance and operational procedures. As the equipment ages and deficient maintenance and operation may take place, the presence of higher concentrations of lubrication oil can occur.

The installed gas-liquid coalescer at the outlet of the plant (outlet of air coolers) had a slightly oversized diameter but did not affect the operation or performance of the system. The overall efficiency (by mass) was lower than is acceptable for a gas stream at the outlet of a compressor station. One of the most likely causes of poor removal efficiency was degradation of the fibrous material in the coalescing element in internal contact with stagnant liquid. A possible improvement is to install XC coalescing elements that have materials in their interiors specially designed to endure intermittent gas flow (cycling) operations. **Figure 6** shows the variation of efficiency of XC coalescers upon cycling. It can be observed that the efficiency is not affected. In many cases the efficiency remains constant up to the ninth cycle of shutdown and start-up. This is critical to ensure that high quality compressed gas is delivered to the gas line and that contamination is properly removed in order to minimise inadequate gas metering and further processing in downstream operations.

Conclusion

The case study shows some of the difficulties and benefits associated with contaminant removal in gas compression systems. Several aspects including gas testing, separation system design, maintenance, and media choice must be done correctly in order to ensure adequate contaminant removal. Properly designing, operating, and maintain-

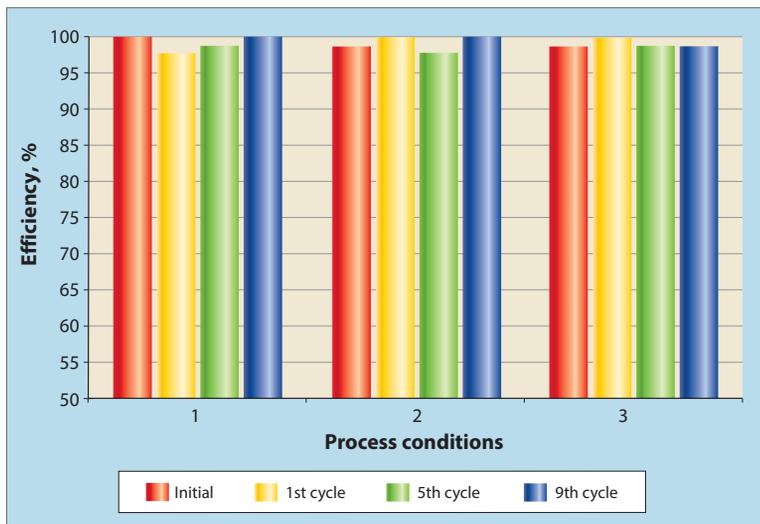


Figure 6 Effect of gas flow interruption on the XC gas-liquid coalescing element

ing a separation system for liquids removal can be complex and challenging, but the benefit of downstream protection outweighs the associated difficulties. Without the protection of a gas-liquid coalescer in the case cited, problems including foaming, fouling, and corrosion of process equipment and inaccurate gas metering would be expected.

Gas compression is a process which requires a holistic approach. Contamination in gas streams varies greatly in both type and concentration, and the best solution for each case varies as well. Proper identification and quantification of contaminants including solids, dissolved species, and liquids must be done, so a better solution can then be designed. Contaminant removal for gas streams requires knowledge of the gas and its contaminants as well as the process itself; many tools including the GASCO system and other methodologies can be utilised, the better to gain that knowledge. When contaminants are identified, source identification and removal is the best option when available. When process protection is needed, as is always the case with injected lubrication oils and additives in compressors, expertise in separation system design is needed in order to

choose and develop the best solution.

Protection of the gas compression system and downstream equipment is critical, and process protection with contaminant removal systems is almost always justified when the cost of failure is high. Many plants cannot function without certain compressors, and downstream equipment failure can be equally detrimental. With advances in technologies for both contaminant identification and contaminant removal, more efficient solutions can be developed for process protection. Plants now have the ability to run at higher throughput with less downtime. Improving process efficiency and profitability is important in every plant, and taking the right approach to contamination problems in gas compression systems now more than ever has a tremendous impact on process stability and economics.

David Engel is Managing Director of Nexo Solutions. He holds a BS in industrial chemistry from the University of Santiago, Chile, a MSc in chemistry from Rochester Institute of Technology, and a PhD in organic chemistry from Indiana University, Bloomington.

Scott Williams is a Staff Process Engineer with Nexo Solutions. He holds a BS in chemical and biological engineering from the University of Colorado at Boulder.

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Amine cleaning in gas treating

Effective amine cleaning requires a three-step filtration system

JAN HERMANS
Sulphurnet

Gas treating or sweetening is a term used to describe the various processes for removal of certain contaminants, primarily hydrogen sulphide (H_2S) and carbon dioxide (CO_2) from natural gas or hydrocarbon liquids. CO_2 and H_2S are also named 'acid gases' because when absorbed in water they form an acidic solution. Reasons to remove these contaminants include toxicity, corrosiveness, freezing problems, and to increase the overall heating value of the natural gas. As a consequence, amine absorption and regeneration equipment are exposed to corrosive and oxidising conditions. This has to be taken into account with the design of the equipment (see **Figure 1**).

Alkanolamine solvents are widely used to remove CO_2 and H_2S from gas and lighter hydrocarbon products. Amine has a natural affinity for both CO_2 and H_2S , allowing this to be a very efficient and effective removal process. Crude oil with low sulphur content is becoming less prevalent and is costly on the mar-

ket while on the other side environmental regulations concerning H_2S and CO_2 content in light hydrocarbon products (fuels) are becoming more stringent. Many processes for the removal of acid gases have been employed commercially and various amines are used, each of the amines offering distinct advantages to specific treating problems.

Depending on the required selectivity, CO_2 or H_2S removal, various solutions of solvent can be used.

The most popular ones are MEA/DGA, MDEA/DIPA, and DEA. This article describes a three-step system for amine filtration.

In **Figure 1**:

- Sour gas passes through an inlet separator and/or a gas-liquid filter/coalescer to
- Remove the majority of the hydrocarbons and solids
- Sour gas flows through the absorber tower and rises through the descending amine
- Purified gas flows from the top of the tower

- The amine solution is now considered rich and is carrying absorbed acid gases

- Rich amine is heated in the regeneration column. The steam rising through the stripper column regenerates the amine

- Steam and acid gases separated from the rich amine are condensed and cooled

- The condensed water is separated in the reflux accumulator and returned to the still

The installation and operation of an appropriate filtration system is one of the key components of all amine systems. The cleaner the amine, the better the amine system operates. Filtration has proven to be the most effective and only protection system for the removal of contaminants such as solids, liquid hydrocarbons, and heat stable salts. Removal of contaminants provides the following benefits:

- Prevention of amine foaming
- Reduced corrosion problems
- Reduced fouling problems in the process

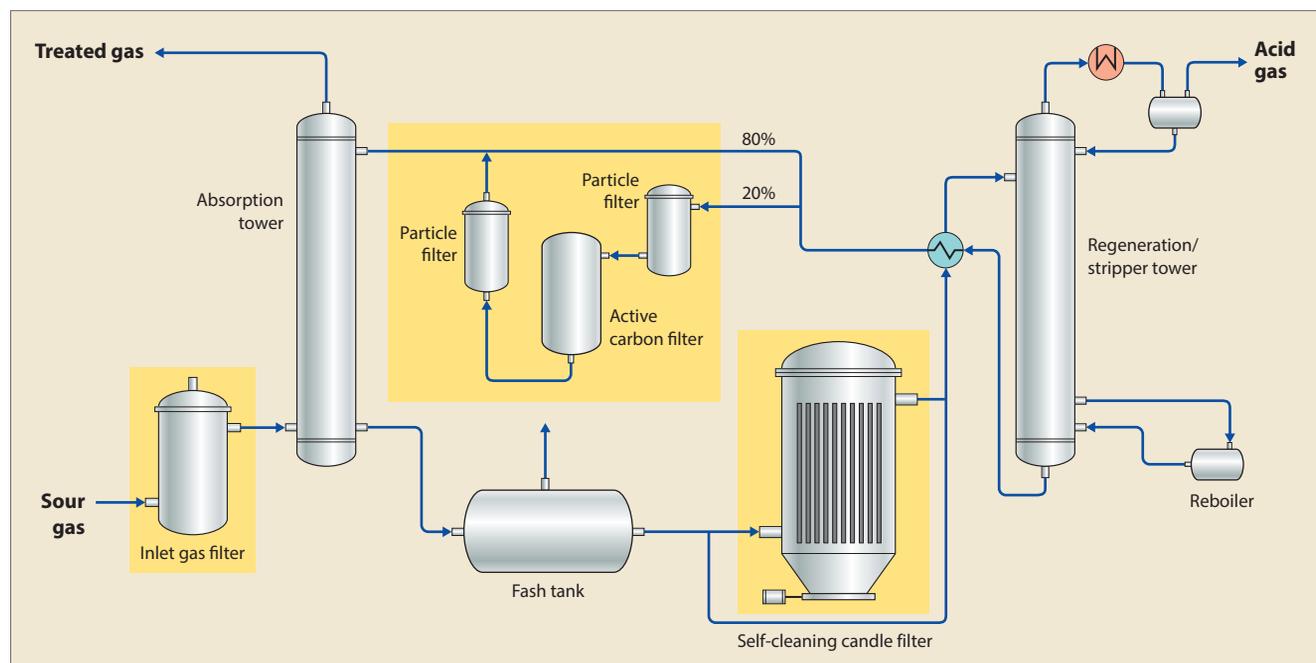


Figure 1 General schematic of sour gas treatment

- Increased lifetime of the carbon bed
- Reduced amine consumption
- Maintaining amine efficiency and plant capacity

If these filtration systems are not designed and operated correctly, then the amine units regularly suffer from several inefficiency problems, such as high operating costs, lean separation efficiency of H_2S/CO_2 , amine losses, and excessive maintenance costs.

Sulphurnet's approach to amine filtration

Adequate amine cleaning includes a three-step filtration system. It starts with a gas inlet filter, followed by a rich amine filtration system. Finally, a mechanical precoat type filter, in combination with an activated carbon filter and a particle filter, is installed in the lean amine side of the process.

Gas inlet filters

The first filter section is the gas inlet filter. Here the liquid hydrocarbons and solids that can upset plant operations are removed. Knockout drums, mist eliminators, filter vanes, or coalescing filters can be used for this process. A combination of various techniques in series is required to provide optimum removal of all levels of particles and liquids.

Rich amine stream

When the amine system is extremely contaminated, filtration of the rich amine may be required. This prevents the heat exchanger from plugging, along with the problem that iron sulphide in the rich amine can dissociate in the regenerator under



Figure 2 A particle filter removes fines at the inlet side of the carbon filter

certain conditions to form soluble iron compounds. Due to its reactivity, iron sulphide cannot be removed during filtration of the lean amine.

Due to the concentration of H_2S in the system, self-cleaning filtration systems are preferred. Self-cleaning strainers are suitable for filtration in the range up to 30 microns. For finer filtration efficiency, and in order to prevent filter cloth from clogging, the concept of precoat filtration is used. Filter elements are protected by depositing a layer of precoat material on their surface, prior to filtration. In order to obtain a layer of precoat material, liquid with precoat material is introduced into the filter vessel, filtered and returned to the precoat tank. The precoat solution is prepared by uniformly mixing part of the amine solution with the precoat material. This can be cellulose or diatomaceous earth. Proper selection

of the precoat media in combination with the filter cloth is a key factor for the successful operation and performance of the filtration unit.

Lean amine stream

In the lean amine stream, a combination of separation equipment is required. Mostly 10-20% of the stream is filtered. This is sufficient to obtain a stable amine system and control the amount of solids in the plant.

Here we have a sequence of three systems: a particle filter in combination with an activated carbon filter, and finally a polishing filter.

Particle filter

The particle filter (see **Figure 2**) is installed to remove fines at the inlet side of the carbon filter, preventing particles from blocking the activated carbon. The particle filter in the lean amine stream is a self-cleaning candle filter. This filter consists of a vertical cylindrical vessel with a conical bottom. The filter is filled with vertically positioned filter candles which are installed in horizontal collecting manifolds. The outside of the candle has supporting rods; inside, a central filtrate discharge pipe. The filter candles are covered with a filter cloth carefully selected for the application. Once the filtrate has passed through the filter cloth, it flows into the support candle down to the bottom of the candle, before rising again in the central filtrate discharge pipe toward the registers. The filter cake is formed on the outside of the filter cloth and over time the pressure differential slowly increases.

When the filtration cycle is completed, cake discharge is initiated by introducing gas in the reverse direction to the inner part of the candle. The quick-pulse gas blow-back lifts the filter cloth from the support candle and the filter cake is released, causing it to fall through the bottom discharge valve (see **Figure 3**). Filtration requirements depend on the micron size and quantity of the particulates. Generally, 5- to 10-micron filtration efficiency is suitable for particulate removal.

Activated carbon filters

Since the rich amine solution is heavily loaded with acid gas, it can



Figure 2 A particle filter removes fines at the inlet side of the carbon filter

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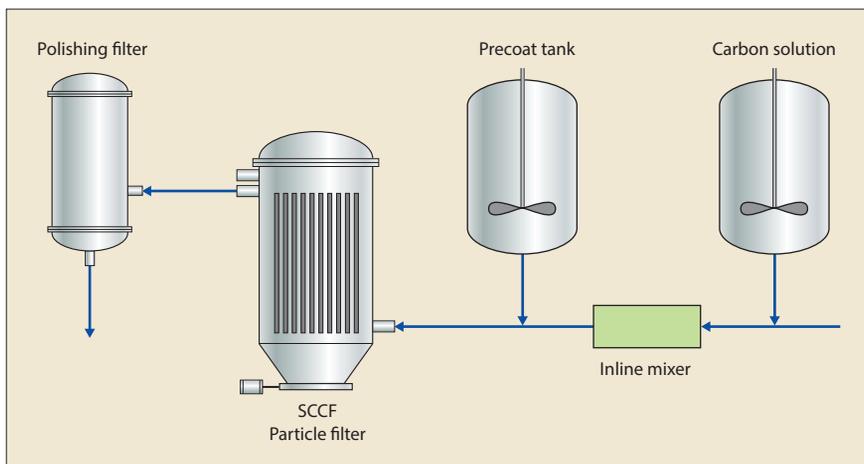


Figure 4 A polishing filter prevents carbon fines from entering the amine loop

form gas pockets in the carbon filter, resulting in a reduced or completely blocked flow. In terms of safety for the workers who dismantle, inspect, and clean out the filters, it is safer to install the carbon filters in the lean amine stream. Carbon filtration removes surface-active contaminants, hydrocarbon corrosion inhibitors, amine degradation products, and oils and reduces the tendency of the amine solution in the stripper to foam.

The activated carbon filter installed is commonly a deep bed filter. The lifetime of a carbon filter will vary, depending on the level of contaminants and the flow rate of the amine through the bed. A typical life is four to six months, although in some cases beds have lasted for many months longer than that.

In determining when a carbon bed should be changed, the following criteria can be used as a guide:

- High pressure drop across the carbon bed
- An increase in foaming tendency
- Colour comparison of the amine solution which has passed a fresh and an old carbon bed

However, it is hard to determine when your carbon filter needs replacing; the only signs are foaming, no colour change or pressure build-up. At that point, the system can be regenerated with low pressure steam and be taken into operation. The operational time of the bed is reduced after the first cleaning cycle, and the regeneration cycles must be repeated at shorter intervals; eventually, the bed must be replaced.

An activated carbon bed will not

always be fully saturated; one meets blocked or dead zones and channeling which reduces the lifetime.

Cleaning a deep bed activated carbon filter is difficult and hazardous work due to the possible presence of H_2S .

Polishing filter

After the carbon bed filter, a polishing filter is installed. This is to prevent carbon fines from entering the amine loop.

Sulphurnet offers an alternative activated carbon filtration method. This is a combination of a particle filter with activated carbon treatment. The process offers the adsorption process in two stages (see **Figure 4**).

First stage

A concentrated suspension of activated carbon is prepared in an agitated vessel. Based on the required activated carbon, a positive displacement dosage pump injects the suspension into the amine. This mixture enters an inline mixer (see **Figure 4**). Turbulence is created within the inline mixer. This enhances rapid suspension of the injected carbon in the amine stream. The design and length of the inline mixer creates the contact time. Application of finer activated carbon in combination with the inline mixer generates a larger contact surface. Advantages of using the mixer over a deep bed filter include the requirement for reduced residence time and improved performance of the injected activated carbon.

Second stage

After the inline mixer, a precoat fil-

ter is installed. The activated carbon fines are retained on the precoat layer and form a filter cake, a layer of activated carbon. The amine has to pass through the filter cake. This filter cake of activated carbon acts as a secondary activated carbon absorption bed. This set-up guarantees good contact time and efficient use of the activated carbon. The carbon will be saturated before cake discharge.

The dosage pump is a highly accurate positive displacement pump and the injected volume of the activated carbon slurry can be adjusted by the speed of the dosage pump. So, based on the process situation, the volume of slurry can be decreased or increased, this depending on the process requirements. Due to the dual stage absorption, the efficiency of activated carbon usage is improved.

Using a self-cleaning candle filter in combination with a low cost inline mixer reduces the investment cost of the appropriately sized carbon filter storage tank as well as the operational maintenance time. This solution offers the following advantages:

- Prevention of amine foaming
- Reduced corrosion problems
- Reduced fouling problems in the process
- Maintained amine efficiency and plant capacity
- Totally enclosed system; operator friendly operation
- Fully automated, assuring repeatability of the sequences

Analysis of the overall project and filtration costs is necessary. The capital cost is the most obvious one when a project is initiated, but one should consider the costs associated with daily operation and maintenance. Operating and maintenance costs include the cost of filter aids and activated carbon consumption, disposal of the waste, as well as the labour costs associated with the selected filtration system. Also, safety and hazard should be taken into account since operators are subject to contact with dangerous and toxic chemicals.

Jan Hermans is the founder of Sulphurnet which focuses on processes including filtration applications for the chemical process industry. He has over 30 years' experience in liquid-solid separation and in 2007 founded Sulphurnet.



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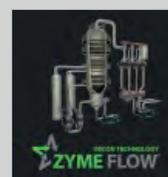
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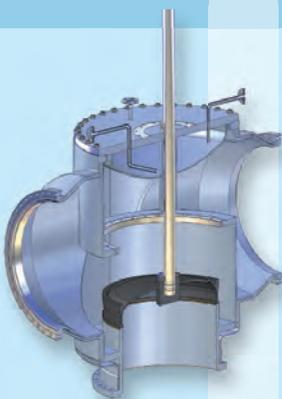
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Revamping the sulphur plant

Expanding the capacity of sulphur recovery and tail gas units requires a thorough review of all plant systems

AVINASHKUMAR KARRE
Worley Group

Sulphur is present in natural gas mainly as hydrogen sulphide (H_2S). Many processes in the refinery produce acid gas which is rich in H_2S . This acid gas is further captured in clean sour water and lean amine. Further, the sour water is processed in a sour water stripper (SWS) and the off-gas produced is sent to the sulphur recovery unit (SRU). The sour acid gas produced, also called ammonia acid gas (AAG), is usually rich in ammonia and H_2S . The rich amine from different refinery units is collected and processed in an amine recovery unit (ARU). The produced gas, also called clean acid gas (CAG), is rich in H_2S . The SRU processes CAG and AAG in order to recover sulphur from the H_2S molecule. The tail gas treatment unit (TGTU) is usually installed downstream of the SRU to capture unreacted H_2S and to meet environmental specifications. The SRU uses the Claus process. **Table 1** shows typical compositions of AAG and CAG.

Typical compositions of ammonia acid gas and clean acid gas		
Parameter	CAG	AAG
Composition, mol%		
H_2O	5.88	26.17
Hydrogen	0.07	0.00
H_2S	93.68	33.91
Ammonia	0.03	39.92
Methane	0.34	0.00

Table 1

High sulphur crude is always needed for higher refining margins. This need in turn drives sulphur projects in the refinery. There is no home for H_2S gas in the refinery other than the sulphur units. H_2S or SO_x cannot be emitted to the atmosphere for reasons of safety and environmental regulations. As a result of this, a refinery's production and profits are at risk when the SRU/TGTU is not operating.

Process flow

Figure 1 outlines the various stages of SRU and TGTU operations and the

areas affected by a capacity increase. The SRU takes acid gas from the amine regeneration units and SWS, converting H_2S to elemental sulphur using the Claus process. Unconverted tail gas from the Claus reactors is routed to a TGTU where sulphur oxides are converted to H_2S and recycled to the Claus reactors, increasing overall sulphur conversion to >99% to reduce SO_x emissions.

The two unit feeds, sour water acid gas and amine acid gas, are separated in the unit with segregated feed knock-out drums. This allows the AAG which is higher in ammonia to be injected at the inlet, increasing ammonia destruction in the thermal reactor. The combined acid gas steam is mixed with oxygen at the inlet burner and combusted. Combustion air is controlled to ensure partial combustion of H_2S . This facilitates the reaction between H_2S and sulphur dioxide (SO_2) to form elemental sulphur. The combustion section generates medium pressure steam.

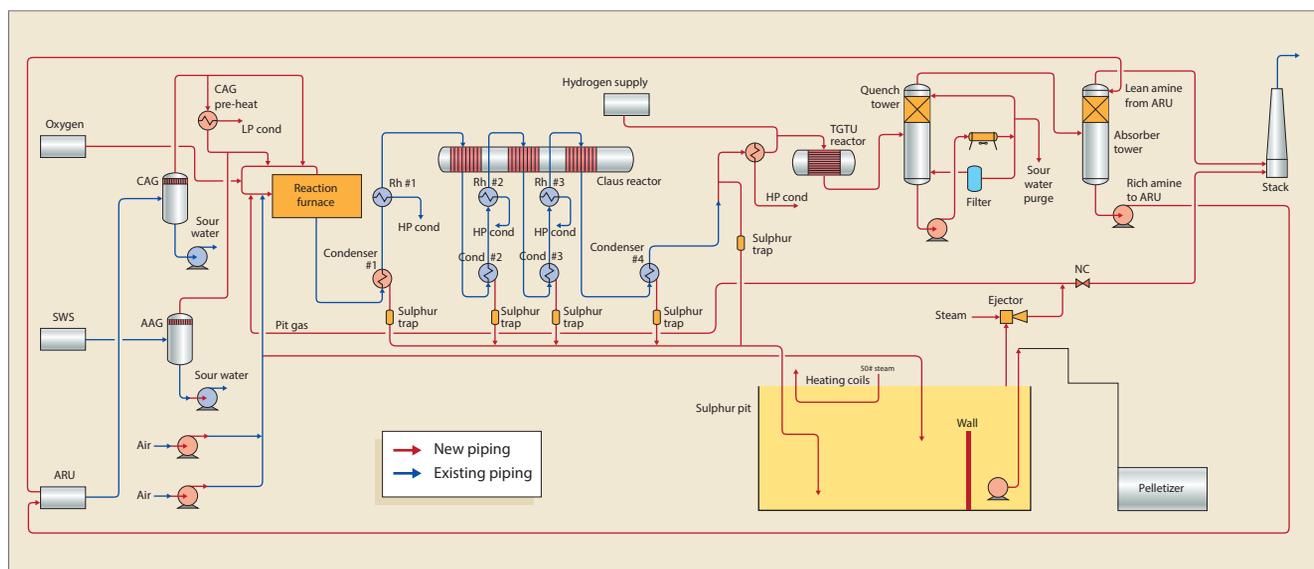


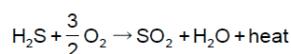
Figure 1 Process flow diagram for a SRU and TGTU. Changes required for a revamp are marked in red

The thermal reactor is followed by a condenser generating additional steam and separating the condensed elemental sulphur from unconverted flue gas. The flue gas is then reheated using high pressure steam to the catalytic reactor. There are three reactor stages, each with dedicated reheat exchangers to control temperature. After each reaction stage, there is a condenser to remove elemental sulphur and generate low pressure steam.

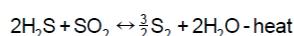
Unreacted tail gas contains 2-8% of inlet sulphur in the form of SO₂ and H₂S. The TGTU uses an amine such as MDEA to collect H₂S. After H₂S is removed, the tail gas is routed to an incinerator. The incinerator combusts any unconverted sulphur components (carbonyl sulphur, carbon disulphide), along with residual H₂S, to SO₂.

Liquid sulphur is condensed and collected by sulphur traps, then collected in the sulphur pit. The liquid sulphur is further cooled and dissolved H₂S in the liquid sulphur is removed by contact with the air. The air and H₂S mixture is vacuumed out using an ejector. This mixture can either be sent to the reaction furnace or the incinerator. The mixture is usually sent to the reaction furnace to increase the efficiency of the sulphur plant, otherwise the unit capacity is limited by SO_x limitations. Reactions for the various stages of the process are:

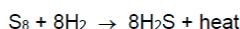
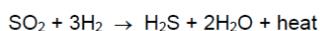
- Reaction furnace



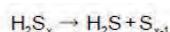
- Claus reactors



- TGTU reactor



- Degassing



Sulphur plant capacity basics

Mass flow limited process

A SRU/TGTU operation is a mass flow limited process; the higher the flow, the higher the pressure drop according to pressure and flow correlation. Pressure drop in the sys-

tem is proportional to the square of flow. The back pressure in the system will increase with the increase in flow needed for a revamp. Burner pressure increases with the increase in back pressure of the system. Nitrogen gas is inert and unwanted in the process; most revamps replace air blowers due to the requirement for higher head and flow. If we replace nitrogen molecules in the process with more oxygen molecules, this favours the hydraulics and the capacity can be enhanced.

All control valves and flow meters should be replaced or evaluated in order to obtain a very low pressure drop for the desired increased throughput. Main gas line pressure losses should be looked at for the increased flow case. The tail gas absorber and quench tower are usually replaced with very low pressure drop packing. Reactors, condensers, and reheaters are evaluated for increased flow rate in order to obtain low pressure drops.

Capacity impacted by hydrocarbons

Hydrocarbons, with their high hydrogen to carbon ratio, are unwanted in CAG and AAG. They take up capacity and consume oxygen which is much needed for the Claus reaction. Excess water is produced by reactions with hydrocarbons and this needs to be removed through the quench tower. Quench tower duty and equipment sizes increase with additional water removal requirements. Large quantities of hydrocarbon in the feed gas interfere with the oxygen demand controller due to the high hydrogen to carbon ratio. If there are aromatics in the feed, they can coke the catalyst and essentially reduce the plant's capacity. Some other carbon and sulphur containing compounds such as COS and CS₂ are difficult to destroy and can make environmental emissions go off-spec very quickly, so these are undesired molecules.

Commonly, all SRU units have CAG and AAG knock-out pots. One can design the appropriate demister pads and hydrocarbon removal capabilities for the knock-out pots so that any carried over hydrocarbons do not compete with oxygen demand in the Claus process. If the

SRU unit does not have knock-out pots, it is necessary to add them to avoid issues with hydrocarbons. Rich amine flash drums, located in ARUs, are often not designed to remove hydrocarbons, so light hydrocarbons as part of the CAG will end up in the SRU. A good design for a rich amine flash drum has a residence time of 30 minutes for adequate separation of hydrocarbons from rich amine. Inefficient operation, for instance not enough reflux, insufficient reboiling of ARU and SWS, can cause hydrocarbon carry-over to the gas streams. The design of a clean sour water storage tank is also crucial in the removal of hydrocarbons.

Capacity impacted by ammonia

AAG tends to contain ammonia from upstream processing units. Ammonia forms salt scaling which can build up over time and cause fouling and scaling. Increased scaling can reduce heat transfer in the reaction furnace and heat exchangers; ammonium salts deposit in the burner nozzles thus reducing capacity. The reaction furnace should be designed appropriately to destroy ammonia in the front chamber. A CAG preheater is often added to new projects and revamps. In addition, ammonium salt formation is favoured below 185°F (85°C). For this reason, AAG and combined acid gas pipes are often steam jacketed or contro-traced to prevent salt formation.

Capacity impacted by design of condensers and reheaters

Redesign of condensers and reheaters is necessary for increased flow and duty requirements. A review of sulphur boot sizing on the condensers and resizing of sulphur rundown piping is also necessary to allow for increased sulphur production following a revamp. The condensers are usually equipped with heat removal capabilities. It is necessary to review the impact of increased condenser loads on relief valve design, steam header sizing, flow meter sizing, and so on. The SRU is a net exporter of steam, so the entire steam hydraulic network should be looked at for increased capacity.

Capacity impacted by reaction furnace design

The heat removal capability of the waste heat boiler located on the reaction furnace should be reviewed with increased process flow rate and duty. A residence time of one second in the main reaction furnace is required to ensure complete destruction of ammonia. Burner back pressure will increase with an increase in plant capacity. A new burner is likely needed to handle higher flow rates. If the revamp involves oxygen enrichments, the existing refractory design may not be adequate. A new refractory design should be looked at in response to increased temperatures in the furnace chamber.

Oxygen addition enhances capacity

As was mentioned earlier, the SRU process is limited by mass flow and the capacity of the unit can be increased if we replace inert nitrogen molecules with much needed oxygen. This is done by adding a new oxygen line to the reaction furnace. A level of 28% oxygen enrichment is very common in all revamp jobs, but it could be increased to 60% if needed for reasons of capacity enhancement. A new burner and new refractory is needed to handle oxygen enrichment. A new oxygen plant will be needed, depending on the utilities available at the site, and the air demand controller should be modified to incorporate new oxygen addition.

Capacity increase by adding a tail gas compressor

The existing air blower design may be slightly under-designed with respect to head but may be adequate for flow rate. Additional head can always be provided by the addition of a tail gas compressor which adds about 1.5-4 psi head to the tail gas hydraulics. This option is only used when trying to avoid replacement of the air blower. Since the tail gas contains H₂S and uncondensed sulphur vapours, consideration should be given to metallurgy when selecting the tail gas compressor. If it is located after the fourth condenser, a tail gas compressor needs steam jacketing due to the presence of sulphur vapours. This option is not so attractive for many plants.

Conclusion

Many options are available to expand the capacity of a sulphur plant. The red line mark-up shown in **Figure 1** summarises the changes required for revamp jobs. The following are the key takeaways for the revamp of a SRU and TGTU:

- Minimise pressure drop in the system by hardware and instrument changes
- Remove or control ammonia
- Go with the oxygen enrichment option and do the necessary changes as required
- Add tail gas compression as a last resort
- Evaluate the upstream hydrocarbon removal systems
- Review sulphur trap capacity and line hydraulics

Avinashkumar Karre is a Process Engineer with Worley Group, Baton Rouge, Louisiana. He has 13 years' experience as a Process Engineer in the refining and chemicals industries. He has extensive experience in refinery revamp operations and water treatment.

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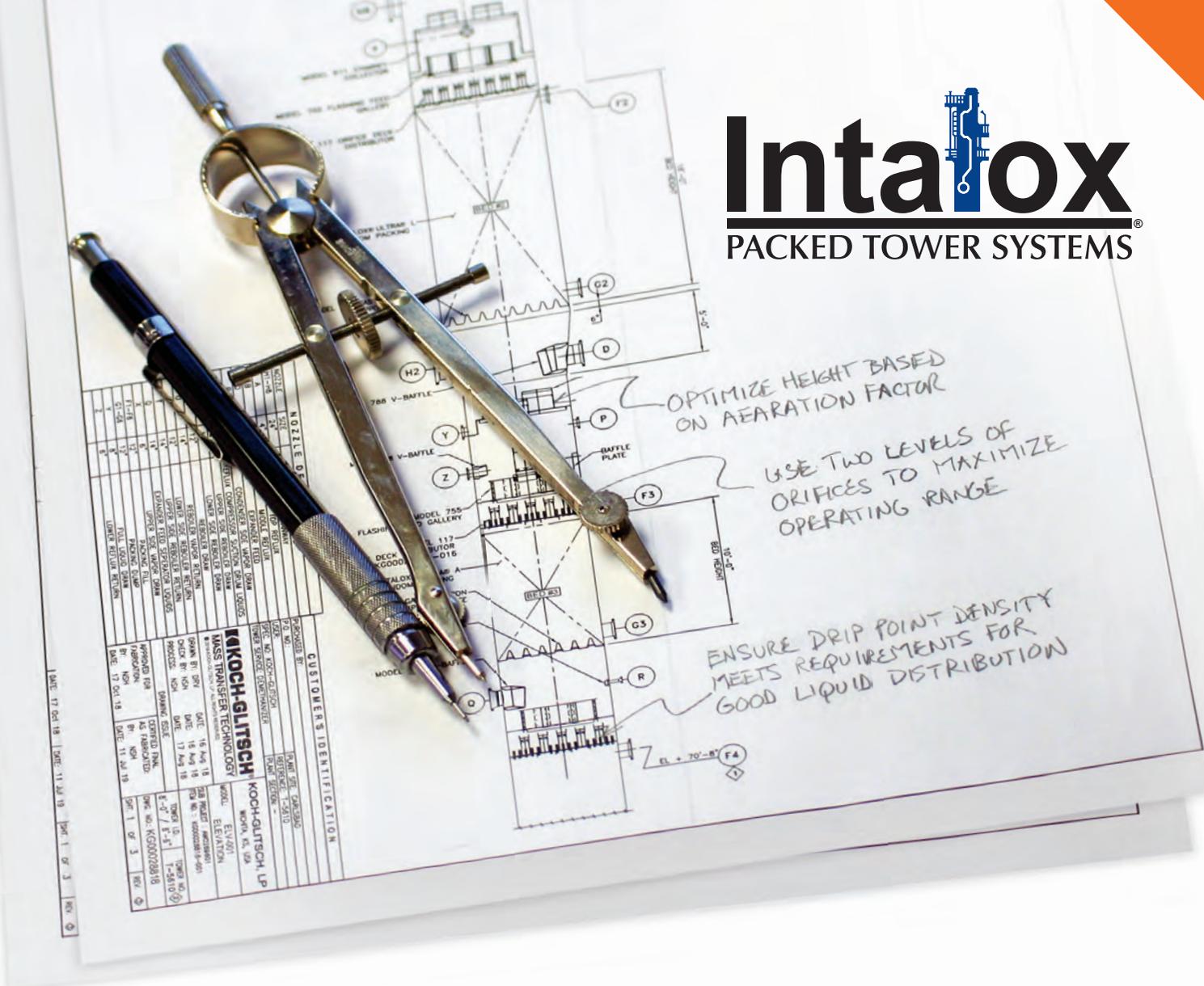
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Efficiency factors in natural gas fired steam boilers

A study to obtain maximum operating efficiency from a set of refinery steam boilers

ELIF GÜL GÖÇER, ELIF MELEK ÖZTÜRK, GÜLŞEN ŞAHİN ANDAŞ and YAHYA AKTAŞ
Tüpraş İzmir refinery

In industry, steam boilers represent one of the areas where energy is consumed intensively. Increasing energy efficiency means decreasing fuel consumption and therefore the cost of steam production. The main parameters that affect a steam boiler's efficiency are boiler load, combustion air, stack gas temperature, radiant heat loss, and acid dew point. In this article, natural gas fired conventional steam boilers are evaluated and potential savings are determined in the power plant of Tüpraş İzmir refinery.

The parameters that affect efficiency are traced and efficiency increase studies are focused on these areas (see **Figure 1**):

- Number 1 represents the fuel system of the steam boiler. Natural gas is used as fuel and the composition of the gas is traced daily.
- Number 2 represents combustion air feed which takes place close to the burners. Combustion air is taken from the atmosphere by forced draft fan and sent to the boiler through the preheater.
- Number 3 represents the isolated surface of the steam boiler. Radiant heat loss is the heat escape from the surface of the boiler and is traced by thermal cameras.
- Number 4 represents the stack gas where burned gases are given to the atmosphere after transferring their heat in the economiser. Stack gas temperature is traced and used in determining boiler efficiency.
- Number 5 represents excess air which is removed with the stack gas. Excess air percentage is traced in order to ensure complete combustion and prevent efficiency loss.
- Number 6 represents acid dew potential in the stack. In order to



Figure 1 Steam boiler general view

prevent acid dew, SO_x and stack gas temperature is traced.

The efficiency of steam boilers can be calculated from:

$$\text{Efficiency} = 100 - \text{Radiant heat loss \%} -$$

$$\left(0.044 + 0.325 * \left(\frac{O_2 \%}{18.16 - O_2 \%} \right) \right)$$

$$* (\text{Stack gas APH outlet temp} - \text{ambient temp}) - 0.8$$

Effect of load on steam boiler efficiency

Maximum efficiency is obtained generally when a boiler is used at 65-75% of load.¹ When the load of the boiler falls below 50%, in order to burn all of the fuel, more excess air

should be fed and this will increase heat losses. Therefore, a boiler load which is under 50% is not suitable in terms of efficiency.³

According to **Figure 2**, actual boiler loads are compared to 65% of the capacity of the boilers which is assumed to enable maximum efficiency in terms of load.

Boiler 1 and Boiler 2 are in a better situation when compared to other boilers due to load values of 65%. Boilers 5, 7, 8 and 9's efficiencies are lowered due to low usage of capacity.

The efficiencies of Boilers 1 and 2 are compared with Boilers 5 and 7 in **Figure 3**.

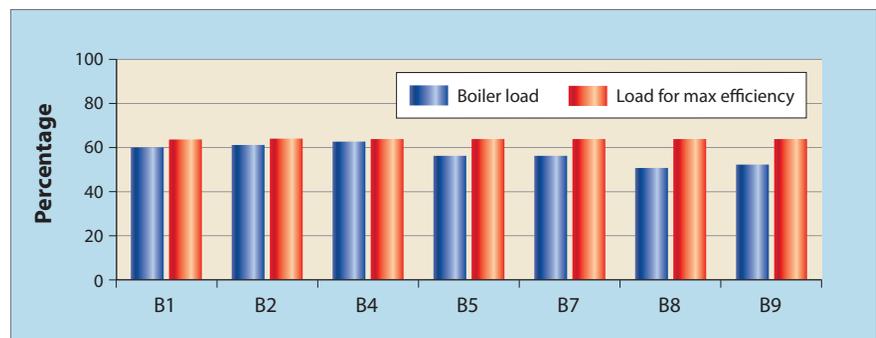


Figure 2 U 900 unit steam boilers' capacity usage

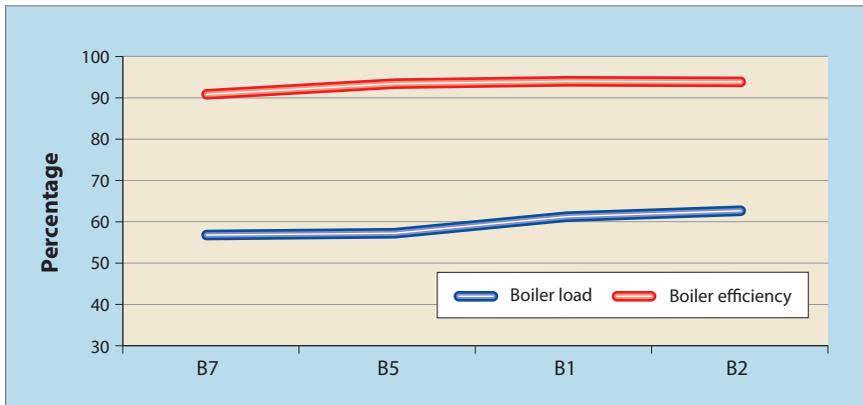


Figure 3 Effect of capacity usage on boiler efficiency

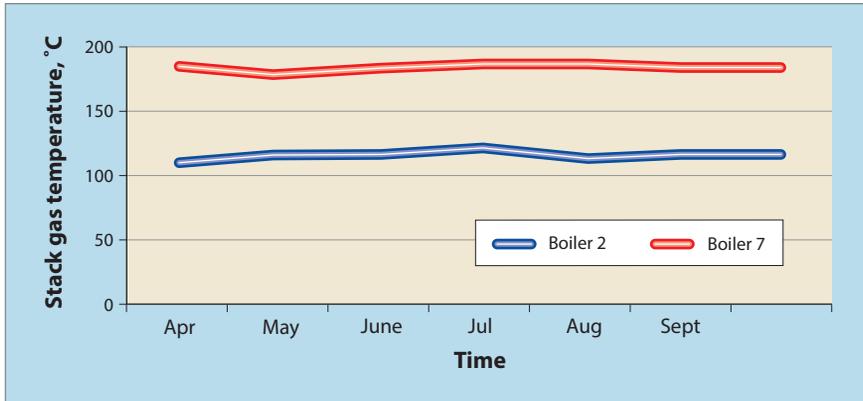


Figure 4 Boiler 2 and Boiler 7 stack gas temperature comparison

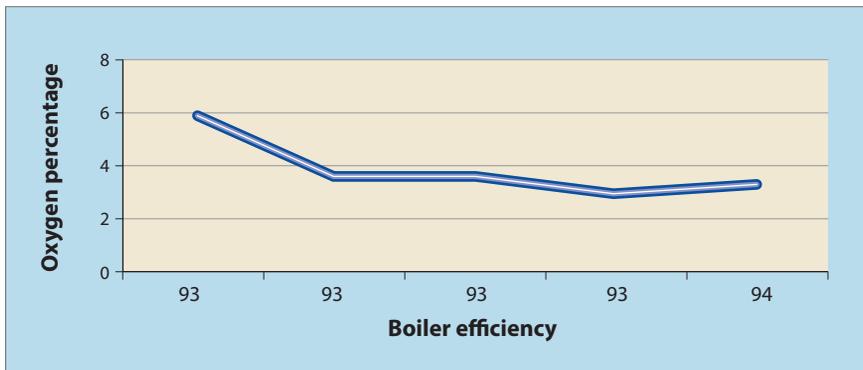


Figure 5 Effect of excess air on boiler efficiency

According to **Figure 3**, boiler efficiency increases with increased usage of boiler load.

When this trend is examined, an increase of 6% in boiler load increases efficiency by 3%. The boilers shown in **Figure 2** have 350 t/h capacity. High pressure steam is produced at 38 bar and 440°C which supplies 4130 Gcal/h of thermal power. However, the average usage of this capacity is 205.4 t/h which corresponds to 2423 Gcal/h. When these boilers produce 2423 Gcal/h, a 72.7 Gcal/h loss is calculated. The total economic loss is \$2394/h if the unit

cost of high pressure steam is taken as \$33/Gcal.

Effect of stack gas temperature on boiler efficiency

Stack gas temperature is a parameter that affects the efficiency of a steam boiler and needs to be traced closely. An increase in stack gas temperature affects boiler efficiency negatively. When the stack gas temperature is higher than the accepted value, heat is lost from the stack to the atmosphere. Every 20°C increase in temperature causes a 1% decrease in boiler efficiency.

The main reason for an increase

in temperature is dirt and clogging of tubes in the radiant area of the boiler. The stack gas temperature should be higher than the acid dew point. In the case of lower temperature values, nitric acid and sulphuric acid forms which leads to corrosion in the stack.

In **Figure 4**, Boiler 2 has the lowest stack gas temperature and Boiler 7 has the highest value. When they are compared, a temperature difference of approximately 70°C is observed. By assuming a 1% decrease in efficiency for every 20°C increase in stack gas temperature, in Boiler 7 an efficiency decrease of nearly 3.5% is calculated.

Boiler 7 has 100 ton/h capacity. High pressure steam is produced at 38 bar and 440°C which represents 79 Gcal/h of thermal power. When this boiler works at 90% efficiency, the thermal power is 71 Gcal/h. Due to the high stack gas temperature of the boiler, a 3.5% efficiency loss occurs and the thermal power reduces by 2.4 Gcal/h to 68.6 Gcal/h. The economic loss is calculated as \$79.2/h.

Effect of excess air on boiler efficiency

Combustion air is a critical parameter in order to enable complete combustion in a boiler. To prevent unburnt hydrocarbons, excess air is fed to the steam boiler.

The excess air ratio should be limited in order to save fuel consumption. A high level of excess air provides complete combustion but increases fuel consumption. A low level of excess air leads to movement of hydrocarbons to the stack and smoke forms.²

In order to understand whether the correct air ratio is applied, the percentage of oxygen is traced in the stack gas composition. At least 2% oxygen should be maintained, however the oxygen level should not be higher than 4%.⁶

Every 1% decrease in the oxygen level in the stack gas means a 0.5% increase in boiler efficiency.⁶

In the case of an increase in air, the stack gas is diluted and CO₂ concentration decreases while the oxygen concentration increases. In safe operation, excess air should be 10-15%.

In **Figure 5**, the oxygen level changes between 3% and 6% in the stack gas. By lowering this ratio to 3%, the saving would be 1.4% in boiler efficiency.

Assuming the boiler has 75 t/h capacity, high pressure steam is produced at 38 bar and 440°C which represents 59 Gcal/h of thermal power. When this boiler works at 90% efficiency, thermal power becomes 53 Gcal/h. Due to a high oxygen level in the boiler, a 1.4% loss in efficiency occurs and thermal power reduces by 0.74 Gcal/h to 52.3 Gcal/h. The economic loss is \$24.4/h.

Effect of radiant heat loss on boiler efficiency

A steam boiler has a higher temperature than its surroundings, therefore heat losses are observed through the surface of the boiler. This heat loss depends on temperature difference and isolation of the boiler's surface. In general, heat losses are accepted as 2-3% of the heat produced in the system. Radiant heat loss can be explained by the Stefan-Boltzmann radiation rule:⁵

$$q''_r = \varepsilon \sigma (T^4 - T_0^4),$$

where q''_r is radiant heat loss per unit area, ε is material emission, σ is the Stefan-Boltzmann constant which is $5.67 \times 10^{-8} \text{ W}/(\text{m}^2 \cdot \text{K}^4)$.

In this formula, radiant heat loss is related to the fourth power of temperature. Therefore, heat loss due to increased temperature gains importance.

In operation, heat loss in boilers is constant. Loss decreases with increased steam production.⁶ Therefore, an increase in boiler load affects boiler efficiency positively. A completely isolated boiler is assumed to produce 1.5% radiant heat loss when working at full load. In the case of 25% working load, heat loss is expected to rise to 6%.⁶

The İzmir boilers' average usage is 205.4 t/h which corresponds to 2423 Gcal/h. Radiant losses can be taken as 2.5% of the heat generated by the boilers. The radiant heat loss is calculated as 60.5 Gcal/h and the economic loss is approximately \$2000/h.

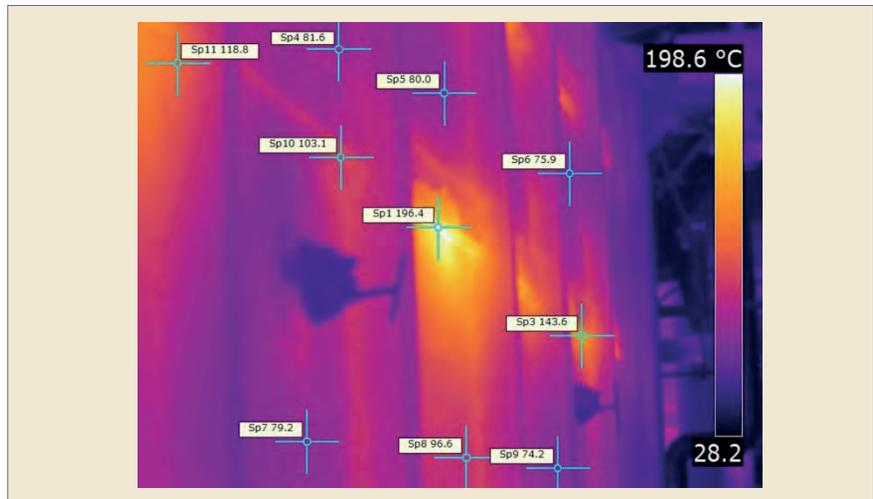


Figure 6 Boiler 2 thermal camera view

In **Figure 6**, an area of a boiler with a 196°C surface temperature has been detected. This area corresponds to the place where tubes are exposed to flame directly. Therefore, control of these areas is important in order to detect isolation distortions and efficiency can be increased by isolating these areas.

Effect of acid dew point on boiler efficiency

After the combustion process, the flue gas follows the radiant zone, convection zone, economiser, and flue path and proceeds by cooling. The fuel used contains carbon, hydrogen, and sulphur. After combustion, sulphur is oxidised to SO_2 and SO_3 .⁴ SO_x compounds react with moisture going from the combustion chamber to the stack. The H_2SO_4 formed presents a danger of

corrosion. H_2SO_4 may stick to the tubes where it is formed and cause leakage in the tubes. Factors that trigger condensation are reduced flue gas temperature, increased oxygen percentage in the flue gas, or the presence of V_2O_5 catalyst when fuel oil is burned.

If the flue gas is below 60°C while natural gas is burning in the boiler, SO_x condensation can be seen. The flue gas temperature should be above 60°C in boilers where natural gas is used, to prevent corrosion. In the economiser zone of the boiler, flue gas and boiler feed water meet and exchange heat.

In the degasser, O_2 in the boiler feed water is stripped and the temperature of the water is 105°C where O_2 is least soluble in water. After the degasser outlet, the temperature of the water that enters the economiser

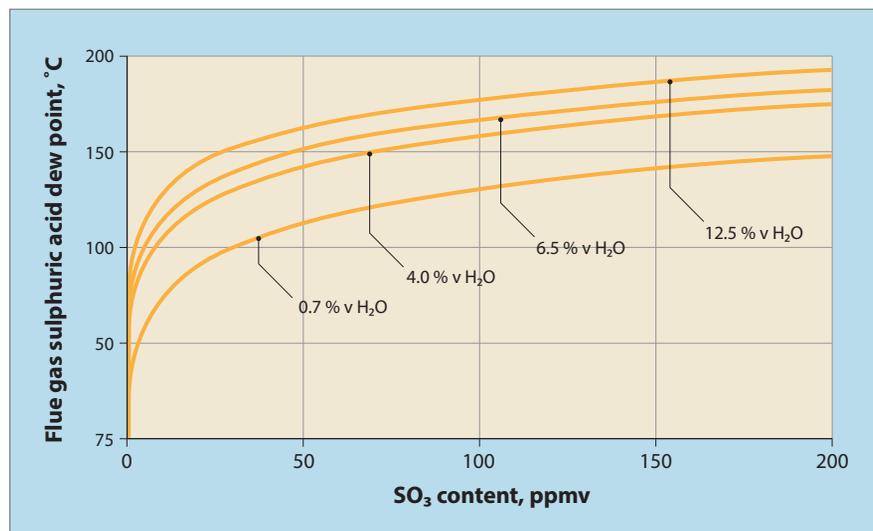


Figure 7 Calculated sulphuric acid dew points of typical combustion flue gases, as a function of SO_3 content and water vapour content

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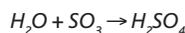
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is heated above 60°C if natural gas is burned, and above 145°C if fuel oil is being burned.

In the dew point calculations shown in **Figure 7**, SO₃ is present because a portion of the SO₂ formed in the combustion of sulphur compounds in the fuel is further oxidised to SO₃. The gas phase SO₃ then combines with the vapour phase H₂O to form gas phase sulphuric acid, H₂SO₄:



Because of the presence of gaseous sulphuric acid, the sulphuric acid dew point of most flue gases is much higher than the water dew point of the flue gases.

Results and discussion

The parameters that affect boiler efficiency, flue gas temperature, capacity utilisation rate, and percentage of oxygen in flue gas, were investigated (see **Figure 8**).

When these parameters are examined:

- The highest boiler efficiency belongs to Boiler 2, which has the lowest oxygen level in its stack gas
- Boiler 2 and Boiler 8 have the highest efficiencies due to low stack gas temperature
- Boiler 7 has the lowest efficiency due to the highest stack gas temperature
- Boiler 4 has high efficiency due to efficient usage of boiler capacity

According to this evaluation, the most important parameters to increase efficiency in boilers can be shown as using boiler load in the most efficient range and reducing flue gas temperature.

Instead of holding lots of low load boilers in operation, keeping fewer boilers at high load is more effective in terms of minimising heat loss and efficiency.

Difference between flue gas temperature and combustion air temperature should be reduced to increase efficiency. This difference is reduced by heating combustion air in the air preheater and transferring the flue gas temperature to boiler feed water in the economiser, so keeping equipment in operation is critical to efficiency. One of the reasons for increased flue gas tem-

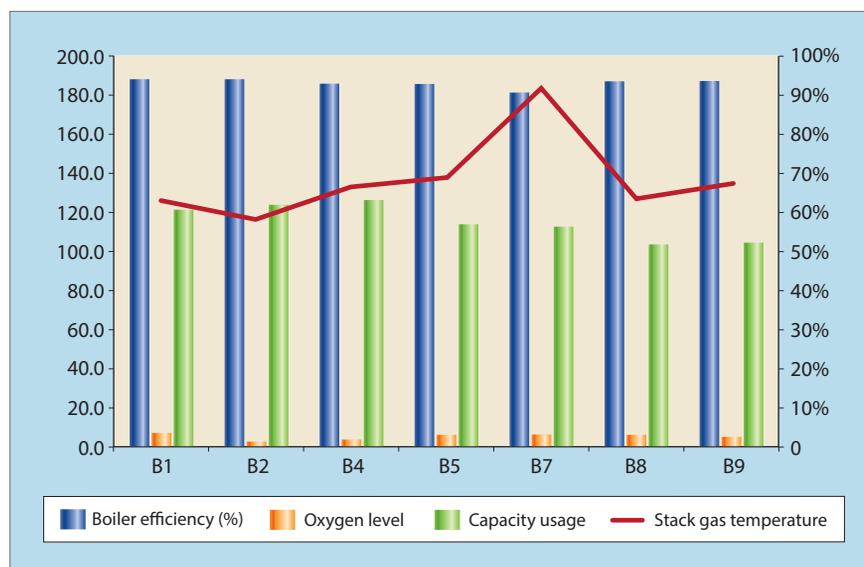


Figure 8 Boiler efficiency parameters

perature is pollution in the tubes. Therefore, the tubes should be cleaned at regular intervals to prevent clogging. Another area for savings is to reduce the percentage of oxygen to save input energy (fuel). Combustion control can increase savings there.

CO emissions and unburned hydrocarbons are factors that determine the required excess air. If the amount of air required for complete combustion is too high, there is the possibility of a malfunction in the air/fuel ratio or burner tip. In addition, deformations of boiler insulation affect efficiency depending on their dimensions. Refractory maintenance should be carried out on time but should not be used more than necessary.⁷

Excessively used refractory slows the rise of steam. When the boiler is switched off, the introduction of cold air must be prevented because there is a possibility of spills on the surface.⁷

Since vanadium and sodium salts in the fuel may interfere with the refractory material and reduce its thickness, the boiler should be fed fuel that is as clean as possible.⁷

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Elif Gül Göçer is an Energy Management Engineer at Tüpraş Izmir refinery. She is a junior chemical engineer receiving orientation at different process units.

Elif Melek Öztürk is an Energy Management Supervisor at Tüpraş Izmir refinery. She has experience in energy efficiency improvements, energy production and consumption optimisation, energy efficiency performance monitoring for different process units, and ISO 50001 energy management systems. She holds a BSc in chemical engineering.

Gülşen Şahin Andaç is an Energy Management Superintendent with nine years' experience in energy efficiency benchmarking and improvement studies of different units, developing short/long term energy roadmaps, online/offline energy optimisation, and ISO 50001 energy management systems. She holds a BSc in chemical engineering and a MSc in engineering management.

Yahya Aktaş is Production Sustainability Manager at Tüpraş Izmir refinery. He has 20 years' refinery experience, mainly in process improvements, furnace and boiler combustion control and safety systems, burners, waste heat boilers, and HC lost control subjects. He holds a BSc in chemical engineering and a MBA.



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Gas analysis in petrochemical production

Accurate gas analysis is critical in the production of PTA

KEITH WARREN and KAREN GARGALLO
Servomex

Purified terephthalic acid (PTA) is, together with ethylene glycol, a key component in the manufacture of polyethylene terephthalate (PET), the most widely used of the polyester type of man-made fibres. PET is also a recyclable thermoplastic resin with US FDA approval for use as food and drink containers and bottles. As such, there is a continuing and growing demand for PTA throughout the world, particularly in fast-expanding economies such as those found in Asia.

Gas analysis plays a vital role in the PTA production process, delivering the measurements that support product quality, process efficiency, and safety.

The PTA manufacturing process

PTA is manufactured from p-xylene by careful and specific air oxidation in a reactor at high pressure and elevated temperature. Liquid acetic acid, which is highly flammable, is used as a solvent for this reaction. The crystalline PTA product is separated from the reaction liquor in separate crystalliser vessels and then recovered and purified.

There are two essential applications for gas analysis in the PTA plant – the oxidation reactors and the crystallisers. Firstly, air is passed into the oxidation reactors, oxidising the p-xylene methyl groups to terephthalic acid and generating carbon dioxide (CO₂) and carbon monoxide (CO). Some oxygen (O₂) remains unreacted, so the most critical gas analysis measurement is to monitor this residual O₂ level in the off-gas, which should be around 4-5% O₂. If the level rises too high, it means a dangerous situation could be developing in the reactor; sudden, runaway oxidation of the flammable materials could occur, resulting in an explosion.

However, if the O₂ level is too low,



Figure 1 Paramagnetic cells consist of two nitrogen-filled glass spheres

then insufficient oxidation occurs, leading to poor efficiency and a low product yield. To achieve optimum results, the O₂ level must be monitored with the best possible accuracy and the fastest response time.

A paramagnetic O₂ analyser is recommended for this application, as this sensing technology is highly specific to oxygen, and so delivers high levels of accuracy in the reaction conditions. It also offers a fast response to changing O₂ concentrations in the reactor.

Paramagnetic cells each consist of two nitrogen-filled glass spheres, mounted on a rotating suspension within a magnetic field (see Figure 1). Light shines on a centrally located mirror, and is reflected onto a pair of photocells. Because O₂ is naturally paramagnetic, it is drawn into the magnetic field, and so displaces the glass spheres, causing the suspension to rotate. This motion is detected by the photocells which generate a signal to a feedback system. This, in turn, sends a current through a wire mounted on the suspension, creating a motor effect. The current produced is directly proportional to the concentration of O₂ within the gas mixture, allowing an accurate and linear percentage reading to be made.

As this technology is non-depleting, paramagnetic cells never need

changing, and the performance does not deteriorate over time, with significant benefits to ongoing maintenance costs and sensor lifespan.

A well-designed sample conditioning system is also required to ensure the analyser is able to cope with the high pressure, high temperature off-gas, which will contain trace p-xylene and significant levels of corrosive acetic acid vapour.

Additionally, many plants require a measurement of the CO₂ level – and sometimes the CO level – in the off-gas, as this reveals more information about the progress of the oxidation reaction. An infrared gas analyser can be used for this measurement, ideally configured to deliver simultaneous measurements of CO₂ and CO.

In the crystallisers, acetic acid vapour is driven off as the PTA product crystallises out of the solvent liquor. This vapour is extremely flammable, and so a measurement of the residual O₂ in the crystalliser vapour is vital to provide a warning of any explosion risk. Monitoring the presence of CO₂ in this vapour can also provide an indication of any post-oxidation that may be occurring, and so is a useful measurement.

Once again, paramagnetic and infrared sensing provides the most effective gas analysis for these O₂ and CO₂ measurements (see Figure 2).

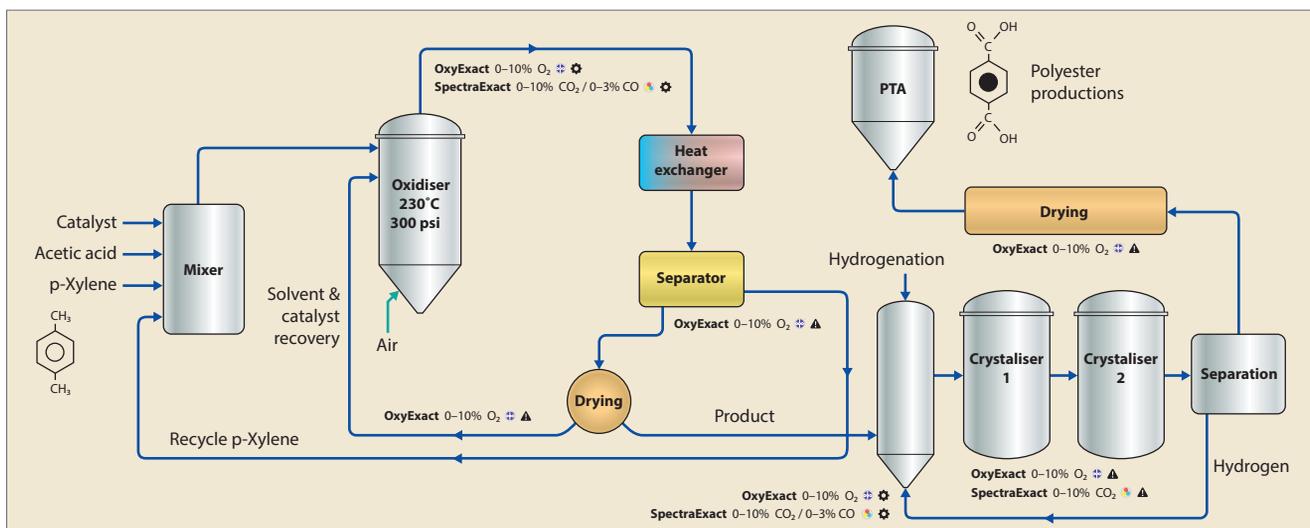


Figure 2 Analyser requirements for a PTA plant

Gas analysis requirements

The reactor off-gas is typically composed of:

- Nitrogen – approximately 90%
- Oxygen – 4%
- Carbon dioxide – 3%
- Acetic acid – 2%
- Water vapour – 1%
- Carbon Monoxide – <1%
- p-xylene, other organics, acid catalyst – trace

The off-gas is generally at a pressure of 20 barg and a temperature of 50-150°C, so the hazardous area classification required may be Zone 1 or 2 depending on the plant conditions.

Gas analysis measurements are normally specified on a dry basis with required ranges between 0-10% for O₂, 0-5% CO₂ and 0-2% CO. Speed of response is critical for gas analysis in this application, particularly for the O₂ measurement. Typically, 30-45 seconds for overall T90 of the complete system is required.

The system must operate with minimal errors, so to ensure reactor safety a voting system may be used to monitor the O₂ concentration. Voting systems use multiple analysers and the process relies on the measurement agreed upon by the majority of analysers. For example, in a three-analyser voting system, if one analyser detects a significant change, it is outvoted by the other two and no action is taken. However, if two of the three analysers (or all of them) detect a change, this reading is held as correct, and action may be taken, ranging from informing the operator to automatically halting the process.

Voting systems provide an extra layer of reliability in safety applications, and also allow a problem with an analyser to be detected at an early stage without endangering the process. If two analysers agree on a measurement and the third differs, it indicates a potential problem that can be investigated and corrected before the process is affected.

For the other measurement needs, a single infrared analyser is usually sufficient. Off-gas applications in the crystalliser are broadly similar and use identical analytical solutions.

For both reactor and crystalliser measurements, the sample conditioning system must be well designed to ensure a fast overall response time, and to handle significant levels of condensibles in the sample, removing them prior to measurement.

Sampling in the reactor off-gas stream also needs to correctly handle the high pressures involved. A water-washing 'lute' system may be used, and highly corrosion-resistant materials (titanium, Hastelloy, for instance) may be specified for construction, because of the presence of acetic acid and possible catalyst traces.

An experienced, expert gas analysis supplier will be able to provide the correct analyser and sample system packages to meet individual plant requirements.

Other applications

PTA plant applications can also include the measurement of water in liquid acetic acid, to assist with con-

trolling the recovery and purification of the acetic acid solvent before recycling. An infrared analyser such as Servomex's Servotough SpectraExact 2500 can be used to make this quality control measurement.

Further applications may relate to ancillary plant operations such as auxiliary boilers. These may require measurements of O₂ and combustibles in the flue gas. Servomex's Servotough FluegasExact 2700 provides accurate measurements for each of these components in a single analyser, using zirconia and thick film catalytic sensing technology.

In addition, emissions monitoring may be needed to show the plant complies with environmental regulations. A variety of sensing technologies exists to support this application. Servomex's Servopro 4900 Multigas provides continuous multi-component measurements of criterion pollutants, greenhouse gases, and reference O₂, using configurable digital sensors to meet plant requirements.

Recommended solutions

For the O₂ monitoring required by PTA manufacturing processes, Servomex has the Servotough OxyExact 2200. This is a paramagnetic oxygen analyser with an optional solvent-resistant cell, delivering an accurate, reliable measurement that is specific to O₂ and unaffected by flammable and corrosive solvent traces.

The OxyExact 2200 complies with Safety Integrity Level (SIL) 2, and is fully certified for Zone 1 or 2 hazard-

ous areas, including use with flammable samples. It operates across a wide ambient temperature range, with a good speed of response, typically delivering a T90 response time of four seconds.

A three-enclosure assembly facilitates simplified and versatile sampling of any flammable gas up to 100% O₂. In many cases, the analyser does not require pre-sample drying, so ongoing costs are dramatically reduced. Up to six O₂ transmitters can be linked to a single control unit, making the OxyExact 2200 suitable for voting systems.

The SpectraExact 2500 is designed for single-component CO₂ analysis while a variant model, the SpectraExact 2550, is used for dual-component CO₂ and CO measurements. Using infrared sensing technology, the SpectraExact 2500/2550 has stable, reliable performance with minimal cross-interference. It has full certification for Zone 1 or 2 hazardous areas, regardless of the sample type, so the certification is not affected by the flammable gases used in PTA manufacture. The SpectraExact 2500/2550 operates over a wide ambient temperature range, with a rugged construction.

Case study

Recently, Servomex supplied an analytical solution for PTA production plants to a major Asian petrochemical manufacturer. This company was planning to use an oxygen enrichment process on two of its PTA plants.

The process involved adding O₂ to the air being fed to the reactors, bringing the O₂ level up to 25%, ensuring a more efficient reaction, reducing catalyst consumption, and improving reactor performance.

A reliable and accurate monitoring solution was required to maintain the O₂ concentration at the most efficient level while ensuring it did not exceed safe levels. Servomex provided three O₂ monitoring systems for each plant, each built around the OxyExact 2200 high-specification oxygen analyser.

The ability of the analyser to operate effectively and reliably in hazardous environments – particularly the resilient enclosure for the transmitter unit – was key to being selected to provide this solution.

Conclusion

In addition to providing analytical instrumentation, Servomex Systems has a comprehensive gas analysis

solution for PTA plants, with project management from design to installation and commissioning.

Using a collaborative approach and employing Servomex's full range of gas sensing technologies, the Systems team ensures a scalable solution that meets individual plant requirements for gas analysis.

This may range from O₂ sampling and analysis for quality and safety in the oxidation reactor, through to a complete solution for the plant that encompasses CO₂ and CO process control analysis, combustion control and continuous emissions monitoring.

Keith Warren is Product Manager for Process Oxygen, Zirconia and Oxygen Deficiency with Servomex. As part of the Industrial Process & Emissions team, he is proficient in Servomex analyser technologies. Based at the UK Technical Centre, he holds a BEng degree from the University of the West of England and is Lean Six Sigma Green Belt qualified.

Karen Gargallo is Applications Manager for Industrial Process & Emissions, Chemical/Petrochemical with Servomex, and is also based at the UK Technical Centre. She has been with Servomex for 13 years, specialising in photometric analysers. She is a graduate of Imperial College London and holds a master's degree in engineering.

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Growth by association

Associated gas can be an important component of future fuel supplies if new gathering pipelines and tighter regulations come into play

Most wells that are drilled for oil also yield a mixture of other hydrocarbons, such as condensates, natural gas liquids, and natural gas. The latter is associated gas, essentially a by-product from an oil well or field, while non-associated gas comes from a well or field that is primarily intended for gas production. In its latest *World Energy Outlook*, the International Energy Agency (IEA) considers the future for associated gas. The IEA's analysis is based on two options for government policies that will determine its prospects: the Current Policies Scenario assumes that governments make no changes to their existing policies, while the Stated Policies Scenario adds current policy intentions and targets to measures that are already in place.

Associated gas is often seen as an inconvenient by-product of oil production: it is generally less valuable than oil per unit of output and is costlier to transport and store. It is often used on-site as a source of power or heat and can also be reinjected into oil wells to create pressure for secondary liquids recovery. Under the right conditions, it can also be stored and sold to the market at a later stage. Associated gas is usually collected via a network of gathering pipelines for further processing or direct injection into gas grids. When the gas is rich in natural gas liquids (NGLs), extra processing is required to separate out the heavier hydrocarbons such as ethane, butane, and propane.

When there is no on-site use for the gas and a lack of infrastructure prevents it from reaching nearby markets, it is vented or flared. Associated gas can also be unintentionally released to the atmosphere as methane emissions. Together, such non-productive uses of gas have significant environmental con-

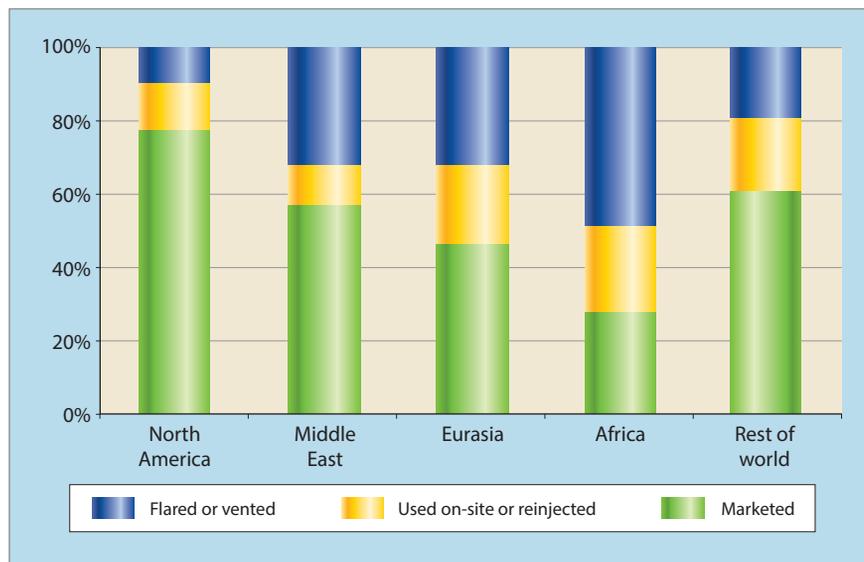


Figure 1 Use of associated gas by region in 2018

Source: IEA

sequences, making up around 40% of the indirect emissions associated with oil production. They also represent a wasted opportunity: the 200 billion cu m that was flared or escaped to the atmosphere or vented in 2018 was greater than the annual LNG imports of Japan and China combined. Globally, only 75% of associated gas is used or brought to market (see Figure 1).

Routine flaring occurs when there is a failure to put associated gas to productive use. This may be because of the remoteness of fields or the topography of the surrounding area or because the local price of gas discourages operators from developing costly gas transportation infrastructure to reach existing or potential new markets. Associated gas also often comes with a combination of water vapour, hydrogen sulphide, nitrogen or carbon dioxide, and the cost of separating out these unwanted elements may be higher than the potential profits from the gas. Although several countries have imposed regulatory measures to restrict flaring, these are

often not enforced. Even in countries with well-developed gas markets, around 10% of associated gas extracted today is flared or vented.

The US is the largest producer of associated gas, accounting for over a third of the global total. In most countries, associated gas constitutes less than a fifth of total marketed gas production, but in some large scale oil- and gas-producing countries, such as Mexico, Saudi Arabia, Brazil, and Nigeria, it has a much larger share. On average, gas makes up around 10% of the energy content of an oil field, but this is subject to wide variation depending on geological conditions, well design, and production method (see Figure 2).

Middle East supply

The Middle East holds nearly 40% of global proven gas reserves, but these are not spread evenly across the region. In the two largest gas-producing countries, Iran and Qatar, natural gas and condensate resources have been developed independently of oil. However, more than 80% of the gas in Saudi

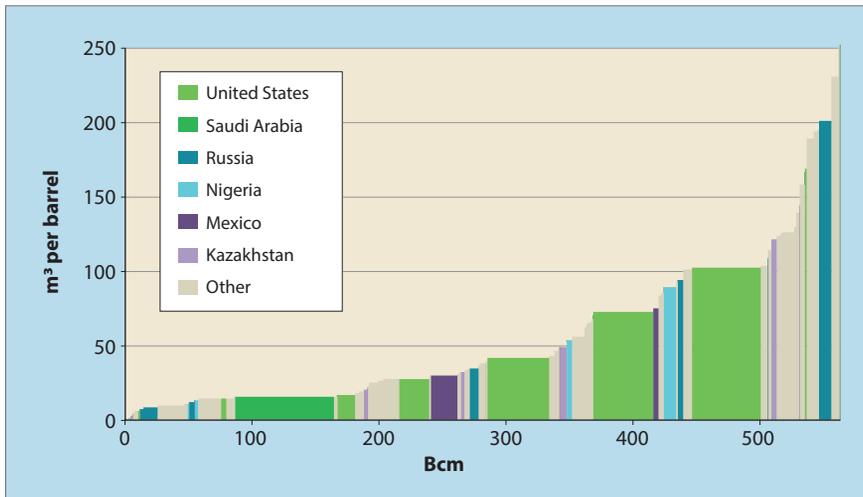


Figure 2 Associated gas volumes in the total output from oil fields in 2018 Source: IEA

Arabia and Kuwait is associated gas, and there are also significant volumes in Iraq and Oman. Associated gas has underpinned the rise of demand for gas in many of these countries since it has largely been available at close to zero cost as a by-product of oil production. It has also provided a basis for economic diversification away from oil.

In recent years, associated gas

production in the Middle East has struggled to keep pace with soaring domestic demand, which has tripled since 2000. Gas has been used as a substitute for oil in the power sector in producer countries because it frees up additional volumes of crude for export. It has also become an important fuel for water desalination plants. These applications cause peaks in consumption

during summer months and, in the absence of significant storage capacity, associated gas has struggled to supply this seasonal variation, hence Kuwait and the United Arab Emirates have resorted to seasonal LNG imports, while Oman has had to cut back LNG exports to redirect supply to the domestic market.

The shortfall in associated gas, combined with the pace of demand, has driven several oil-rich countries to develop non-associated gas fields, particularly those containing NGLs. Since 2000, the Middle East has quadrupled non-associated gas production. This has supported the development of new gas value chains and has underpinned Qatar's rise to become the world's largest LNG exporter (helped by the liquids-rich North Field). It has also led to integrated gas and NGL projects in the United Arab Emirates and Saudi Arabia that have spurred the development of heavy industries and petrochemical complexes.

Some countries are facing a need to raise gas prices to support fur-

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ther upstream development of more complex non-associated gas projects. They face a balancing act on price given their overall macro-economic reliance on low cost gas supply. Saudi Arabia is planning a pricing regime that differentiates associated from non-associated gas to reflect the higher development cost of non-associated gas. End user prices for non-associated gas are likely to be up to eight times those of associated gas. Even prices at the higher end of this range are unlikely to cover the long-run production costs of these resources, which are located in difficult to develop fields. The kingdom has also created incentives to Saudi Aramco for gas production, a sign of the priority assigned to domestic gas development. Oman, Bahrain, and the United Arab Emirates have put similar measures in place.

In the Stated Policies Scenario, some countries in the Persian Gulf achieve marginal gains from associated gas production, as oil output grows by a predicted 3.9 million b/d up to 2040. However, the majority of growth comes from non-associated gas resources, with production nearly doubling to reach 250 billion cu m by 2040. Saudi Arabia derives most of its incremental production from non-associated gas, which allows the country more or less to keep pace with growth in demand from the power, petrochemical, and desalination sectors.

Overall, natural gas's share of total marketed oil and gas production in the region rises from 26% today to nearly 33% by 2040, according to the IEA. The brisk pace of non-associated gas production allows the Middle East to develop upstream oil and gas supply chains that are increasingly separate from each other. It also accelerates the displacement of oil in electricity generation. At the same time, oil and gas remain tied together by investment in petrochemical and refining complexes in several parts of the Middle East, since these require an integrated hydrocarbon processing chain consisting of gas, oil, and NGL feedstocks.

The development of non-associated gas has important implications

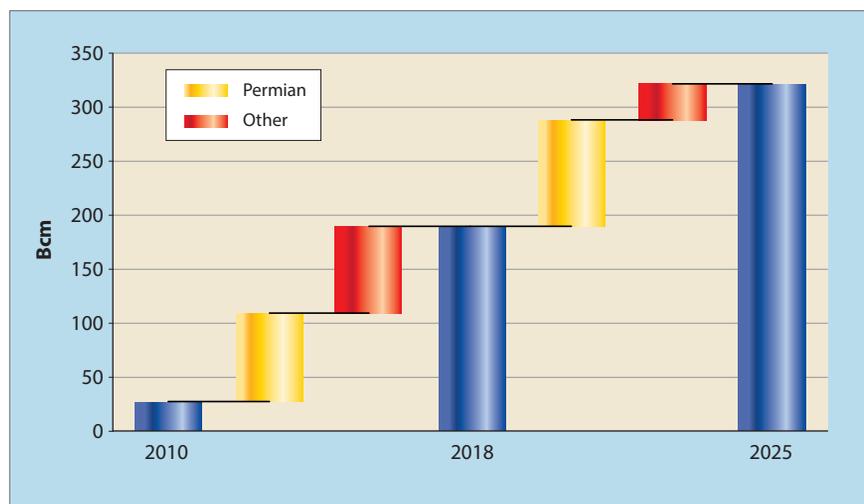


Figure 3 Associated gas production in the US, 2010-2025

Source: IEA

for the region's ability to adapt to the demands of the Sustainable Development Scenario, where oil production begins to decline very soon while gas demand continues to grow until 2030. The divergent paths in this scenario raise questions about how investment is divided between associated and non-associated gas, and about how countries in the Middle East reconcile declining crude oil exports with continued robust growth in domestic gas demand.

The Permian factor

Associated gas production in the US has doubled over the last decade, reaching nearly 200 billion cu m in 2018 and accounting for around 20% of the gas produced in the United States today. More than half of associated gas production comes from tight oil plays and significant further growth is expected (see **Figure 3**). The Bakken formation in North Dakota and the Eagle Ford play in Texas were the first basins to yield significant quantities of both gas and oil from horizontal drilling. Since 2017, the Permian Basin in southwest Texas has been the main source of growth, reflecting a huge increase in drilling activity with gains in productivity that have increased the amount of oil and associated gas output per well. As drilling has increased, so have estimates of remaining technically recoverable resources: the Permian is now estimated to hold nearly 7 trillion cu m of gas, alongside 80 billion barrels of oil.

Drilling in the Permian primarily targets more valuable liquids; gas is essentially a low cost by-product of this activity. This has created a number of dilemmas for US producers. While crude oil can be transported by road or rail, associated gas must be transported through dedicated pipelines; strong growth in production in recent years has outpaced mid-stream processing and pipeline transport capacity, creating bottlenecks that have put strains on upstream operations. Companies have responded by leaving drilled wells uncompleted and selling off associated gas at very low, sometimes negative prices.

They have also increased the amount of flaring; in the Permian alone, levels of flaring have risen more than 20-fold since 2011, when total flared volumes were estimated at 250 million cu m. Recent data suggest that as much as 7 billion cu m could be flared in the Permian in 2019. Flaring on this scale invites a regulatory response.

Constraints on pipeline capacity to transport associated gas away from where it is extracted are visible in widening price differentials between associated gas-producing basins and natural gas transported via the Henry Hub pipeline in Louisiana which sets a benchmark price. These differentials make a case for investment in new connecting pipelines, but the scale of projected growth in associated gas production in the Permian would require a doubling of take-away capacity by 2025.

It is not clear which demand centres have the greatest capacity to absorb low cost gas. Pipeline exports to Mexico have increased more than four-fold since 2010, but the prospects for exporting additional quantities are limited by the need for further development of pipeline infrastructure within Mexico, as well as by Mexico's own gas production.

LNG export terminals are expected to be the main outlet for associated gas. Around 80% of liquefaction terminal capacity in operation in the US today is on the coast of the Gulf of Mexico. New pipelines that link low cost Permian gas to these export facilities, such as the Gulf Coast Express, have a role to play in relieving the pressure on upstream producers by providing a route to market for their associated gas. Several proposed LNG export projects have made sourcing lower cost gas from the Permian a key part of their business model, which means that new pipelines will also help support the commercial case

for the next wave of LNG export expansion.

The implications of a possible rise in oil prices are likely to reinforce the desire of producers to send associated gas to LNG terminals for export. Any increase in the oil price would be likely to stimulate additional tight oil production, which would lead to more low cost associated gas, thereby putting downward pressure on domestic gas prices. At the same time, higher oil prices would increase LNG prices, enhancing the competitiveness of LNG exported from the US.

An answer to imports

Associated gas has an important role in the future energy mix of Brazil. The development of offshore pre-salt fields has led to increasing quantities of associated gas production. Today, every barrel of oil extracted from pre-salt fields is accompanied on average by 20 cu m of gas, which means that associated gas accounts for around 10% of total output in energy terms. In

the Stated Policies Scenario, offshore gas production rises from 21 billion cu m today to over 60 billion cu m by 2040.

Despite growing production from this significant resource, Brazil today relies in part on imports to meet its domestic gas demand. It could potentially make much more use of its own gas, but it lacks the necessary pipeline infrastructure. Pipeline capacity is sufficient to land around 8.5 billion cu m of associated gas, while gross production is running at around 32 billion cu m. Producers reinject over a third of the associated gas into the pre-salt fields.

There is also a mismatch between associated gas supply and demand. Gas demand for electricity generation varies considerably from one year to the next in Brazil because gas is used to balance the annual availability of large-scale hydropower. As a result, demand for gas from the power sector over the last decade has varied from as little as 3 billion cu m to nearly 20 billion



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cu m. This means that producers of associated gas do not at present have a relatively constant source of demand to justify building additional pipeline capacity to bring gas onshore.

Significant storage capacity could potentially provide such a constant source of demand, but it would be difficult to obtain finance for this because of the annual unpredictability of gas demand. New power projects linked to associated gas that would typically run as baseload supply could also potentially provide a stable source of demand. Currently, Brazil's power market is over-supplied, meaning that the delivered cost of associated gas to such power projects would need to be low enough to justify new investment in plants that need to run as baseload. Meanwhile, expanding wind and solar capacity adds a further challenge to the investment case.

Petrobras is exploring other technologies that potentially avoid the need for offshore-to-onshore pipeline infrastructure, such as floating LNG, gas-to-liquids processes, or CNG for the transport sector. It is not yet clear whether these technologies represent cost-effective alternatives to conventional infrastructure.

Conclusion

The major hurdles to finding markets for associated gas are the need to build additional infrastructure and the need to match a stable supply of output with demand in situations where many sources of demand are variable. In most parts of the world, in the absence of action by regulators, operators have greater incentives to flare associated gas than to curb more valuable oil output. Efforts to reduce flaring bear fruit, with rates declining by half even as oil production increases. The US dominates the rise in associated gas over the next decade, accounting for 75% of total growth. Production becomes more evenly distributed after 2030, reflecting a greater diversity in oil supply during this period. Associated gas increases from 565 billion cu m to 680 billion cu m by 2040, but its share of total marketed gas production drops to 13%, as global oil demand levels off while natural gas demand continues to rise.

In the Sustainable Development Scenario, flaring rates decline faster (as do methane emissions) and the share of total gas output accounted for by associated gas drops more quickly. Global demand for crude oil declines through the early 2020s, while demand for gas continues to rise throughout most of the rest of the decade; demand for natural gas then falls away more slowly than demand for oil. This creates a variety of challenges for operators: in a world of reduced revenue from oil, they face an even stronger imperative to invest in gas capture, and minimise flaring and venting. Some emerging technologies, such as small-scale LNG, may offer a commercially viable alternative to the reduction of flaring and venting of associated gas.

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Rupture discs for cryogenic containers

The pressure relief of cryogenic containers for liquefied gas transport is vital if unexpected evaporation occurs due to a collapse of the insulation vacuum, uncontrolled heat rise or excessive pressure rise in the inner container.

As a special form of pressure vessel, cryostats have particular requirements for the leak-tightness of their protective systems. The basic layout of a cryostat consists of two containers: a container with the cryogenic medium and an insulation container.

The inner container, also known as the product container, is often secured with a safety valve and a rupture disc. The additional secondary protection with a rupture disc ensures sufficiently fast pressure relief even during very high or fast pressure increases. Depending on the requirements for leak-tightness or corrosion resistance, various types of rupture discs are used, for instance reverse or forward-acting rupture discs, as well as 'plugs' – rupture discs with a thread connector.

The outer containers of cryostats are often designed for a pressure of less than 0.5 bar so that they do not fall under the Pressure Equipment Directive. Nevertheless, high demands are placed on pressure relief here: a combination of high vacuum, low burst pressure and high leak-tightness requirements (low leakage rate) is not feasible for standard pressure relief devices. Therefore, these outer cryostat containers are protected by so-called compact rupture discs.

Customised rupture discs for pressure relief

Rupture discs are typically made to order because the material type, thickness, disc size, and other properties are selected based on process parameters such as burst pressure, burst temperature, working pressure, operating temperature, process medium, and so on.

They are divided into various categories, one being compact rupture discs. While, for example, the term 'reverse-acting rupture disc' actually only refers to the rupture disc, the term 'compact rupture disc' usually includes both the actual rupture disc and the housing in which the rupture disc is enclosed.

Due to their small dimensions, these units are referred to as compact. High-quality compact rupture discs are characterised by extraordinary leak-tightness (leakage rates $<10^{-9}$ mbar l/s) and are also available in corresponding versions for sterile applications and containers.

An example of such a compact rupture disc is the UKB LS from the German rupture disc manufacturer REMBE. They consist of a housing, a burst membrane, and an opening aid, similar to a three-part knife. If the working pressure exceeds the defined maximum and

reaches the bursting pressure, the rupture disc presses against the three-part knife welded into the outlet part of the housing and cuts itself open. The largest possible vent area will become available immediately. Through the integrated three-part knife, predetermined breaking points on the rupture disc itself can be omitted, which makes the rupture disc itself more resilient. Leak-tightness is also increased by the weld connection of the rupture disc and housing, whereby both elements become one unit. At the same time, this unit is particularly easy to handle during installation and removal, thus preventing damage to the rupture disc during installation and normal operation. This ensures reliable protection of the system for operators, and guarantees the defined burst pressure over the long term. Premature response is thereby prevented – this protects against product loss and unnecessary downtime.

Cryostats and other containers for cryogenic media can become a great danger to people and the environment if there is insufficient protection with regard to pressure relief

In addition to the advantages already mentioned, welded compact rupture discs have two features to further increase the leak-tightness: if a so-called reverse-acting rupture disc (bulge of the rupture disc faces the process) is installed, relatively thick material can be used even at very low response pressures, which prevents diffusion of the process medium. In addition, these rupture discs are vacuum resistant even at very low burst pressures without the need for an additional vacuum support. This is important because vacuum supports make sterilisation impossible. However, this is exactly what is required for sterile, demanding processes or ultra-pure gas applications.

Cryostats and other containers for cryogenic media can become a great danger to people and the environment if there is insufficient protection with regard to pressure relief. Last but not least, there is a high monetary loss for operators. Special safety valves and rupture discs are therefore necessary to ensure adequate long term protection.

REMBE

For more information: sandra.drawe@rembe.de

Steamboat on stream

Commissioning of the Steamboat I gas processing plant in Wyoming has been completed to more than double Meritage Midstream Services' natural gas processing capacity in the Powder River basin. The owner-operator of the plant is Thunder Creek, a subsidiary of Meritage.

The aim of the Steamboat plant is to improve overall product recoveries, optimise system run times, and maintain system pressures. This additional processing capacity will further Meritage's goal of providing Wyoming's oil and gas producers with access to the largest and most advanced natural gas and NGL midstream facilities in the Powder River basin.

Meritage has also entered into a multi-year gas gathering and processing arrangement with a large independent oil and natural gas producer in the Powder River Basin. This contract provides Meritage with a minimum volume commitment supporting a "substantial portion" of the company's gas gathering and processing capacity, says the company.

Meritage is a leading midstream provider in the Powder River basin with 380 MMCFD of processing capacity, 1600 miles of gas gathering pipeline, 120 miles of NGL pipeline and 168 000 hp of compres-

The aim of the Steamboat plant is to improve overall product recoveries, optimise system run times, and maintain system pressures

sion, serving more than a million acres of production. Currently, 47% of the rigs operating in the Powder River Basin are operating on acreage committed to Meritage Midstream's Thunder Creek system.

The new cryogenic processing plant has a nameplate capacity of 200 MMCFD. Additionally, the Steamboat I plant is located on a site large enough to accommodate two additional 200 MMCFD cryogenic processing plants as future demand warrants expansion.

Seasonal gas storage and recovery

Samsung Engineering is to build a \$1.85 billion gas injection and reprocessing plant for storage and recovery of sales gas. The project is for the Aramco Hawiyah Unayzah Gas Reservoir Storage (HUGRS) project in Saudi Arabia.

The project is located at Hawiyah, 260 km east of Saudi Arabia's capital Riyadh, and includes a gas injection facility for 1500 MMSCFD and a gas reprocessing facility with a capacity of 2000 MMSCFD. The injection facility will introduce surplus sales gas into existing wells during the winter months. The stored

gas will then be used to match increased demand for gas in the summer. Samsung Engineering will execute the whole engineering, procurement, and construction process and expects the Aramco HUGRS to be completed in 2023.

The scope of work includes gas injection with booster compressors and injection compressors, and gas recovery with compressors and slug catchers, as well as utilities and offsite facilities.

Since its initial presence in Saudi Arabia in 2003, Samsung Engineering has carried out more than 30 projects worth about \$15 billion, half of which are Aramco projects.

Developing hydrogen for sales gas

Sales gas distributor Australian Gas Networks Limited (AGN) has received federal and state funding to support the Australian Hydrogen Centre (AHC) and explore the feasibility of blending hydrogen into natural gas networks. The company will join other members of AHC, including gas and energy infrastructure business AusNet Services, and renewable energy companies ENGIE and Neoen.

The AHC will develop feasibility studies to inject renewable hydrogen at levels of up to 10% into the gas distribution network of selected regional towns in South Australia and Victoria.

Building on the feasibility studies for regional towns, the AHC will also develop feasibility studies to inject hydrogen into the gas distribution networks of South Australia and Victoria, and develop a pathway to make the transition to 100% hydrogen networks.

In addition, the AHC will publish knowledge sharing reports covering insights and data from the operations of AGN's flagship project, Hydrogen Park South Australia (HyP SA). It will be Australia's largest renewable hydrogen production facility, expected to be operational by mid-2020, where renewable hydrogen will be produced and blended into the gas distribution network in Adelaide. Approximately 710 households will be receiving 5% renewable gas – a combination of natural gas and renewable hydrogen.

The ARENA grant will cover approximately 31% of the total estimated cost of \$4.15 million to complete the work programme of the AHC by January 2022. AGN says that its strategy is to deliver substantial and measurable ways to minimise the current carbon across its national gas distribution business.

The \$11.4 million HyP SA hydrogen production facility includes a 1.25 MW electrolyser to produce about 5% by volume of hydrogen for injection into the existing natural gas network, to deliver the renewable gas product. AGN received an A\$4.9 million grant from the South Australian Government's Renewable Technology Fund to build and operate the project. The proton exchange membrane (PEM) electrolyser will use renewable electricity to split water into oxygen and hydrogen.

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