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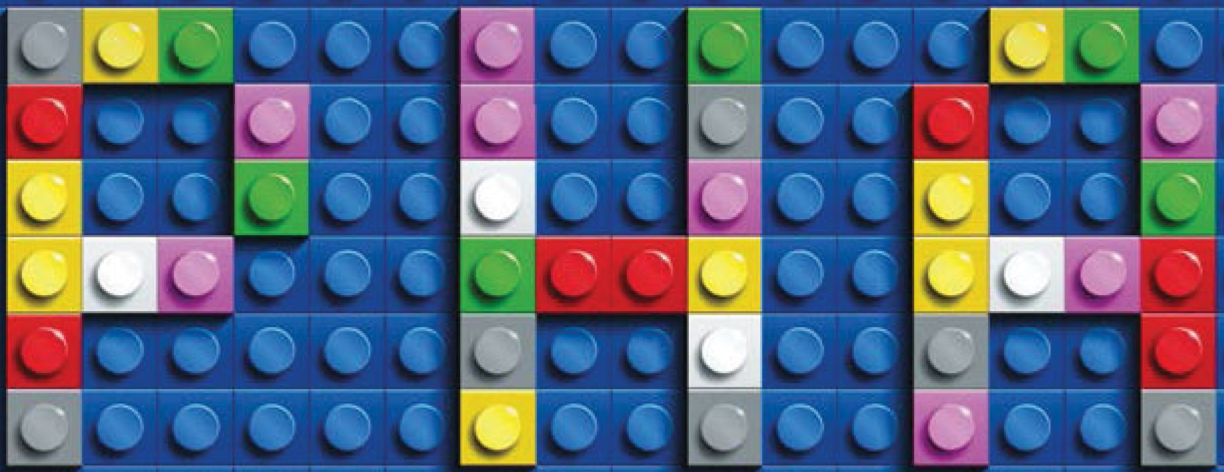

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OCTOBER 2020

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ADROITLY ADDRESS
WASTEWATER CHALLENGES

REFINERY TAMES
TOUGH SEALING SERVICE

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ALKY-ONE gasket in Hydrofluoric Acid

The Challenge

Hydrofluoric acid (HF) is one of the most difficult sealing challenges in modern refining. In addition to its potential to do bodily harm (NIOSH considers it dangerous at 30-ppm), it can corrode carbon steel flanges from the inside, leading to a condition called "taper corrosion", which – when advanced – requires a costly repair or replacement of the flanges. With some gasket options, the repair/replacement fraction can run as high as 30%.

The Opportunity

In 2015, a Midwest refinery with a HF Alkylation unit was undergoing a major upgrade. To reduce the occurrence of taper corrosion, they chose to upgrade their HF flange gasket to the ALKY-ONE gasket, which was engineered to provide an ID-to-OD seal across the flange face. During their turnaround, they installed 3,119 ALKY-ONE gaskets. With assistance by ERIKS, the refinery put in place a 100% inspection/QC procedure to ensure that the proper protocols were followed at every flange. Upon startup, all flanges were leak free.

The Results

At the next turnaround in 2019, the refinery opened 1,320 flanges in which the ALKY-ONE gasket had been installed. A full inspection of each flange was performed, along with photographs of each flange. Each was in "great condition", with no replacement or repair required. This 0% repair/replacement fraction is unprecedented, and speaks not only to the capability of the ALKY-ONE gasket, but to the excellent management of the installation/QC process instituted by the refiner. The combination of the right gasket, bolts, lubricant, training and procedures kept all 1,320 flanges in pristine condition over the course of four years.

A combination of the right gasket, bolts, lubricant, training, process and procedures kept 1,320 flanges in great condition over the course of four years.

To have the same solution implemented at your HF plant, email GasketPBUGroup@eriksna.com

FAST FACTS

Customer Profile:
An HF alkylation refinery with 6000 bpd of alkylate output.

Challenge:
Hydrofluoric acid (HF) is one of the most difficult sealing challenges in modern refining. In 2015, a Midwest refinery with HF Alkylation units was undergoing a major upgrade.

Opportunity:
During their turnaround, they installed 3,119 ALKY-ONE gaskets.

Results:
At the next turnaround in 2019, the refinery opened 1,320 flanges, which were found to be in pristine condition after four years of service.

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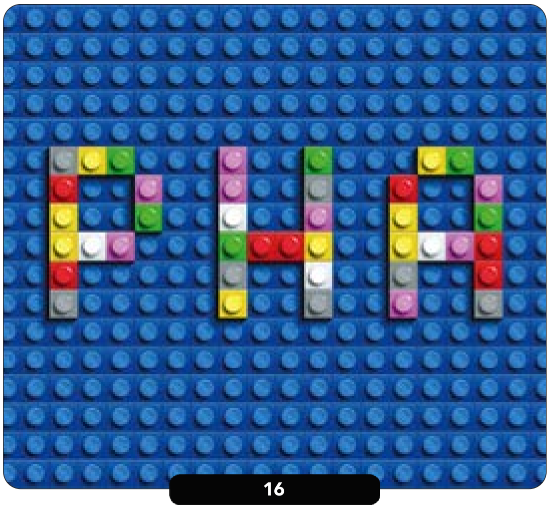

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COVER STORY

16 PHA Data Can Work Smarter

Process hazard analysis data can provide more insights than usually gotten — for instance, about how risk mitigation differs between sites. However, PHA data often pose barriers in accessibility and structure. Here are some pointers to overcome such issues and take fuller advantage of the data.

FEATURES

DESIGN AND OPTIMIZATION

23 Carbon Dioxide Developments Fizz Up

Concerns over carbon dioxide emissions are spurring work to develop processes that can use the gas as a feedstock to make chemicals or fuels. This articles looks at key developments in industry and academia.

SOLIDS AND FLUIDS HANDLING

27 Adroitly Address Wastewater Challenges

Better understanding regulations and taking advantage of advanced technologies are key to optimizing wastewater management. Here are six issues to focus on to ease wastewater compliance and minimize recurring costs.

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32 Refinery Tames Tough Sealing Service

A midwestern refinery upgrading its hydrofluoric acid alkylation unit opted for a new gasket designed specifically for this severe service and adopted stringent installation procedures. This led to impressive results.

COLUMNS

DEPARTMENTS

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BPA WORLDWIDE

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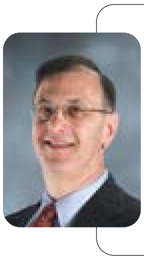
Folio Editorial Excellence Award Winner

Focus More on Safety Data

Leverage and augment existing hazard assessment information



PROCESS SAFETY isn't capturing headlines the way personal safety is during this pandemic. However, it, of course, remains a top priority; chemical makers always should strive for ways to improve process safety performance.

As our cover story "PHA Data Can Work Smarter," p. 16, highlights, processors can gain additional important insights from the massive amount of data they collect during process hazard assessments (PHAs). However, this requires a paradigm shift. "We must begin thinking of PHAs as less of a snapshot and more like a gigagpixel satellite image that allows you to zoom in and out at different altitudes and from a variety of vantage points," the authors stress. "This macro-level perspective would enable us to compare and crosscheck different PHA results both across similar processes and facilities," they explain.

As that article illustrates, such a perspective would allow a company to more easily spot the sometimes significant inconsistencies in how different plants rank the same risk. Moreover, it can show for a risk that sites rank similarly if mitigation approaches vary markedly. Glaring disparities should prompt questions as to why.

The way data now are handled in PHAs hampers getting a macro-level perspective. So, the authors recommend ways to overcome current barriers.

Another improvement — dynamic real-time risk identification and management — is gaining momentum, spurred by the pandemic and fluctuating oil and commodity prices, according to the 2020 "Process Safety Management and Operational Risk Management" survey conducted by Sphera, Chicago. Companies increasingly are considering technologies that can provide such capabilities, notes the report, which points to a shift from static to dynamic and simulated risk management.

"Many companies found themselves wondering if they had embraced simulated dynamic risk management tools earlier whether they would have seen less of a shock manifest itself throughout industry when the pandemic accelerated and oil prices ran out of steam," says Scott Lehmann, a coauthor of the report.

"The technology which connects the dots, joins the disparate processes and workflows, and illustrates the operational reality in real time simply has not existed until now," he adds. "Companies that embrace these technologies will finally be able to achieve a holistic, end-to-end view of their operational risk."

Real-time risk identification and management is gaining momentum.

Besides take-up of new approaches to risk visualization and mapping, respondents expect high rates of adoption over the next three years for fog/edge computing (over 600% increase) and digital twins (more than 300% growth).

This fifth annual report (for key points of last year's survey, see "Process Safety Demands Perseverance," http://bit.ly/39OYwSt) includes a section "Debates & Challenges" that cites four common process-safety failings: 1) use of outdated audits and inspections to decide on safety-critical priority; 2) incomplete audits and inspections; 3) deficiencies in the quality and consistency of audits; and 4) lack of awareness of vulnerability to major-accident-hazards risk exposure.

The report also covers a variety of other process-safety-related factors. One of its key conclusions is "...People need access to data and tools that deal with safety and risk in a dynamic, across-the-board way."

You can download a copy of the 2020 report via https://bit.ly/3k1Lghk. ●

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Make Your Vote Count

Online polls can give you and us valuable insights

Poll questions probe challenges.

IT'S THAT time of year; time to ignore the elephants and donkeys in the room and think about *Chemical Processing*'s polls instead.

Every month, we pose one multiple-choice question to gain insight on a topic pertinent to chemical engineers or the chemical industry. The results provide a quick, real-time view of readers' opinions and help us better understand the challenges faced by engineers designing and operating plants in the chemical industry. We share these results every issue via an illustration that appears in the In Process section of the magazine (see p. 10). We also house all the results online (chemicalprocessing.com/poll-questions). In addition, these polls serve as useful inputs in planning editorial content.

Over the last 12 months, we've asked everything from outreach efforts in the local community to interest in using renewable power. If you're wondering, more than three-quarters (75.9%) of survey respondents consider outreach efforts to be "effective" or "very effective" and just over half (55.3%) note that their site's interest in renewable power is "moderate" to "high."

Every year, we also like to ask several safety-related questions. When we posed the question, "How effective do you consider your site's current communications with local first responders?," we learned that only 38.8% consider communications "very" effective. Nearly a quarter of respondents (23.5%) stated that communications were only "somewhat" effective, 7.7% said "slightly" effective and 2.8% responded the communications were "not at all" effective.

Poor communications with first responders can lead to fatalities, as we discussed in a recent Process Safety With Trish & Traci podcast ("What Have We Learned From Significant Safety Incidents?" https://bit.ly/3m387Ls). Trish Kerin, director of the IChemE Safety Centre, spoke about the lessons learned from the West Fertilizer Plant incident in April 2013 where an ammonium nitrate explosion killed 15 people — most of them first responders.

"Emergency responders need to know what they're dealing with so they can adequately respond to look after themselves and keep themselves safe," says Kerin. "If they're hurt or injured, they can't respond on our behalf."

In this incident, Kerin noted that first responders thought they were putting out a simple fire. They had no idea they were dealing with ammonium nitrate stored in huge volumes.

The main lessons learned, according to Kerin, were "understanding the hazards of ammonium nitrate, how it should be stored, what to do with contamination, and how it should be segregated into smaller quantities was really important. And then being able to communicate that information to the emergency responders."

Another poll question probed a different communications issue: "How would you characterize your company's effectiveness in sharing safety learnings among its various sites?"

The news is better here. More than two-thirds (69.5%) of the poll respondents noted that safety learning sharing was either "good" or "excellent." Only 2.7% stated "poor" and 18.6% noted their site had "adequate" safety learning sharing.

In the same podcast about lessons learned, Kerin cautions: "It's easy to judge and we jump to judgment very, very quickly. But judgment of what happened doesn't necessarily help us. We need to really unpack why the decisions were made. Then we can try and do something different.

YOUR POLLING STATION

For more poll results, and to vote in the current poll, visit chemicalprocessing.com/poll-questions.

"We also often hear people say, 'Well, that can't happen here.' And to me, 'That can't happen here,' are the four most dangerous words we could ever put together in the English language when we're talking about process safety. The moment you say them, you're actually setting yourself up for it to happen because that's complacent... The better question to ask is, How can that happen here? And what controls do I have in place to prevent that? How can I manage that?"

Obviously, these poll questions help us understand you better. But they also allow you to voice your opinion on important issues and to benchmark your responses with those of your peers. So, when you see a new poll question, go ahead and participate. You might learn something. ●

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Pipeline Cleaning Demands Care

The way you do the job and what you use really matters

Looking at drainage and dead legs is important.

THE PIPELINE that carried 50% caustic solution needed cleaning. I reckoned this called for a flow of at least 30 gal/min in the 500-ft 2-in. line to maximize velocity — and, so, minimizing the ¾-in.-hose connections. Instead, operations opted for 150 ft of hose and water from the hot water system; this produced a paltry 9.4 gal/min, as I confirmed with a bucket test. After a few hours, the pH had dropped from 14 to 11. That, as I informed operations, was the easy part; the U.S. Environmental Protection Agency mandates a pH of 8 for caustic at landfalls. So, the flushing began again the next day. After a few more totes, operations claimed to have reached a pH of 9.4. I had my doubts, though, because I'd calculated a 1%-by-volume caustic residual in the pipeline and gotten field measurements of pH 11.

Based on dilution alone, I estimated it would take 10 totes, at 275 gal/tote, to achieve a pH of 10.94 and 789 totes to reach a pH of 9. However, the actual amount of water required depends on its applied velocity and the way the contaminant bonds to the surface.

Disgruntled, operations blew out the pipe again to remove the residual. I captured a sample of the spray at the end of the hose — the pH was 10.96, as confirmed with two pH meters.

CHECK OUT PAST FIELD NOTES

More than a decade's worth of real-world tips are available online at www.ChemicalProcessing.com/field-notes/

For additional practical pointers, check out the online roster of Plant InSites columns at www.ChemicalProcessing.com/plant-insites/

Operations staff had another trick up their sleeves. They filled up the pipe, let it soak for an hour, blew it out again and then flushed for a third time. Finally, after 16 totes (4,100 gals, as the totes weren't full), we achieved a pH of 9.6. A final test of the water used for the hydro-pressure test that followed the construction showed a pH of 9.3.

My report concluded that blowing took the place of the velocity I was seeking but, without flushing, the caustic residual would have remained in the pipe.

Several factors can prompt the need to clean a line: 1) tie-points require clean welds; 2) the safety of the construction crew; 3) decommissioning or mothballing; or 4) to eliminate sources of food for biological contaminants.

I spent five years in industries — food, consumer product and pharmaceutical — where cleaning is an everyday affair. I've learned that salts, acids, bases and other ionic compounds are the most difficult to remove from pipes. Of course, scaling from hard water and material that sticks to a surface like caramelized molasses require harsh treatment, perhaps even abrasive cleaning that can endanger the texture of polished surfaces.

Measuring the efficacy of the cleaning of contaminants from acid and base lines is much easier than assessing the removal of bacteria — because pH meters provide instantaneous results that are easily and quickly duplicated. However, complications can arise in operations that use the same batch tanks in different campaigns.

Chemicals sometimes can improve cleaning but also may result in product contamination, a problem that can occur in any type of process plant. I remember a hydrotest on a chlorine system that took over a month to dry with nitrogen; opting instead for pneumatic testing would have made much more sense. In addition, a chemical that is highly toxic or has a pH greater than 10 or less than 4 will be more difficult to take to a landfill. Then, there's the safety angle: acids and bases aren't the only combinations that are exothermic — carefully consider venting in such situations. These are reasons why water often is the best choice. That said, a chemical that can be recycled or easily disposed of might work as a cleaning agent in some circumstances.

Looking at drainage and dead legs is important in all process and utility pipe designs. A good practice is what I call the "fit test." It involves loosely assembling pipe components on a bench. Operators and engineers then can look at the spool and define the proper orientation and location of the components. For example, it's best to place bleed and drain valves as close as possible to isolation valves.

Also, just once, I'd like to find a pipeline subdivided to make cleaning easier. ●

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Photocatalyst Splits Tough C-F Bonds

Use could reduce cost and energy involved in breaking fluorine-containing compounds

ENGINEERS FROM Rice University, Houston, and collaborators have created a light-powered catalyst that can break carbon-fluorine (C-F) bonds. The process has potential for applications in high-value chemical transformations, as well as in abatement of chlorofluorocarbon, hydrofluorocarbon and perfluorocarbon pollution, reckon the researchers.

"The hardest part about remediating any of the fluorine-containing compounds is breaking the C-F bond; it requires a lot of energy," says Naomi Halas, a Rice University engineer and chemist whose Laboratory for Nanophotonics specializes in creating and studying nanoparticles that interact with light.

Based on the antenna-reactor photocatalyst platform technology developed by Halas' lab, the catalyst uses tiny spheres of aluminum speckled with palladium to break C-F bonds via hydrodefluorination, a catalytic process that replaces a fluorine atom with a hydrogen one.

Syzygy Plasmonics has licensed the photocatalyst technology from the Halas lab and will focus on scale up and commercialization.

"In the past few years we have achieved a dramatic scale up and improvement in efficiency. We are even in the design stages for our first micro chemical plant based on the technology," says Trevor Best, the firm's CEO.

Best adds: "When applying the antenna-reactor to a chemical process using Syzygy's reactor we are seeing a dramatic reduction in the operating pressure and temperature of the reactor. We are able to achieve the same conversion, etc., but while operating at hundreds of degrees Celsius lower temperature. This allows us to build our reactors out of aluminum, glass, and plastic, which dramatically reduces our costs. Also, because we are powering the reaction with light that can be generated with renewable electricity, we no longer need to burn fuel to power many of these reactions. This results in a dramatic reduction in carbon emissions."

Furthermore, scaling up the catalyst manufacturing process has been remarkably simple, notes Best.

Applying the antenna-reactor technology to industry involves a few steps. "First, we created the photocatalytic cell and surrounding reactor enclosure. This reactor uses high efficiency artificial lights to drive the chemical reactions. … the company … is now working on constructing multi-cell reactors. Finally, after the multi-cell is complete then we will combine many of those together into the final chemical systems that make product at scale…We have even automated the process to take out the potential for human error. We have a solid plan to produce catalyst at any scale," he explains.

The catalyst also shows good stability in terms of its light response. "There are many different types of antenna-reactor photocatalyst. In general, we have seen that they are highly resistant to many forms of catalyst decay including coking, oxidation and sintering. However, they are susceptible to sulfur poisoning so sulfur must be removed from the feedstock gas," cautions Best.

The company's future work focuses on two segments: the platform itself and the reaction.

"The next steps for the platform are to continue scaling up and optimizing the photocatalytic reactor that Syzygy is working on. We are currently at a large bench-scale unit in our lab and plan an integrated demonstration as part of a hydrogen production system in the next few years.

Best says Syzygy will assess market interest in the C-F breaking catalyst, and how it compares against other options. If there is significant commercial interest, the company will commit resources to scaling up the reaction.

"This general reaction may be useful for remediating many other types of fluorinated molecules," Halas believes.

"… Because the antenna-reactor photocatalyst is a platform, and it has now shown capability with flouromethane, it is very possible it can be adapted to break other types of C-F bonds. This would allow it to be applied in different ways in industry," Best adds. ●

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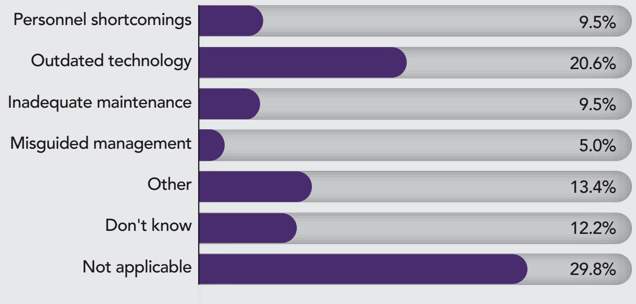
What issue most undermines your site's ongoing performance?



Outdated technology was by far the most cited particular failing.

New Option Beckons for Propylene Separation

POROUS LIQUIDS (PLs) based on a metal organic framework (MOF) represent a breakthrough for separating propylene from other compounds, claim researchers at Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany. Moreover, the approach promises to have far broader applicability, they say.

PLs are nanoparticles that typically float, finely distributed, in a solvent. Only molecules of a certain size can pass through their empty pores.

However, MOFs' highly crystalline structure and lack of processability have limited their application in gas separation. The KIT workers have overcome these issues by using N-heterocyclic carbene ligands to functionalize the outer surface of a MOF called zeolitic imidazolate framework 67 (ZIF-67).

The team systematically modified the surface of ZIF-67 nanoparticles to vary the size of the pores from their original 0.34 nm and then finely dispersed the nanoparticles in liquids such as cyclohexane, cyclooctane and mesitylene.

So, for example, a gas with larger molecules such as propylene takes much longer to pass through a column filled with the PL than methane does.

"We want to exploit this property of the dispersion in the future to produce liquid separation membranes," says Alexander Knebel of KIT's Institute of Functional Interfaces.

The researchers also managed to produce solid membranes by embedding the modified ZIF-67 (Figure 1) in a plastic material. Once the ZIF-67 content of the membrane reached 47.5%, they passed a mixture of propylene and propane over two membranes arranged in series — and obtained propylene with a purity exceeding 99.9% despite the barely 0.2-nm difference in size between the two molecules. The team reports their results in a recent issue of *Nature Materials*.

Knebel believes that a separation process such as this could replace energy-intensive distillation commonly used now.

"Our selling point is the processability. And, of course it is scalable; nanoparticles can be made and hollow fiber membranes can be spun. We have a patent filed and are looking for industrial partners to scale it up with," he notes.

All small-pore MOFs should be processable in a similar way to form PLs and the approach can be extended to other MOFs and applications, he reckons.

POROUS FRAMEWORK

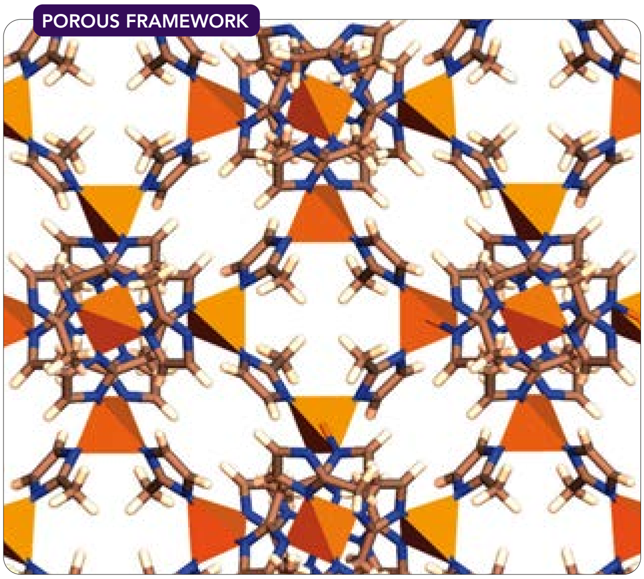
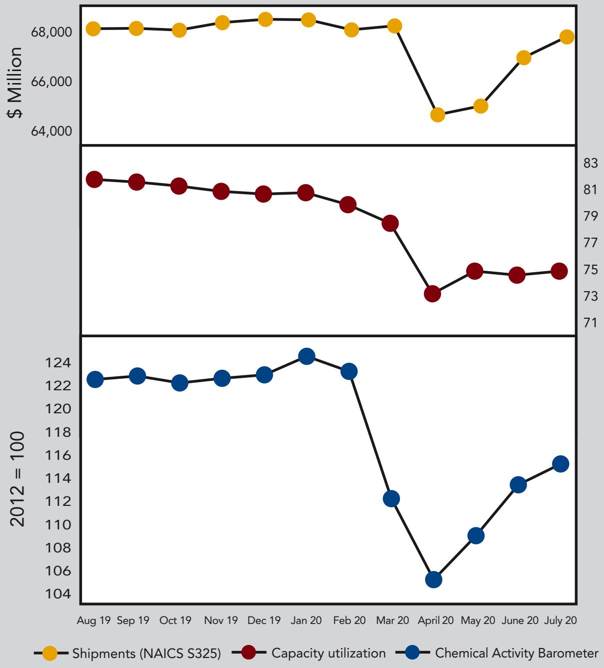


Figure 1. In ZIF-67, methyl imidazolate (rods and rings) connect the metal centers of cobalt (pyramids) to each other. *Source: R. Ahmad, KIT.*

Knebel has spoken with BASF's start-up funding agencies — who showed a major interest in the research — and also is looking to get other parties involved. ●

ECONOMIC SNAPSHOT



All three metrics rose. *Source: American Chemistry Council.*

Learn from Your Electric Bills, Part 1

Scrutinizing utility charges and rate tariff structures can enable reducing energy costs

28 states have some form of sales tax abatement for manufacturing-related energy purchases.

MOST OF us are familiar with our home's electric bill charges for energy (kWh) usage. The bills for larger customers, including manufacturers, contain other components, such as demand and power factor (we will cover this next month in Part 2). They also show the individual charges that lead to the final dollar amount, and whether or not you are paying sales taxes. Understanding these items, together with rate tariff structures, provides valuable information that can lead to significant savings.

Demand is the rate of energy use per time, which equates to power. It is measured in kW or kVA; the demand charges are in \$/kW or \$/kVA. Utilities measure the energy usage in discreet windows of time, often for 15 minutes, and determine the demand by dividing the kWh by 0.25 hour. They do this for every 15-minute period in the billing month. Many billing tariffs use the single highest demand as the billed demand for a month.

Many utilities have multiple rate tariffs to better serve different classes of customers, with certain tariffs suggested given the electric demand. For instance, a gas services (GS) tariff is suggested for plants with a demand of less than 400 kW. The large general service (LGS) tariff is used for higher demand levels. The GS may feature higher energy costs and lower demand cost, compared to the LGS which has lower energy costs but higher demand costs. Depending upon the exact nature of your plant's energy and demand usage, your final bill may be less on one tariff or the other. Texas A&M University's Industrial Assessment Center recently evaluated a large manufacturing plant with many meters and found that switching two meters to different tariffs could save \$305,000/yr. You can find the rate tariffs offered on your utility's website or by requesting assistance from your account representative.

Your final billed cost will include several energy (\$/kWh) and demand (\$/kW or kVA) charges, plus fixed charges for metering and customer charges. To correctly determine your net costs for both energy and demand you need to look at the sum of the energy-based charges, and separately the sum of the demand-based charges.

Common methods to reduce demand usage include searching the demand usage pattern to find the peaks, determining what production operations are taking place, and looking for some operation that can be moved out of that peak time period, into another shift perhaps. To determine your demand history, visit your utility's website and download that history, or request the "15-minute demand history" from your utility account representative. Another common method is power factor correction, which reduces the billed demand by installation of capacitors. We will look at this method in more detail in Part 2.

At least 28 states have some form of sales tax abatement for manufacturing-related energy purchases. So, if you see sales taxes shown on your bill, you may be able to reduce the final cost by eliminating all or part of those sales taxes. My experience is in the state of Texas, so I will speak for the rules there. A PE can perform a "Predominant Use Study" to determine the tax-exempt and non-exempt energy use for each meter. If the usage is over 50% tax-exempt, sales taxes can be completely eliminated for that meter. This could amount to the full 8.25% charged for sales taxes in Texas. Once the tax-exempt certificate is provided to the utility, it will stop collecting sales taxes. A real "kicker" in Texas is that a site can recover up to four years of past paid taxes from the state. The Texas Administrative Code discusses sales tax abatement (see, https://bit.ly/3hwF2EO, paragraphs 3.287 and 3.295).

The states with this tax abatement are: Ark., Colo., Conn., Fla., Ga., Idaho, Iowa, Ill., Ind., Kan., Mass., Md., Maine, Mich., Minn., Mo., Miss., Neb., N.M., N.Y., Okla., R.I., Tenn., Texas, Utah, Vt., Wisc., and Wyo. Notice also in Texas that includes sale taxes on natural gas used for manufacturing!. ●

JIM EGGEBRECHT, PE, Guest Contributor
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Editor's note: This article was written by a colleague of our regular columnist, Alan Rossiter (pictured). Jim Eggebrecht, PE, has worked at the Industrial Assessment Center (IAC) at Texas A&M University in College Station, Texas, for over 27 years as the assistant director. The IAC is a national program of the U. S. Department of Energy's Advanced Manufacturing Office. Eggebrecht has completed over 450 energy assessments for a range of manufacturing facilities. He is also the executive director of the Industrial Energy Technology Conference, hosted by the Texas A&M Engineering Experiment Station, the Texas State Energy Conservation Office, and the Louisiana Department of Natural Resources.

EPA Tells Businesses to Pay Up

Agency releases list of manufacturers subject to a $1.35-million TSCA risk evaluation fee

ON AUGUST 26, 2020, the U.S. Environmental Protection Agency (EPA) released the much-anticipated interim final list of businesses subject to risk evaluation fees for the 20 chemicals designated as "high priority" under the Toxic Substances Control Act (TSCA). Making the interim final list available now gives businesses and other stakeholders an opportunity to review the list for accuracy. It also provides time for businesses to reach out to form consortia to share in fee payments. That is a fancy way of saying the race is on to try to get off the list or find others to share in the not-so-trivial cost of $1.35 million — the EPA's fee for work on the risk evaluation.

BACKGROUND

Congress passed extensive revisions to the TSCA in 2016. One of the most significant changes involved TSCA Section 6 requiring review of active existing chemicals identified as high priority and mitigating the adverse effects of each chemical's uses and applications determined to pose significant risk to human health and the environment.

Congress recognized this task would take time and money and authorized the EPA to assess fees to recoup a portion of the government's costs in undertaking TSCA-related actions. The EPA published a notice on January 27, 2020, identifying the "preliminary" lists of manufacturers (including importers) of the 20 high-priority substances for risk evaluation and on which the EPA assesses fees. Manufacturers also were required to self-identify as "manufacturers" of a high-priority substance whether or not they were included on the EPA's preliminary lists. The agency used this information, along with feedback received during the public comment period, to develop the interim final list.

The EPA intends to publish the final list of businesses subject to fees for the 20 high-priority chemicals concurrently with the release of the final scope documents for these chemicals. Companies on the list have 60 days to notify the EPA of the formation of consortia. The EPA plans to begin invoicing for the fees after those 60 days have passed. Due to the public health emergency, and resulting cash flow issues for many businesses, the EPA is exploring payment options.

DISCUSSION

Now that the list is out, affected businesses are focusing in earnest on what this initiative means. The EPA has published a very public list of businesses presumptively responsible for a portion of the $1,350,000 fee. So, what are the takeaways?

First, it is important to see if your company is on the list. If many manufacturers of the chemical are identified and listed, the financial hit is less consequential. If not, the fee is significant and is due in full early in the process. The fee, of course, is just that, an administrative assessment paid to the EPA. Depending upon the EPA's determination of what chemical use patterns pose the greatest risk, stakeholders must spend much more on disabusing the EPA of any misinformation on which any such finding is based, and otherwise participating actively in the risk evaluation process. The process is at least three-years long, and manufacturers and brand managers must address issues along the way. The success of any advocacy effort can save product lines; however, failure risks product lines becoming commercial casualties of the process. The court of public opinion has a way of compromising products even without the benefit of a final risk evaluation. In 2018, for example, Lowe's voluntarily removed 19 products containing methylene chloride before the EPA's prohibition of methylene chloride in consumer paint strippers. This cautionary tale is unlikely to be an isolated incident.

Second, the fees rule experience demonstrates TSCA's wide reach. For decades, TSCA was thought of narrowly as an arcane "chemical manufacturer" law with little relevance to the broader value chain. Not anymore. The EPA's broad grant of authority under TSCA to regulate chemical manufacturers, importers and processors, coupled with its authority to include entities that "manufacture" targeted chemicals as byproducts or impurities and importers of chemicals in finished articles, includes thousands of unsuspecting commercial businesses.

Stakeholders with even tangential chemical interests are wise to know the law, appreciate its broad implications, and anticipate the law's application to commercial operations. Failure to do less could prove costly. ●

$1.35 million is not a trivial amount.

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Lynn is managing director of Bergeson & Campbell, P.C., a Washington, D.C.-based law firm that concentrates on chemical industry issues. The views expressed herein are solely those of the author. This column is not intended to provide, nor should be construed as, legal advice.

Tap True ROI Of Digital Transformation

CHAD BRIGGS
vice president and
general manager of
Honeywell Thermal
Solutions

> As the industry continues to evolve, Honeywell is at the forefront in technology.

MOST COMPANIES are looking for meaningful ways to embark on a digital transformation. According to Chad Briggs, vice president and general manager of Honeywell Thermal Solutions, picking potential problems like regulatory, safety or efficiency and applying a solution that not only connects the user and collects the data, but also takes that data and helps the user visualize it, analyze it and provide a way to act upon it is where the true ROI is found.

Chemical Processing spoke with Briggs about how to reap the benefits of digital transformation. "I think there's a lot of data that is collected today. Very little of that data actually goes into a system where it can predict or prevent failure," he says.

Here is the rest of that conversation, including insight into hydrogen combustion and its sustainability impact:

Q: How can plants take fuller advantage of thermal process data they already are gathering?

A: The whole thermal process industry is taking steps toward significantly improving data availability. While there is data available to a control system or a historian, that's simply data gathering. That doesn't meet the need of digital transformation, which would use that same data to help companies transform their business, competencies and revenue models.

There are obviously a lot of ways you can connect data. Honeywell harnesses the power of a cybersecure connectivity platform, advanced data analytics, and machine learning technologies to process that pool of data. Companies can use the connected devices and the integrated systems they have and capture real-time, process and analytics-based information to overcome several challenges prevalent across the thermal process industry. Top of mind for everyone is the need for enhanced safety and regulatory compliance, as well as the lack of visibility to critical thermal process information and the decreasing number of combustion specialists across the industry.

Q: What sorts of insights on process efficiency and optimizing operations can this approach lead to?

A: With a connected plant solution, customers are able to bring together historical and real-time process data from different systems in one place; and connect it to the cloud. The data can then be easily accessed, retrieved and analyzed by the stakeholders.

Using this approach, thermal process plants can reduce the complexity of their assets and realize efficiency and operational benefits by leveraging multiple insights such as:

- Critical safety, reliability and performance related parameters, alarms and trends — revealing insights on thermal processes, which can be visualized by users on respective dashboards accessible on mobile devices and desktop computers, to quickly act before the breakdown happens;
- Benchmarking analysis between regions, plants and individual assets enabling quick identification of the bad actors; e.g., an air heating system in plant A is running at 20% lower efficiency than exactly the same systems in plant B and C);
- Capability to drill down to these bad actors and see the relevant performance KPIs and real time analytics driven recommendations to improve the asset performance;
- Fault-modelling analysis to provide insights on the repeatability of such anomalies.

Honeywell's response to the demand for better remote monitoring is Thermal IQ™, a platform designed for organizations with limited tracking and limited remote access capabilities.

With Thermal IQ data, users can closely monitor thermal processes without being on site, get real-time alerts when key parameters stray outside normal limits, track historical data over time to identify when and why something happened and provide actionable recommendations.

Q: What role can it play for proactive maintenance?

A: Honeywell offers two different solutions based on the Thermal IQ platform: Thermal IQ Operate, an equipment- and process-level remote monitoring solution that provides process operators with real-time asset performance data on smart devices; and Thermal IQ Optimize, an enterprise-level, desktop-based remote monitoring solution that delivers real-time analytics and fault modelling with early event detection.

Thermal IQ is designed to improve remote monitoring of thermal processes.

By using Thermal IQ Operate users can stay ahead of faults or potential failures, that can lead to downtime, with early alerts. That visibility also enables technicians to arrive at the equipment with the correct tools to fix the problem, while reducing maintenance costs.

With advanced analytics and fault modelling offered by Thermal IQ Optimize, thermal process users can now see failure coming even before they happen and hence plan the maintenance activities proactively without affecting the plant production significantly thus saving thousands of dollars in downtime.

Q: How is the increasing emphasis on greener approaches to reduce emissions and improve sustainability affecting combustion processes?

A: There are two or three main drivers. There are obviously the environmental permits, but I think most manufacturers have moved beyond just compliance and are working on internally driven metrics to reduce their own consumption. Some of that is efficiency and financial driven but there's a lot of corporate sustainability and responsibility goals that we see coming into each of our customer bases.

With the deepest, broadest portfolio of products in the industry for reducing both NO_x and CO_2 emissions, Honeywell is the only supplier with an end-to-end solution incorporating burners, valves, sensors and controls.

Complementing its product portfolio, Honeywell Thermal Solutions applies deep application knowledge to fine-tune each solution to achieve optimum results for specific use cases, from high-temperature metal and glass applications to low-temperature automotive and food manufacturing. For example, when firing a burner on hydrogen, the flame characteristics will be different compared to the same burner firing natural gas. The difference in flammability, speed of the combustion reaction, flame luminosity, flame length and changes in the flue gas composition will all have an effect on the process. This will have an impact on how the product is heated and how the combustion chamber or oven should be constructed.

Q: What is happening as far as burners for hydrogen?

A: We have been producing hydrogen burners for quite some time, so the concept of a hydrogen burner is not at all new to Honeywell. I think what is new in the market are the ideas around using hydrogen as a fuel in place of natural gas. And certainly, we have the expertise and capability to design those types of burners. Hydrogen combusts differently than natural gas. It's a different fuel with many different criteria: combustion, speed, luminosity of flame, there's a lot of unique challenges to combusting hydrogen.

I think the market is moving in a direction, particularly in Europe, to have hydrogen mixed with natural gas. It's a bit like ethanol mixed with gasoline in several countries, including in the U.S. That would enable reduced emissions when hydrogen is produced in a green manner from renewables or other sources — that represents an opportunity to reduce CO_2 in that fuel stream. The challenges we see are for high temperature or high-heat-load applications where mixing in a new type of fuel with a very different caloric value will cause disruption if not managed well.

The best approach to thoroughly understand how a burner operates with hydrogen-based fuels is to actually fire the burner and measure the results. The extensive testing capabilities of its R&D labs allow Honeywell Thermal Solutions to verify the performance of its burners and controls to ensure they fire these hydrogen fuels safely and reliably.

Honeywell has invested significantly in lab-based simulations and studies on how to best adapt burners for hydrogen firing. These learnings — together with extensive customer application testing and best practices gleaned from deep experience with thermal processes — have been channeled into its portfolio of hydrogen solutions.

Honeywell Thermal Solutions offers both hydrogen-ready and hydrogen-capable burners designed for a wide range of applications in markets like automotive, chemicals, construction, environmental, food, glass, metals, ceramics, gypsum, paper, power generation, printing and textiles.

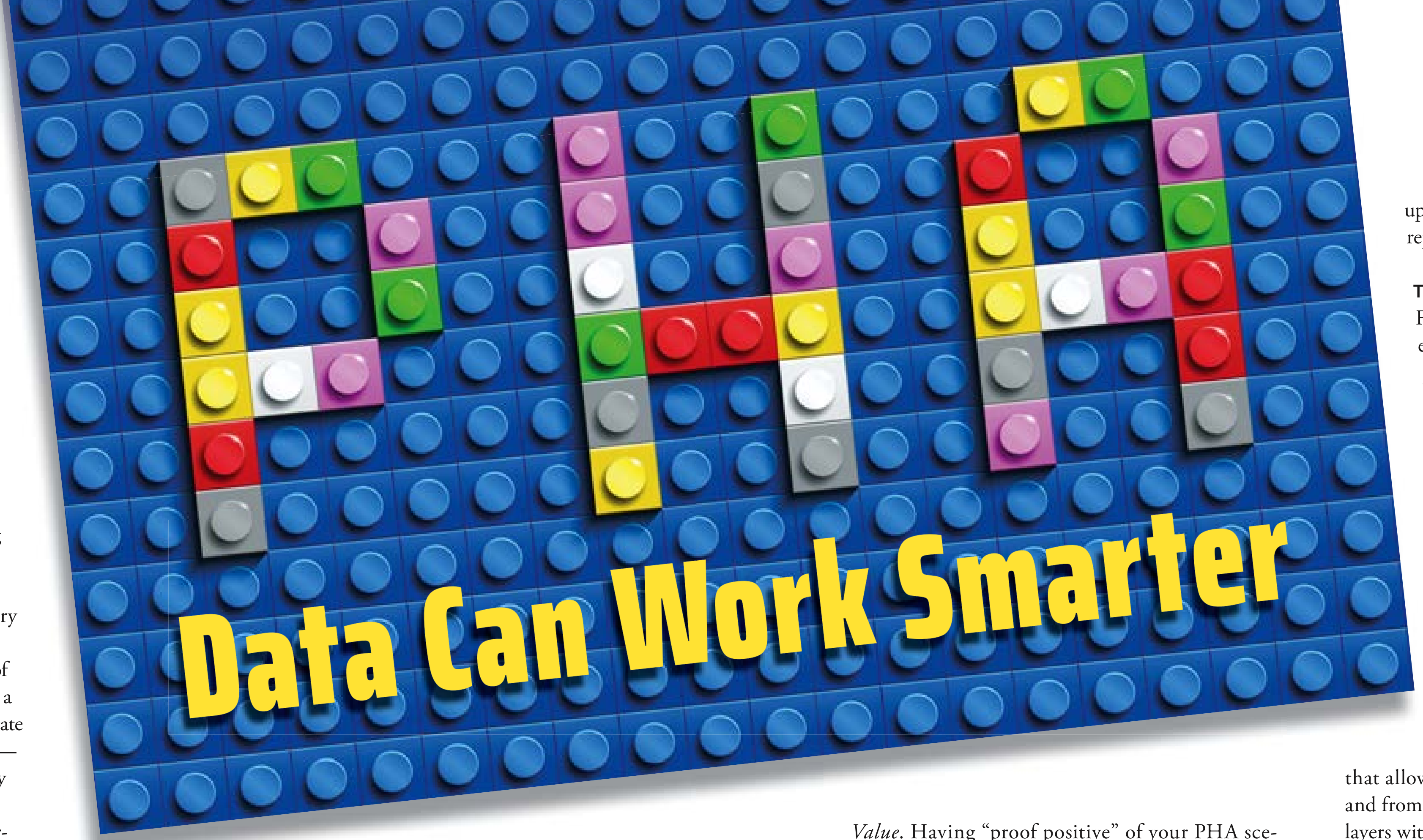
Q: What sort of reductions in carbon dioxide emissions can hydrogen combustion provide?

A: Green hydrogen as a fuel would reduce 100% of the CO_2 produced. I think the challenge with that is there's not a lot of ways to produce fully green hydrogen in quantities to replace natural gas. So, we see hydrogen being used in some applications, but I don't think it will be able to fully replace natural gas in most heating applications. Therefore, the blending solution that I talked about would allow higher natural gas networks to take only a part of hydrogen blended in with the natural gas. For example, if we took a blend of 20% hydrogen and 80% natural gas, and we took a continuously fired process around 10 million Btu/h, or about 3,200 kW, we'd get a reduction of about 1.1 tons per day of CO_2, which would be equivalent to 400 less tons of CO_2 per year (visit **bit.ly/H2graphic** to calculate your own CO_2 saving with hydrogen).

Q: What differentiates Honeywell from other solutions?

A: We have a comprehensive offer. We have everything from the combustion equipment to the sensors. We have the ability to securely connect that to the cloud to do analytics on the data that is provided. I think whatever the application would be, we can provide a solution. As the industry continues to evolve, for sustainability reasons or for digital revolution reasons, Honeywell is at the forefront of all of those things in technology.

For more information, visit: ThermalSolutions.Honeywell.com.



Data Can Work Smarter

More effectively piece together information you already have

By Patrick Nonhof, Provenance Consulting, and Heather Feimster, Trinity Consultants

THE TERM "big data" conjures up thoughts of countless sensor data points, real-time manufacturing processes or predictive modeling. Process safety isn't usually in the mix — but it should be.

Most facilities take process hazard analyses (PHAs) very seriously, devoting considerable resources and staffing to produce a comprehensive and valuable report. The PHA of a single unit can generate upwards of 2,000 scenarios and a company usually has multiple units at a site and may operate several plants; so, the amount of data available is massive — and multiplied by the requirement to conduct PHAs every five years. The result is an enormous "data lake."

This resource certainly fits the definition and purpose of big data. However, getting full value from this information long term requires addressing some of the current limitations of the data as well as a paradigm shift in use of the data.

Let's consider the example PHA scenario on a simple distillation column, a debutanizer, given in Figure 1. Regardless of the technology used, the final PHA data usually are organized similar to the way shown. The two most informative fields — cause and consequence — generally are free text fields with no set structure. So, too, is the listing of safeguards. However, other key fields — severity, frequency and unmitigated risk ranking — may follow a pretty structured format.

Now, let's define "big data." Generally, it requires volume, variety and velocity. You must have ample amounts of information in diverse formats and generated at a rapid pace. Using a tool to capture these data in a usable way helps you ensure the veracity of what the information indicates so you can drive value.

UNDERSTANDING PHA AS BIG DATA

Using that protocol, let's examine PHA data.

Volume. On average, a PHA of a unit at a large-scale petrochemical plant will have anywhere from 1,500–2,000 scenarios. If that facility contains 30 units, it could have an estimated 45,000 PHA scenarios. Now, considering that PHAs are completed every five years, a plant with 30 years of PSM records could amass 270,000 scenarios.

Big data also involves individual data fields. Each scenario could have 15 data fields. Multiply your scenarios by the fields of data and a single petrochemical facility conservatively could have over 4 million fields of PHA data in its archives.

Variety. PHA data include scenario information (structured and unstructured), spreadsheets and PDFs as well as piping-and-instrumentation diagrams and other drawings. These various types of data also are captured in different ways.

Any free texts fields allow for variety of inputs. This lack of structure can prove to be a problem. We'll address this issue and potential solutions later.

Velocity. This is one of the key components of big data. The capturing of pressure, temperature, flow and other process measurements on a periodic basis — as frequently as every few seconds — leads to rapid data accumulation.

The velocity of PHA information may not rival real-time sensor data, for example, but you could compare the high-velocity sensor data collected before/during/after a consequence with what the PHA team predicted.

Veracity. Making data connections enables you to check the validity of your PHA evaluation. Did the cause/consequence in the scenario end up the way predicted? Did safeguards operate as intended? Does a gap exist in risk mitigation?

Value. Having "proof positive" of your PHA scenarios allows you to do additional evaluations with confidence. In particular, consider conducting data comparisons focused on capturing and leveraging the knowledge in all PHAs for high-level decision-making.

However, including PHA information in a big data model requires addressing several limitations.

For the past 25 to 30 years, the industry has done an excellent job at facilitating PHAs. This generally results in up-to-date process safety information and a massive report that's put on a shelf, either real or digital.

THE NEED FOR A PARADIGM SHIFT

Facilities most commonly rely on two PHA deliverables — the recommendations list with action plans and independent protection layer (IPL) or safeguard lists — to mitigate the risks identified.

As currently designed, a PHA is a snapshot. While that's a start, it's only a single point in time with few benefits.

Other than the list of safeguards or IPLs and recommendations, the PHA sits on a shelf. It represents an immense amount of time, effort and energy and the thinking of some of your brightest and most capable people but it's barely used.

To fully leverage that information, we need a paradigm shift — we must begin thinking about PHAs as less of a snapshot and more like a gigapixel satellite image that allows you to zoom in and out at different altitudes and from a variety of vantage points. It consists of multiple layers with depth of detail.

This macro-level perspective would enable us to compare and crosscheck different PHA results both across similar processes and facilities. However, two notable barriers now prevent us from realizing this potential: lack of accessibility and lack of structure.

Lack of accessibility. Today's PHA files aren't easily searchable. Because there isn't any structure to the data in the files, even electronic ones, you can't search effectively.

EXAMPLE SCENARIO

Cause				Consequence	Unmitigated Risk Assessment			Safeguards	Mitigated Risk Assessment		
Unit	Node	Deviation	Cause	Consequence	Severity	Frequency	Unmitigated Risk (UMR)	Safeguards	Severity	Frequency	Unmitigated Risk (UMR)
HF Alkylation Unit	Debutanizer Tower	No flow	Overhead liquid control valve FC-109 loses instrument air and fails closed	Increase column pressure to vapor pressure of overhead fluid at reboiler steam temperature i. Overpressure: greater than 3 x MAWP ii. Vessel failure	Cat.	Occasional	5	1. Shutdown PSD-301 2. RV-305 set at 175 psig	Cat.	Very improbable	2

Figure 1. Risks from lack of flow in distillation column require mitigating actions.

If you're looking for specific failure, doing a free text search on your PHA may not return the results you hoped — you can't "google" within your PHAs. You may not be able to search a single word because you may not be able to guarantee how the information was captured. For instance, a team may have used "debutanizer" instead of "vessel 100," hampering getting relevant or comprehensive results.

Additionally, those data usually are stored in standalone software, and most common systems restrict access. They don't allow just anyone to look at the information as a matter of data integrity and avoiding corruption.

Furthermore, a company may not use the same software at all its sites or may have changed software between PHA seasons. Data structures may differ.

Digging through the data — let alone aggregating and analyzing all this information — usually is a daunting task, to say the least.

Lack of structure. Today, most data reside in free text fields without structure and categorization. You can't even run simple filters. We must change from embedding important information in free text fields to breaking it out into structured data categories. The difference is building a data structure where you capture details like process fluids, equipment involved and safeguard type.

Lack of accessibility and structure results in a lack of consistency. Ask yourself, "How consistent are your PHAs for the same process? For the same technology and equipment? Do they have similar causes, consequences or risk levels?"

Without an intentional structure, I would argue you can't easily answer these questions.

Consider this: a company has two hydrofluoric acid alkylation units — one in the Middle East and one in the United States. How do the PHA evaluations for the units compare? I can confidently predict that they didn't evaluate the same scenarios, let alone come to the same conclusions. As engineers we'd like to think teams will follow the same course of logic but it isn't always obvious how a team arrives at its scenario consequence.

This issues also arises when examining the same technology at similar facilities. A large petrochemical owner/operator may use a single technology to produce a specific type of plastic at ten comparable facilities throughout the world. What does the risk look like for those ten plants? Can you even compare them?

Most companies currently can't do that type of analysis — at least not cost-effectively or quickly. However, if we change the way we structure PHA data, we open up some fascinating possibilities.

Imagine being able to query: "Every time we overpressure a distillation column across our company, what's the most frequently employed safeguard? Is it a relief device, an operator alarm or the basic process controls?" No one option likely suits all operations but the types of safeguards shouldn't be all over the board either.

These are the types of questions you can start to answer at a corporate level to identify and address inconsistencies in your process safety departments.

THE START OF A SOLUTION

To remove the barriers to big data, we must address the structure problems first. Let's examine that distillation column example.

Figure 2 contains all the information captured previously. It also shows suggested fields (shown in blue) to add for better structure. Essentially, doing so breaks out some of the information currently inside each free-text field to capture it in a more analysis-friendly way.

Let's now look at the specific data fields to add under cause, consequence and safeguards.

Cause. Specify technology, a cause category, the process fluid and the location.

Consequence. Include a simplified consequence and the equipment involved. I suggest pulling these category fields from a master list built from the facility information. This ensures the data are linked to one master data set and will foster accurate and comprehensive filtering and analysis.

Safeguards. Stipulate safeguard type and priority level for the given scenario. Ideally, the "safeguard type" should come from a preset list specific to the company or facility. This would avoid the confusion that can arise from different descriptions of a safeguard, e.g., "RV-305," "relief device 305"

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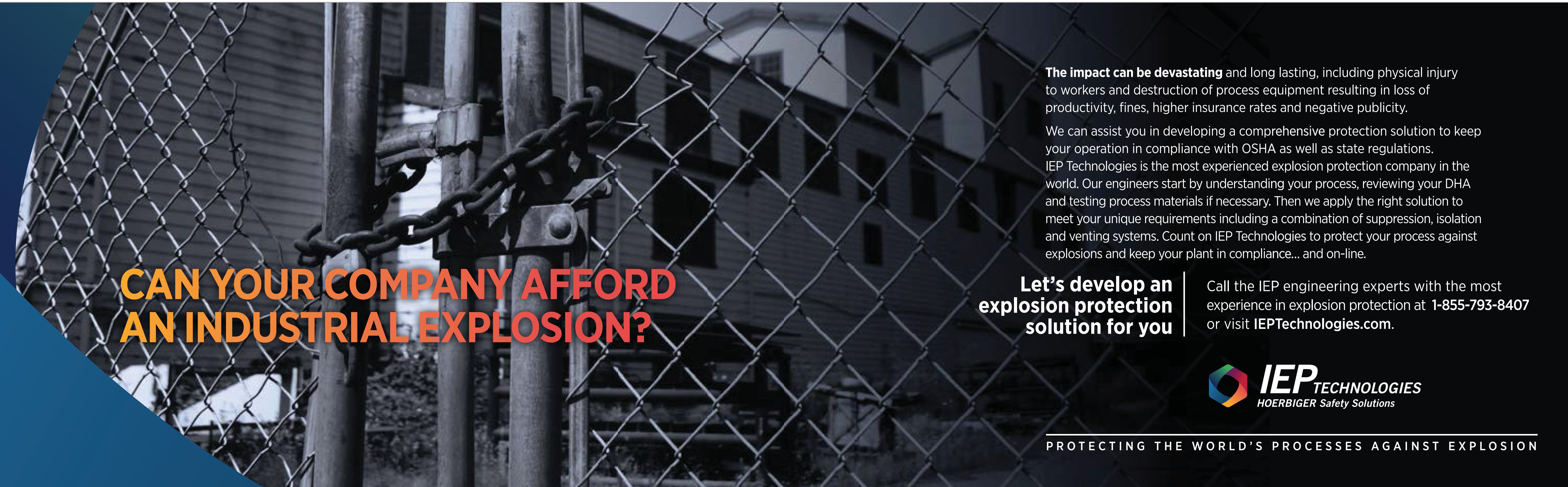


IMPROVED STRUCTURE

A

Unit	HF Alkylation Unit
Node	Debutanizer Tower
Deviation	No Flow
Cause	Overhead liquid control valve FC-109 loses instrument air and fails closed
Technology	HF Alkylation
Cause Category	Blocked outlet
Process Fluid	Butane
Location	Overhead of debutanizer

B

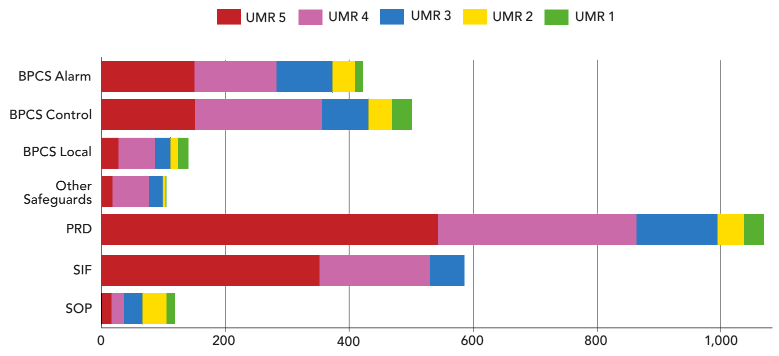
Consequence	Increase column pressure to vapor pressure of overhead fluid at reboiler steam temperature i. Overpressure: greater than 3 x MAWP ii. Vessel failure
Simplified Consequence	Tower overpressure
Equipment	Debutanizer V-300

C

Safeguard 1: Description	1. Shutdown PSD-301
Safeguard 1: Type	Safety Instrumented System
Safeguard 1: Priority	1
Safeguard 2: Description	RV-305 set at 175 psig
Safeguard 2: Type	Pressure relief device
Safeguard 2: Priority	2

Figure 2. Adding fields (shown above in blue) to cause (A), consequence (B), and safeguards (C) provides a better structure.

SAFEGUARDS IMPLEMENTED



Most common/frequently used safeguards for unmitigated risk levels 1–5 for entire facility:

- Basic Process Control System (BPCS) Alarms, Controls and Local
- Pressure Relief Device (PRD)
- Safety Instrumented Function (SIF)
- Standard Operating Procedure (SOP)
- Other Safeguards

Figure 3. Comparing safeguards by unmitigated risk level can lead to significant insights.

or “relief device on the debutanizer.” Such inconsistencies, while acceptable for PHA documentation, hinder filtering and analyzing the data.

Once you improve the data structure, you can run novel analytics to identify interesting patterns within the information.

Let’s consider a company that operates identical alkylation units at several sites and wants to compare evaluations done for a blocked outlet. The process fluid is butane on the overhead of the debutanizer.

Filtering by those parameters, the company quickly could identify matching units in the Middle East and Texas: the same technology, cost category and process fluid as well as similar equipment.

For this client, we performed a consequence analysis and found a marked variation in the consequence evaluation: the team at Plant 1 predicted a catastrophic vessel failure while the team at Plant 2 expected a gasket failure. By seeing this information side-by-side, the client could identify the discrepancy in evaluation techniques between the two PHA teams that generated vastly different severity levels.

Interestingly enough, the American Institute of Chemical Engineers’ book “Guidelines for Initiating Events and Independent Protection Layers in Layer of Protection Analysis,” https://bit.ly/35AeFvh, specifies the appropriate evaluation method (for this scenario, see Appendix E, p. 393, of the electronic version). Obviously, one team didn’t consult the guidelines.

The company didn’t realize the plants used different evaluation methodologies until it could compare similar scenarios. Without intentional data structure, this exercise invariably would have required incredible amounts of work.

Beyond consequence, we could compare how different teams mitigate similar risks. If one team includes a relief system expert, it might opt for a relief

device. In contrast, the other team, if it has safety instrumented system (SIS) specialist, might specify an SIS. Now, quite honestly, we don't lose much sleep about the choice between a relief device and an SIS from a risk-reduction perspective.

However, what if one team instead mitigated the risk for the same hazard scenario with alarms or procedures? That type of discrepancy should at least trigger a second look, not just to verify its adequacy as a safeguard but also for the cost differential of implementing and maintaining those very different types of safeguards.

Being able to compare these scenarios allows you to identify points of differentiation.

GAINING IMPORTANT INSIGHTS

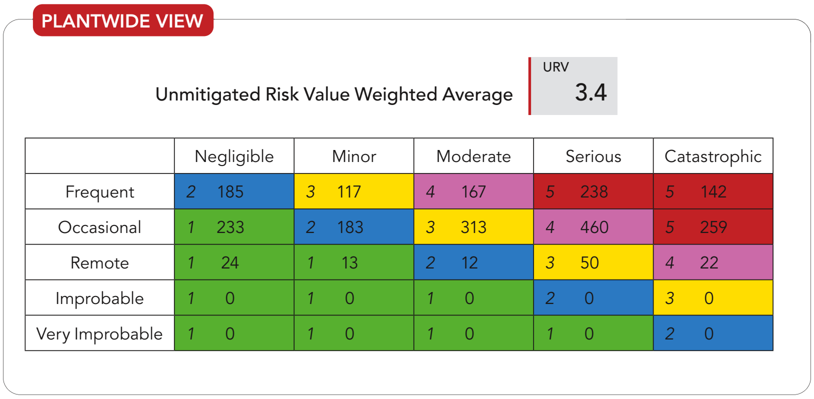
Looking at the data comprehensively enables you to start to compare the unmitigated and mitigated risk at different levels or between similar scenarios.

Let's examine high-level analysis of all scenarios that result in losing feed to a specific type of column. When we filtered the consequence for "loss of feed," we efficiently observed major differences in the unmitigated and mitigated risk rankings. While this doesn't explain "why" you have these discrepancies, it helps you focus on where to look further.

These data also could show patterns in how you mitigate your risk. Figure 3 groups all scenario unmitigated risks by safeguard type (one of the categories we added to our data). Red indicates any scenario or group of scenarios with the highest unmitigated risk (level five). We clearly see that pressure relief devices are most frequently used to mitigate these riskiest scenarios.

When you start to analyze all these data together, you've got to remember that snapshot (micro) versus satellite picture (macro).

Consider an entire facility: "What does the Texas plant rely on most often for an unmitigated risk of five? Does it use relief devices? What does the Middle East plant use?"



PLANTWIDE VIEW

Unmitigated Risk Value Weighted Average

URV
3.4

	Negligible	Minor	Moderate	Serious	Catastrophic
Frequent	*2* 185	*3* 117	*4* 167	*5* 238	*5* 142
Occasional	*1* 233	*2* 183	*3* 313	*4* 460	*5* 259
Remote	*1* 24	*1* 13	*2* 12	*3* 50	*4* 22
Improbable	*1* 0	*1* 0	*1* 0	*2* 0	*3* 0
Very Improbable	*1* 0	*1* 0	*1* 0	*1* 0	*2* 0

Figure 4. Looking at the quantity of scenarios and their risks gives an indication of the overall situation at the site.

By zooming in and out of your PHA data — because the data now are structured in a way that allows you to do that — the analytics begin to get interesting.

If we just look at that example Texas plant (Figure 4), you can view the quantity of scenarios that started in each of the different areas of our risk matrix for the entire facility (not just a single PHA). There are 142 highest risk scenarios. You could average all these to come up with the unmitigated risk value at the facility

level. In this example, the weighted average of the scenarios gives us an unmitigated risk value of 3.4.

You could do the same by looking at the mitigated risk value, which reflects the risk with your safeguards applied. The difference between the two essentially is your risk reduction.

Now that you can view your data in a macro-level way, you can look at one specific plant and ask, "What's our average on unmitigated risk?" Here, it's 3.4. "What is the mitigated risk value?" It's 1.9 for the site. In this case, we are reducing our risk on average on most scenarios by 1.5 levels.

Now, let's take things one step further and examine those average risk metrics a few different ways.

When we look at the aggregate data for the entire company, we have a 2.7 unmitigated risk and a 1.7 mitigated risk (Figure 5). So, the corporation has achieved a risk reduction value of 1.0.

Let's zoom in on two separate facilities. Plant 1 has a risk reduction value of 0.6 while Plant 2 has one of 1.5. If these are for the same technologies with similar throughput, does that sound right? (Hint: It probably isn't right.)

COMPANY-WIDE RISK PROFILE

	URV		MRV		RRV
Overall - Corporate Risk Profile	2.7	-	1.7	=	1.0
Plant 1 Unit Risk Profile	2.0	-	1.4	=	0.6
Plant 2 Unit Risk Profile	3.4	-	1.9	=	1.5

URV = Unmitigated Risk Value, MRV = Mitigated Risk Value, RRV = Risk Reduction Value

Questions to ask:
- Is Plant 1's URV too low?
- Why is Plant 2's unmitigated risk so high?
- Is Plant 2 taking too much credit for safeguards?
- Does Plant 2 have more-robust safeguards?

Figure 5. Comparing the overall corporate situation to that of individual plants can spur some important questions.

So, you should pose some questions. Start with an "I wonder…" statement: "I wonder if I have any alarms for more than one scenario. How many times do I use this specific alarm? Do we mitigate the highest risk scenarios with alarms? Do we want to mitigate them with alarms?"

You can ask those questions today — but, unless you have better data structures, you can't answer them.

Another starting point is to key in on critical scenarios, most often high-risk ones. Then, you can ask: "Based on the risk levels of these given scenarios, are we allocating our resources appropriately? Should we budget the same resources (time, effort, energy and capital) to alarms as we do relief system design? What should our operator training focus on? Is our mechanical integrity program and inspection schedule prioritized to our more critical safeguards?"

Unless you can pull, filter and analyze your data comprehensively, you may be misallocating or wasting money.

REALIZING THE POTENTIAL OF PHA DATA

In the end, we as an industry need a paradigm shift to embrace big data concepts within PHA data. We no longer can view PHA data as that "snapshot in time." Instead, we must consider how to organize and structure PHA data better so we can realize the potential of those macro-level analyses.

We must start comparing data between similar processes, sites and failures so that we can discover what these data tell us about how we are mitigating risk in our facilities.

Big data tools can help move us forward but they can't think for us. We must begin to think differently about the value our PHA data can bring to our risk mitigation strategies. ●

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Carbon Dioxide Developments Fizz Up

Efforts to productively use the gas are advancing on various fronts

By Seán Ottewell, Editor at Large

THE QUEST to turn carbon dioxide into a valuable raw material has spurred significant efforts for some time. Attention certainly isn't flagging as ongoing activities of some chemical companies and research groups attest. For instance, Evonik, Clariant and Neste all are investing in technologies with that aim. At the same time, research breakthroughs are giving glimpses into how the next generation of catalysts to convert the greenhouse gas might look and work.

Evonik, Essen, Germany, has joined forces with specialty chemicals company Beiersdorf, Hamburg, Germany, in a joint research project to use CO_2 as a raw material in the manufacture of personal care products including skin moisturizers and sun creams.

The aim is to apply Evonik's artificial photosynthesis technology — electricity from solar energy together with bacteria — to produce raw materials for such products and then test them in different applications (Figure 1).

The project has attracted €1 million ($1.18 million) in funding from Germany's Federal Ministry of Education and Research (BMBF).

"This work is taking place on a laboratory scale and in parallel with the Rheticus II project being carried out jointly by Evonik and Siemens Energy. Rheticus II is focused on industrial scale-up of artificial photosynthesis," says Thomas Haas, who is responsible for the project within Evonik's strategic research department Creavis.

LABORATORY BIOREACTOR

Figure 1. Research project focuses on using artificial photosynthesis technology to make raw materials for personal care products. *Source: Evonik.*

With €3.5 million ($4.13 million) in funding from the BMBF, Evonik and Siemens Energy are constructing a test facility in Marl, Germany, that comprises an electrolyzer and a bioreactor.

"The official starting date for joint test operation of the electrolyzer and bioreactor is end-September 2020. The composition of the synthetic gas and the interaction of electrolysis and fermentation will be tested and optimized in the coming weeks," he adds.

For the moment, the focus is on the design/dimensioning of the interfaces between the electrolyzer and bioreactor.

"As soon as these have been optimized, it will be possible to ensure stable and reliable operation of the individual modules and, ultimately, the entire platform. After that, the impact of load changes caused by fluctuations in power supply based on renewable energy during operation will be investigated," notes Haas.

The first target molecules are butanol and hexanol; work continues on fine-tuning process conditions to investigate fully their significant effect on production of the alcohols.

"That said, the Rheticus project is about developing a platform facility. In other words, it is conceivable that different organisms could be used in the future for other target products. The selection of the organisms and the process conditions are the main variables for the different target products this platform could be used for. The key features of this technology are flexibility and modularity," he stresses.

Rheticus II finishes towards the end of 2021 and, if successful, Haas believes the first commercial facilities could be designed and built to manufacture specialty chemicals from CO_2 and electricity a few years after that.

COMPACT TECHNOLOGY

In July, Clariant, Muttenz, Switzerland, joined forces with Ineratec, Karlsruhe, Germany, to develop and commercialize novel technologies to produce renewable fuels and chemicals.

Ineratec's technology is based on modular reactors with micro-structured cores that provide a large surface area for heat and mass transfer. Highly exothermic reactions, such as methanol synthesis and CO_2 hydrogenation, achieve high conversions per reactor pass in compact container-sized plants, claims the company.

Clariant brings three of its specialist catalysts to the table: HyProGen R-70, which produces renewable syngas via reverse water-gas-shift — an essential step in the conversion of green hydrogen and CO_2 to green fuels; its signature methanol catalyst MegaMax; and Meth 134, which supports the efficient hydrogenation of CO_2 to methane.

"One focus is on syngas production from CO_2 and hydrogen via reverse water-gas-shift. A second is the production of renewable methanol directly from CO_2 and green hydrogen. Methanol can serve as fuel additive or as raw material for other chemical products. Clariant's methanation catalyst has been proven as catalyst of choice for Ineratec methanation technology," says Ineratec cofounder and managing director Tim Boeltken.

Strategic partnerships between catalyst and reactor specialists are essential for the technology to develop, he believes. "A perfect fit between the highly active and selective catalysts and the innovative micro-structured reactor technology is crucial for efficient and robust power-to-X systems to enable affordable renewable fuels and chemicals for everyone."

For its part, Clariant will track the performance and operational lifetime of its catalysts in Ineratec's modular reactors.

"As part of our collaboration, Clariant provides access to existing as well as next-generation materials and catalysts from Clariant's power-to-X catalyst portfolio as they are available and provides technical support to Ineratec regarding specific operational challenges," notes Thomas Cotter, business development manager, Clariant Catalysts.

"Generally speaking, the modular reactor concept provides greater heat control and homogeneity of process parameters to the catalysts, which enable them to perform optimally under given conditions. Where we can identify clear mutual opportunities to improve the combination of reactor and catalyst, we consider entering joint catalyst development in order to address larger markets," he explains.

Currently, the Ineratec system's CO_2 recycling capacity ranges from 1,000–10,000 mt/y, with the higher capacities reached by linking several plant modules.

"We are continuously improving and adapting the reactor technology. The current focus is the further scale-up of the reactor modules while maintaining the already achieved reactor properties," adds Boeltken.

ELECTROLYZER TEST SITE

Figure 2. Trials of high-temperature unit are taking place at refinery in Porvoo, Finland. *Source: Neste.*

HIGH-TEMPERATURE ELECTROLYSIS

Meanwhile, Neste, Espoo, Finland, has acquired a minority stake in high-temperature electrolysis technology specialist Sunfire, Dresden, Germany, whose patented technology allows production of renewable hydrogen as well as direct conversion of water and CO_2 into raw materials for petrochemicals.

Sunfire's key technology is its PowerCore solid-oxide cell stack that can convert both electrical energy into chemical energy, and liquid and gaseous fuels based on hydrocarbons, such as natural gas and liquefied petroleum gas, into electricity and heat.

"As part of Neste's strategy, we are developing business platforms for new growth. Renewable hydrogen and power-to-X is one of these platforms. Power-to-X technologies enable the utilization of CO_2 as raw material for synthetic fuels, such as aviation fuel, and chemicals. We see Sunfire's high-temperature electrolysis technology as a promising technology for power-to-X solutions and so decided to invest in the company," says Lars Peter Lindfors, senior vice president, innovation at Neste.

Both companies now are working together to demonstrate the production of renewable hydrogen at Neste's Porvoo, Finland, refinery using Sunfire's high-temperature electrolyzer (Figure 2).

In a separate development, SunFire has joined Norsk e-Fuel, a new consortium headquartered in Oslo, Norway, focused on industrializing power-to-liquid technology in Norway for the European market.

Its state-of-the-art project at Herøya, Norway, will allow conversion of the country's extensive renewable electricity resources into renewable fuels.

The first plant, with a production capacity of 10 million l/y of renewable fuel, should begin operation in 2023. The plan is to boost capacity ten-fold to 100 million l/y before 2026. This scaled-up plant then will serve as a blueprint for a nationwide rollout of the technology.

Meanwhile, in March, Finland's Technical Research Center (VTT), Espoo, and business partners launched the €5-million ($5.9-million) bio-energy--based CO_2 for polyols and fuels (BECCU) project. It will produce olefins through reverse water-gas-shift and Fischer-Tropsch (FT) reaction steps. The olefins will undergo conversion to epoxides through oxidation reactions by peroxides, with the epoxides then polymerized together with CO_2 to obtain polyols. Hydrogen for the process will come via renewable electricity or from industrial byproduct sources. The team will test each stage of the process using VTT's pilot and laboratory equipment and assess the techno-economic requirements for the entire lifecycle. It also will compare the concept with other power-to-X processes that produce chemicals and fuels from CO_2 and hydrogen.

"Many tasks have progressed as planned and capture tests for CO_2 begin in September. Also, the only part now needed for the FT-synthesis lab device is the recirculation compressor. The technical economic assessment and lifecycle analysis work is progressing well," notes VTT senior scientist Janne Kärki.

"If we can show in small-scale that the concept is feasible, the aim then is, of course, to scale it up," he adds.

Part of the project focuses on developing a multipurpose synthesis unit (MOBSU) for CO or CO_2 upgrading to energy carriers, fuels and chemicals that could be transported to sites where CO_2 emissions and energy are available. The capacity of the first MOBSU is expected to be 3–5 l/d for liquid hydrocarbons and 6–9 l/d for solids such as waxes.

"Current funding for BECCU runs for two years and we will be looking for new opportunities along the way for continuation, hopefully more on the demonstration side with interested companies," concludes Kärki.

COMING CATALYSTS

A research collaboration between the U.S. Department of Energy's Argonne National Laboratory, Lemont, Ill., and Northern Illinois University, DeKalb, Ill., has discovered a new electrocatalyst that converts CO_2 and water into ethanol.

The catalyst, which consists of atomically dispersed copper on a carbon powder support, breaks down CO_2 and water molecules and selectively reassembles them into ethanol under an external electric field.

"Tested under ambient temperature and pressure, the catalyst maintained 90% selectivity during the 16-h

durability test and showed no significant change in current density," notes Di-Jia Liu, chemist and principal investigator in the catalysis and energy conversion group at Argonne.

"We found that the metal dispersion in the catalyst is very important in controlling the selectivity. When the copper cluster size becomes bigger, the selectivity toward conversion to ethanol drops significantly. This probably explains why other studies did not report >90% selectivity," he adds.

The study, reported in a recent issue of *Nature Energy*, used a half cell and solely focused on the electrochemical reduction of CO_2 to ethanol at the cathode.

"To make a large-scale industrial production, the catalyst needs to be integrated into an electrolyzer. Challenges here include how to produce high current density at low voltage through extended period of operation — so more engineering research on electrode design — together with mass-charge transport, product separation, etc., [is needed]," explains Liu.

The work already has attracted industrial interest, although details remain guarded.

Meanwhile, researchers at Heriot-Watt University, Edinburgh, Scotland, and Murdoch University, Murdoch, Australia, have found a new way to fabricate a complex nanostructured photocatalyst for solar fuels.

The resulting raspberry-like microspheres have a core-shell nanostructure that can capture CO_2 and convert it into methane.

PHOTOCATALYSTS SHEET

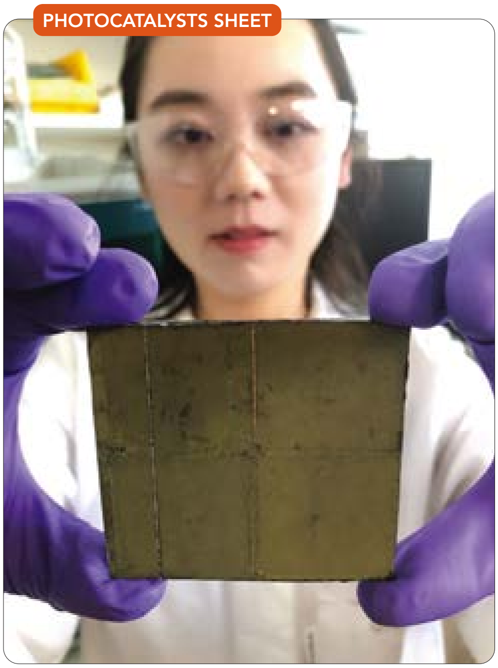

Figure 3. Test sheet is 20 cm^2 but researchers say scale-up is easy. *Source: Sarah Collins, Cambridge University.*

"The discovery of this project has demonstrated the importance of the photocatalytic active site on the photocatalyst," notes Jeannie Z.Y. Tan, a research associate in the Research Centre for Carbon Solutions (RCCS) at Herriot-Watt.

The initial study, described in a recent issue of *Chemistry & Sustainability*, used a 2-cm^3 photoreactor that gave conversion rates of 0.2 µmol/g of catalyst in one hour.

"The aim of the research is practical application and commercialization. To achieve this, both the cost and efficiency need to be considered," stresses Tan.

"In the published paper, the observation on the formation of photocatalytic active site and the role it played provides important information for future investigation. We will continue to explore this characteristic and extend the work to other photocatalysts," she adds.

Scale-up challenges include actual CO_2 uptake by the catalyst, product selectivity, product separation, deactivation of catalyst and reactor design, Tan says.

The RCCS also is pursuing other CO_2 utilization projects, including generation of cyclic carbonate or polycarbonates from epoxides, and photoelectrocatalysis of CO_2 to formic acid/formate.

Finally, researchers at the University of Cambridge, Cambridge, England, have developed a standalone device that uses a cobalt-based photocatalyst to convert sunlight, CO_2 and water into oxygen and formic acid, a storable fuel that either can be used directly or converted into hydrogen. The device doesn't require any additional components or electricity.

The photocatalysts are embedded in 20-cm^2 test sheets made of readily available semiconductor powders (Figure 3).

"We were surprised how well it worked in terms of its selectivity — it produced almost no byproducts," says Qian Wang of Cambridge's department of chemistry. "Sometimes things don't work as well as you expected, but this was a rare case where it actually worked better," she adds.

The researchers now are experimenting with a range of different catalysts to improve both stability and efficiency of the sheets. ●

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Adroitly Address Wastewater Challenges

Focus on six key compliance and water consumption issues

By Tim Hanna, PRAB

WASTEWATER MANAGEMENT is one of the most challenging operational issues facing chemical, petrochemical and other process plants today. Three primary factors contribute to this: wastewater compliance standards are growing increasingly strict, water consumption costs are rising, and a water shortage is looming in many areas.

The U.S. Environmental Protection Agency (EPA) assessed a staggering $69 million in pollution penalties in 2018 alone. Meanwhile, the cost of water is getting higher throughout the United States. In addition, more and more processors are treating effective and efficient processing of fluid byproducts as much as a corporate sustainability imperative as an environmental responsibility. This is a pressing issue for all chemical processing operations but smaller facilities may feel improved wastewater management is out of reach because they lack in-house compliance expertise or advanced wastewater-treatment technologies. What's more, understanding a facility's wastewater compliance obligations can be difficult because dense regulatory terminology permeate wastewater standards and mandates may depend upon the particular local publicly owned treatment works (POTW).

Chemical processors that take steps to better understand wastewater regulations and deploy advanced technologies to reduce recurring costs associated with wastewater compliance will position themselves for a stronger future. Here are six areas to focus on to take control of wastewater compliance.

1. CRITERIA BEHIND REGULATIONS

Wastewater discharge regulations include a fair amount of complexity. Lack of a high-level understanding of their framework and enforcement can pose a real barrier to effective and efficient compliance management.

Since 1972, the United States has pursued an increasingly stringent water control program. From the EPA's perspective, two kinds of wastewater discharges need to be regulated under the Clean Water Act (CWA): direct discharges into "waters of the United States" and indirect discharges that pass through a POTW for treatment prior to being released into the water supply.

Indirect discharges are regulated through a national pretreatment program that is a cooperative effort of federal, state and local environmental regulatory agencies. The objective of the program is to protect POTWs' infrastructure and reduce the amount of industrially generated pollutants discharged into the municipal sewer system and the environment.

The EPA has established three primary kinds of pretreatment standards:

- general and specific prohibited discharge standards for all industrial users;
- categorical pretreatment standards for particular industrial categories, including inorganic chemicals, ink formulating, oil and gas extraction, organic chemicals, plastics and synthetic fibers, paint formulating, pesticide chemicals, petroleum refining, pharmaceutical manufacturing, rubber manufacturing, and soap and detergent manufacturing; and
- local limits that are site-specific to ensure the POTW will not process waste that passes through to the water supply or interferes with operations.

Standards outside of the CWA also factor into wastewater compliance. Under the Resource Conservation and Recovery Act (RCRA), the EPA regulates the transport, treatment, storage and disposal of solid waste (including oils and sludges). While not a direct component of discharge regulations, U.S. Occupational Safety and Health Administration (OSHA) standards also impact a chemical processor's approach to wastewater management. Toxic and other hazardous gases can arise when certain inorganic pollutants in wastewater mix in the discharge collection system. OSHA sets exposure limits on toxic and air contaminants to protect worker health. POTWs will reduce this risk by controlling the maximum level of pollutants discharged.

Tip: When it comes to understanding the scope of wastewater requirements for a plant — and optimizing solutions to manage wastewater treatment — operators must appreciate that air discharge limits also play a role. For example, a wastewater treatment system requires proper ventilation. If a wet scrubber removes toxic substances from gases, the toxic substances will collect in the wastewater generated by the scrubber, creating an additional wastewater stream to manage.

2. THE PURPOSES OF PERMITTING

At a minimum, the EPA requires all significant industrial users (SIUs) to have permits. The EPA defines SIUs as:

- industrial users (IUs) that fall under categorical pretreatment standards due to their industry;
- IUs that discharge an average of 25,000 gal/d or more of process wastewater (excluding sanitary, noncontact cooling and boiler blowdown wastewater) to the POTW;
- IUs that contribute a process waste stream that makes up 5% or more of the average dry-weather hydraulic or organic capacity of the POTW;
- IUs that the control authority identifies as having a reasonable potential to adversely affect the POTW's operation; and
- IUs that have violated any pretreatment standard or requirement.

The permitting process usually is one of the clearest illustrations that the onus of proactive wastewater compliance falls on the process plant. Not only can local wastewater authorities define SIUs in their jurisdiction more stringently than the federal EPA but also EPA counsels local wastewater authorities to communicate pretreatment standards *during* the permitting process. In "The Industrial User Permitting Guidance Manual," https://bit.ly/3k8fpg1, the EPA states that, in its experience, "the permit is the most effective means of ensuring that industrial users are aware of all applicable pretreatment requirements."

Most permit applications require plants to disclose a

broad range of details about their wastewater management, such as a description of operations, wastewater generating and discharge activities, and the pollutants potentially in the wastewater and on-site. From the chemical processor's perspective, it would seem that the operator must supply all the details of its wastewater management practices prior to learning which discharge regulations will apply. This approach compromises the operator's ability to initiate pollution abatement practices that may streamline permit approvals and reduce surcharges levied by the POTW to cover costs for treating wastewater with excessive pollution levels.

Tip: For plants that add an in-house wastewater treatment system, the permit application will need to clearly state where the system will be located within the facility and the location of the sample port so regulators can perform testing. Some suppliers of wastewater treatment technology will work with plants and wastewater regulators to submit and obtain the necessary permits on behalf of the facility.

3. RECURRING COMPLIANCE COSTS

Wastewater compliance can incur many costs such as treatment expenses, labor investments and fines that can erode a chemical processor's bottom line.

Wastewater compliance lapses, for example, can lead to serious financial liability. A facility negligently or knowingly discharging to a POTW in violation of federal or local pretreatment standards can face significant penalties:

- negligence violations — initial penalty: 1 year and/or $2,500–$25,000/d, subsequent convictions: 2 years and/or $50,000/d; and
- knowing violations — initial penalty: 3 years and/or $5,000–$50,000/d, subsequent convictions: 6 years and/or $100,000/d.

If a discharge introduces a pollutant or hazardous substance into a POTW and the person knew or reasonably should have known such pollutant could result in injury or damage the system, or the discharge causes the plant to violate its own permit, the penalties are the same as those for a discharge to a POTW in violation of a local pre-treatment program.

Chemical processors have two choices if they are to avoid such compliance fines: treat wastewater to meet local POTW standards prior to discharging it to the sewer or pay to have wastewater hauled away and treated, which easily can total several thousand

dollars per week. The costs to transport (either by bulk drums or tankers) and treat wastewater are increasing and likely will continue trending upward. According to data from the U.S. Bureau of Labor Statistics, costs for waste collection and remediation services rose 12% from June 2014 to June 2019.

Tip: Facilities that have an in-house wastewater treatment system and a discharge permit are not exempt from monitoring and testing. These plants still must perform regular visual tests and send samples out for an official analysis (usually twice a year). Additionally, failure to pay fees, charges or surcharges typically are viewed as compliance lapses and also are subject to legal action.

4. WATER USE COSTS

While wastewater compliance is a necessary aspect of chemical manufacturing, reducing water consumption expenses is a related component of cost-effective wastewater management.

According to estimates in 2017 research from the American Council for an Energy-Efficient Economy, https://www.aceee.org, among all U.S. manufacturing sectors, chemical making accounted for the third greatest volume of water withdrawal, behind only pulp and paper and primary metals. More important, though, the chemicals subsector ranked highest in consumptive use, followed by primary metals and petroleum refining.

With water costs rising and water demand expected to exceed the current supply by 2030, taking steps to reduce water consumption through wastewater recycling and re-use could dramatically impact chemical processing facilities for the better.

Tip: Recycling or repurposing washdown water can cut water consumption substantially. For example, a chemical blender of industrial metalworking fluids uses as much as 20% of its incoming water to clean out the facility's mixing vats. Treating this water enables its reuse, markedly reducing incoming water usage.

5. OUTSIDE EXPERTISE

Achieving wastewater compliance in a cost-effective manner requires a balance of technology and compliance expertise. An ability to work with local control authorities to become familiar with applicable regulations and adopt measures to meet the regulations underpins this.

Unfortunately, chemical companies — whether new or long-established — can find pursuing pre-emptive compliance measures extremely challenging when their primary information liaison is also the enforcing party. An experienced, trusted supplier of industrial wastewater treatment technology will be familiar with local and federal pre-treatment standards and, in some cases, can act as an "information agent." For example, when a plant operator poses questions to wastewater regulatory officials, it may risk inviting followup requests from the regulator. As a neutral third party, a wastewater equipment supplier may be able to answer the questions itself or consult with regulators without disclosing specific details.

THOROUGH EVALUATION

Figure 1. Selecting the most appropriate treatment system requires a detailed and accurate analysis of the wastewater.

Furthermore, wastewater treatment systems for chemical plants are not one-size-fits-all. Determining the most cost-efficient and effective technology for the specific application requires a thorough understanding of the wastewater's makeup (Figure 1). For example, correctly specifying and optimizing a reverse osmosis system demands the following data: pH, total dissolved solids, chemical oxygen demand, biochemical oxygen demand, operating temperature, chloride, ammonia, oil and grease, total suspended solids, sulfates, calcium, magnesium, and emulsified oil and grease.

Tip: Do not exclusively rely on historical wastewater data. Carefully evaluate the current wastewater in the context of the plant's current operating parameters, which are subject to change as production goals fluctuate. An experienced and trusted supplier of industrial wastewater technology can evaluate a facility's wastewater stream by running tests and obtaining a laboratory analysis of samples before and after various treatment options. From those results, the supplier can recommend the proper equipment and treatment methods to recycle or repurpose the permeate.

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6. ZERO-LIQUID-DISCHARGE TECHNOLOGIES

The EPA's Effluent Guidelines, https://www.epa.gov/eg, set technology-based numerical limitations for specific pollutants on an industry-by-industry basis, including several chemical processing applications. The guidelines don't require the use of a specific technology to achieve reduction.

Several available zero-liquid-discharge technologies can be installed on-site to cut water pollution and prepare water for repurposing within the production facility. In many instances, a plant may need to deploy multiple modular technologies to optimize wastewater treatment and recycling. Three of the most common processes for chemical plant wastewater treatment are ultrafiltration, vacuum evaporation and reverse osmosis.

- Ultrafiltration uses low pressure to push wastewater through a semipermeable membrane. The technology filters out organics, emulsified oils and suspended solids, reducing oily water volumes by as much as 98% without chemicals. Ultrafiltration systems can cut the cost of washwater and detergents by as much as 75% and decrease haul-away costs by 90%. Such systems can help manufacturing facilities meet a goal not hauling away any wastewater and provide them the ability to meet RCRA requirements and state and local discharge regulations.
- Vacuum evaporation is one of the most effective methods for mitigating the risks and costs associated with chemical manufacturing wastewater. This process removes salts, heavy metals and a variety of hazardous components. It restores 90–95% of the original distillate (water), cuts the cost of washwater and detergents up to 75%, and reduces water costs up to 99%. Vacuum evaporation also has a low carbon footprint.
- Reverse osmosis is a low-maintenance method that removes dissolved solids by using high pressure to push wastewater through a semipermeable membrane. The technology removes up to 99.5% of dissolved salts and impurities. Often this technology serves as the final process after ultrafiltration or chemical treatment of wastewater.

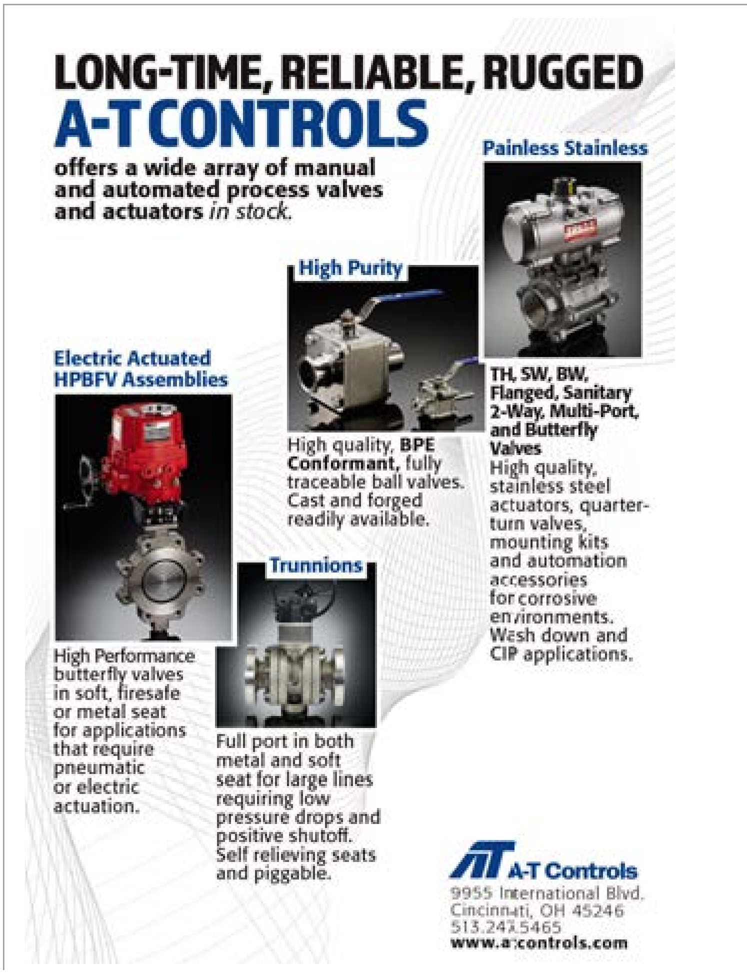
Tip: Partner with a wastewater treatment system supplier that offers all types of technology and that will work in lockstep with plant operators throughout the entire equipment acquisition — from sampling and permitting to testing and installation. Also, be sure to pursue testing and feasibility studies before equipment selection. Equipment suppliers that collect wastewater samples from the plant, run those samples through their proprietary wastewater treatment systems and then verify the results of the processing through a certified laboratory not only have proof of projected water quality improvements but also will have collected data required for a new discharge permit application.

Figure 2. This technology can remove up to 99.5% of dissolved salts and impurities, and often serves as the final step in a treatment system.

BUOY YOUR BOTTOM LINE

Wastewater regulations almost will certainly grow increasingly stringent. Chemical processors that partner with wastewater treatment experts to establish improved compliance practices will benefit from lower discharge fees, labor costs and haul-away expenses. In addition, by recycling wastewater to the production line for use, a plant will lower fresh water expenses. Chemical manufacturers that leverage this potential will make wastewater compliance less of a drain on their operation. ●

TIM HANNA is the vice president of business development for PRAB, Kalamazoo, Mich. Email him at thanna@prab.com



Refinery Tames Tough Sealing Service

Gasket designed specifically for HF alkylation delivers unprecedented performance

By David Clover, ERIKS North America

ALKYLATION UNITS are critical in petroleum refining — not only for producing high-quality gasoline but also for processing one of the most dangerous chemicals in the industry, hydrofluoric (HF) acid. Safely and reliably sealing flange connections in the piping systems of HF alkylation units is an issue that's plagued refineries for decades.

Refineries that operate HF acid alkylation units are keenly aware of the unique challenges and costs associated with HF acid. Broadly, these break into two categories:

1. *Environmental, health and safety*. HF acid is among the most dangerous acids commonly used in refineries. While it's not considered a strong acid (in terms of its disassociation in water), even small splashes on the skin can prove fatal. The U.S.'s National Institute for Occupational Safety and Health considers it harmful to life and health at airborne levels as low as 30 ppm.

2. *Internal corrosion of pipe flanges*. While anhydrous hydrogen fluoride is easily sealed and contained within carbon steel flanges, the addition of even small amounts of water results in the creation of aggressive HF acid, which can corrode carbon steel flanges from the inside.

Both challenges create imperatives for refineries relying upon HF alkylation, and each directly impacts gasket-related decisions in HF acid service.

First, the heightened health and safety risk posed to plant personnel and surrounding communities by HF acid means that no release is acceptable. The primary function of any pipe flange gasket is complete containment of HF acid.

Second, to prevent the failure of flanges due to internal taper corrosion, sealing the inner diameter of the flange to stop the intrusion of HF acid across the flange surface demands deliberate care.

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ONE REFINERY'S RESPONSE

In 2014, a refinery based in the U.S. Midwest was preparing for a major upgrade in its HF acid alkylation unit. This required the tie-in of new equipment to improve both the process and capacity. The engineering staff knew that the gasket the site historically used on the alkylation unit did not properly address the two imperatives of sealing HF acid. While the refinery had achieved reasonably good external leakage control, it regularly incurred damage to the pipe flanges — a problem common to other HF operators.

To combat this problem, some refineries regularly cut off and replace up to one third of all flanges opened during turnaround activities. To reduce the number of flanges swapped out, others prefer to weld-build damaged gasket surfaces and then machine them in the field to the ASME B16.5 specification. With either method, the tab for repairing corrosion damage is huge but accepted as a standard cost associated with using HF acid.

Engineers at the Midwest refinery were unwilling to accept the status quo and, so, undertook a study of emerging gasket technologies to determine if any could satisfy the two key imperatives — first, to tightly protect against external leakage with a highly loaded primary seal and, second, to simultaneously seal a soft conformable material to the interior of the flange to block acid intrusion — all with the available stud stress. The study took the refinery engineers to three prominent North American gasket companies, where they reviewed each organization's latest sealing advancements and audited their manufacturing capabilities.

After completing the study, the engineers determined that only one product, the Alky-One gasket designed and manufactured by Advanced Sealing (an ERIKS company), Norwalk, Calif., met their designated performance criteria.

Designed specifically for HF-acid service, the Alky-One gasket has a patented design that generates very high seating stresses on the external primary seal to prevent release of HF acid. That design includes a two-stage inner barrier pillow that effectively seals to the interior diameter of the flange, preventing taper corrosion.

The engineers also contacted end-users of the Alky-One gasket; their positive testimony provided the field verification needed to confirm its effectiveness.

IMPLEMENTATION

The tie-in project took place in 2015 as part of a planned alky-unit turnaround. Preplanning for the event was extensive and well-coordinated, involving engineering, inspection, operations and maintenance personnel and contractors. Advanced Sealing, the gasket manufacturer, conducted two on-site seminars, one for the engineering group that detailed the gasket's design principles and test results, and another that covered inspection so refinery personnel could gain a thorough understanding of potential quality issues.

GASKET IN PLACE

Figure 1. Proper flange separation allows for uninhibited insertion of gasket.

To further ensure plant safety, the refinery developed a targeted quality control/inspection plan that tagged every flange. The plan also required sign-off by the pipe fitter and quality control inspector for each of the following elements:

- the cleaning and inspection of the flange faces;
- proper flange alignment;
- verification of gasket type, size and condition;
- correct fastener type, condition and lubrication;
- the presence of hardened washers;
- verification of tool calibration; and
- proper torqueing procedures used to generate correct target torque.

Extra inspectors were hired to enable following this intense inspection and sign-off protocol for every flange.

THE RESULTS

The refinery installed 3,119 Alky-One gaskets during the 2015 turnaround. On startup, all flanges were leak-free; they continue to run leak free to date.

During the next scheduled turnaround in 2019, the refinery opened 1,320 (more than 40%) of the flanges in which the Alky-One gaskets were installed and fully inspected each opened flange. It found that all were in like-new condition, with no need for repair or replacement. This 0% repair/replacement fraction is unprecedented for the refinery — and the industry in general.

Combining excellence in engineering design and exceptional attention to installation practices, the Alky-One gasket has proven its ability to provide unmatched sealability and flange protection in the industry's most hazardous application. The refinery's next turnaround is scheduled for 2023. ●

DAVID CLOVER is a senior product/application specialist for ERIKS North America, Pittsburgh. Email him at David.Clover@eriksna.com.

Repair the Reactor Right

Identify operational issues that led to tube failure

THIS MONTH'S PUZZLER

We manufacture formaldehyde using DuPont's Formox process in a 30-yr-old system. Methanol is oxidized over a molybdenum-iron oxide catalyst at 600°F in a fixed-bed reactor: $CH_3 + ½O_2 \rightarrow CH_2O + H_2O$. We replaced the catalyst several months ago — we had stretched the service life of the old catalyst to 18 months from the usual year because of the pandemic.

We recently suffered a tube failure in the cooling water (boiler feedwater) surrounding the reactor. The downtime finally allowed us to inspect the reactor. We'd wondered for three months why methanol conversion dropped from 88% with fresh catalyst to a paltry 79%; the methanol registered downstream had crept up slowly. (We had ignored this because the old catalyst gave 83% conversion.) In addition, we saw more paraformaldehyde fouling of downstream equipment as we raised the reactor temperature to 690°F from 620°F. We also increased the oxygen content to the reactor by 25% to push the reaction. The effect was negligible in improving conversion. However, we noticed an increase in trace formaldehyde in the absorber downstream.

We run our boilers at 400 psig. The recovered steam produced by the reactor feeds into the main feedwater tank. Some engineers at corporate call it "dirty steam" and worry the boilers are being fouled. One suggestion was to sample the feedwater tank and discuss additional chemical treatments to prevent a plantwide problem with steam.

What do you think caused the cooling water leak? Is there really a problem with the boiler feedwater? Did our attempt to raise conversion lead to any lasting damage? Is there a way to identify this problem before it prompts major problems?

FOCUS ON A FEW POSSIBLE CULPRITS

In a broad sense, tube failure could stem from one or combination of the following:

1. Vibration caused by vortex formation due to boiler feedwater flow around the reactor tubes — or fatigue (from exceeding the useful life of the tubes);
2. Vibration from water hammer caused by flow of steam (formed by heat transfer of reaction heat to feedwater) and boiler feedwater; and
3. Poor water chemistry resulting in inadequate removal of dissolved oxygen, CO_2 or hardness, and lack of pH control.

Without information about the material of construction of reactor tubes and pressure on the boiler feedwater side (at the reactor tubes), I only can offer some general observations:

Visual and metallographic examination of leaking tubes and leak locations will help identify the root cause of the leak or leaks. However, finding the culprit — especially in complex situations — may require considerable sleuthing and possibly inputs from vibration and metallurgy experts. For many situations, though, visual clues are immensely helpful.

Visually, you generally will not see loss of metal with leaks caused by vibration or water hammer. If boiler feedwater (BFW) pressure at the reactor tubes is less than the saturation pressure of steam, steam could form at the reactor and could cause water hammer. On the other hand, if there is a back-pressure control with set pressure sufficiently high, then steam will form downstream of back-pressure control (in the BFW tank) and there is less chance water hammer will take place at the reactor tubes. For flow-induced vibration, if the vortex-causing frequency coincides with the natural frequency of the tubes, then vibration will intensify.

Typically, dissolved oxygen will prompt pitting corrosion — which is visible by indentations on reactor tubes. On the other hand, CO_2 causes groove corrosion and thinning of reactor tubes (loss of metal). Low pH also will entail metal loss due to acidic corrosion. High pH, on the other hand, could lead to caustic corrosion. Scale can result in under-deposit corrosion and CO_2 corrosion by scale decomposition.

If these are the causes, then the broad strategy is to control water chemistry:

- determine allowable levels of dissolved oxygen at the BFW pressure at the reactor tubes; consider deaeration or oxygen scavenger treatment with hydrazine substitutes;
- control CO_2 by amine treatment, scale by zeolite bed operation, and solids by conductivity controlled blowdown; and
- consider placing the BFW tank under a nitrogen blanket. If nitrogen is not available or suitable, use natural gas — of course, you must address the flammability issue.

You quite possibly may determine that a combination of mechanisms caused the tube leaks. You then can develop corrective action.

You also state that conversion dropped from 83% to 79%. This is to be expected because water vapor (leak-caused ingress of water/steam to the catalyst bed) inhibits oxidation of methanol to formaldehyde (H-CHO an aliphatic aldehyde).

GC Shah, senior advisor
Wood, Houston

DON'T BE HANS BRINKER

Old equipment often is poorly maintained. Managers don't see a problem for many years and, so, give up on routine inspections. Then, they become a plant version of Hans Brinker — plugging holes as they spring up, in tubes rather than dikes.

Fouled steam can degrade performance of reboilers throughout your plant. In addition, operating at >300 psig will affect the water quality of the steam condensate recovered. (The allowable impurity of Fe^{2+} and Cu^{1+} for boiler feedwater is half of what's tolerated for <300 psig boilers: 0.05 ppm versus 0.100 ppm for Fe^{2+} and 0.025 ppm versus 0.05 ppm for Cu^{1+}.) You can add tens of thousands of dollars' worth of chemicals to counteract the fouling, with side effects. Or you can spend a lot of money buying equipment to trap the foulant before it affects the boiler and plant exchangers; most powerhouses I've seen don't have that kind of space.

Dumping the steam might seem tempting but it's far too valuable to an operation like this. When considering steam condensate recovery, the cutoff for a 4-yr payback (~25% return on revenue) is about 600 lb/h based on a cost of \$22/1,000 gal of steam condensate.

Instead of plugging holes in the tubing as they spring up, you can bite the bullet — shutting down for the week it will take to identify the leaks and make a plan to repair them all. Do a thickness reading as part of your inspection, although alloy steels don't tend to thin from corrosion. If the thickness is reasonable, then cut out a section of the coil for dye penetration testing followed by electron microscopy. The results might prompt you to buy a new vessel — a decision you couldn't reasonably make before such testing.

Once you've repaired the obvious leaks, plan for a longer outage to: replace the vessel and the coil; replace only the coil; or, hopefully, just repair the coil.

You may want to run a fluorescent dye test at low pressure to detect any small holes or check sections of the coil difficult to inspect, like right next to the vessel wall. At low pressure, the dye will accumulate where it escaped. Run this

test once, cut out the affected coil and replace; then run it again to identify any holes that were missed the first time. It's amazing how long you can extend equipment well past its zero depreciation point with vigilant inspections and effective repairs.

One problem you will have to live with for a while: the foulant is all through your plant from the boiler feedwater tank to the individual heat exchangers. It will be decades before that problem is behind you.

Like most, this episode has a positive side. At least, you learned that increasing the O_2 rate and raising the temperature had negligible effect on the reactor conversion. In fact, a high temperature might have exceeded limits on the coil. Also, seeing product downstream in the column may be useful in predicting the limits of the distillation tower.

Dirk Willard, consultant
Wooster, Ohio

DECEMBER'S PUZZLER

We completed an engineering package for a de-ethanizer system (Figure 1) that is part of an overall expansion of a refinery. This involved replacing some lower trays because of fouling and capacity limitations and repairing corrosion in the feed tray and tubes in the air heat exchanger and water condenser. Construction is done. However, the pressure relief system — I did its initial design a few years ago but that has been significantly modified — troubles me.

I noticed the following changes to my design: 1) a block valve was added in front and back of the water (thermal) expansion relief valve (RV); 2) that valve is upside down and someone left the cap at the discharge; 3) the RVs that were located on the reboiler, condensate knockout drum, condensate tank and water condenser have been removed and capped; 4) the pilot RV has been moved from the top of the vessel to the condensate pipe; 5) an isolation valve has been added to a long inlet pipe and the discharge pipe was extended to a duct leading to the flare stack; and 6) the reboiler RV has been replaced by a restrictive orifice on the steam supply (or so I am told by one of the client's engineers working on the project). These changes really concern me, not the least because my name is on the calculations if something goes wrong.

My managers are telling me the refinery is happy and, so, not to rock the boat.

What do you think? What should I do? Should I ask for the new calculations for my files?

Send us your comments, suggestions or solutions for this question by November 6, 2020. We'll include as many of them as possible in the December 2020 issue and all on ChemicalProcessing.com. Send visuals — a sketch is fine. E-mail us at ProcessPuzzler@putman.net or mail to Process Puzzler, *Chemical Processing*, 1501 E. Woodfield Rd., Suite 400N, Schaumburg, IL 60173. Fax: (630) 467-1120. Please include your name, title, location and company affiliation in the response.

And, of course, if you have a process problem you'd like to pose to our readers, send it along and we'll be pleased to consider it for publication.

DE-ETHANIZER COLUMN

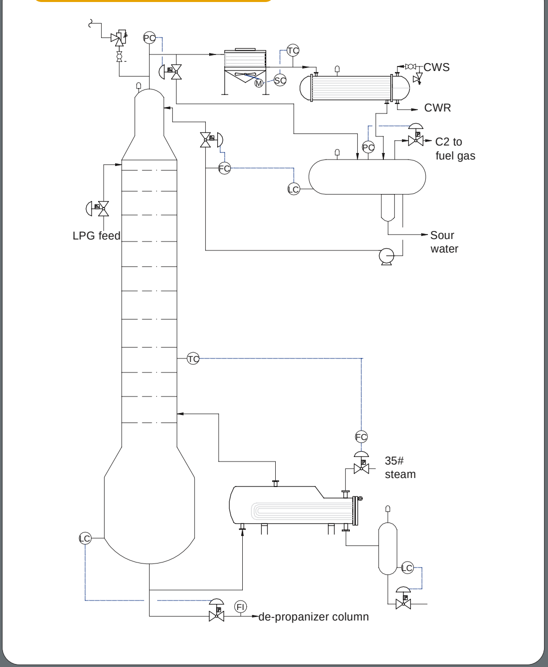

Figure 1. Changes to pressure relief system cause concerns for original designer.

Choose the Correct Thermosyphon Reboiler

Both horizontal and vertical designs boast benefits for specific situations

Three technical issues can influence the choice.

AN EXPERIENCED colleague recently needed to design a horizontal thermosyphon reboiler. Until then, he had dealt exclusively with vertical thermosyphon reboilers. His latest assignment, though, required copying part of an existing plant that had a single horizontal thermosyphon reboiler amid lots of vertical ones.

"Why was that one service an exception?" he wondered. This spurred a broad discussion that covered a number of practical issues about thermosyphon reboiler design. These merit a wider audience, hence this column.

I asked my colleague if he knew the history of that reboiler. One reason one-of-a-kind equipment shows up in plants is that the item was a rush replacement or surplus equipment just sitting around. The concern here is whether this item, which differs from everything else, actually suits the future service. While copying lowers engineering costs and shortens the schedule, it's counterproductive if the unit really wasn't a good choice for the service.

Both horizontal and vertical exchangers will work fine as thermosyphon reboilers. The configuration of the exchanger and its piping will differ but there's no fundamental reason why either can't handle a specific service. So, why was one horizontal thermosyphon reboiler among all the vertical ones?

Some plants, companies or industries strongly prefer one or the other based on previous experience. This historical bias influences future choices. If a plant already has 30 or more horizontal thermosyphon reboilers that work, it very likely will make the next thermosyphon reboiler a horizontal exchanger as well.

Bias aside, three technical issues can influence the choice between a horizontal and vertical thermosyphon reboiler:

- physical size and weight of the exchanger;
- maintenance and replacement requirements; and
- vacuum operation.

In general, economics favor the vertical design for smaller thermosyphon exchangers. The foundation and steel to put the exchanger up by the tower cost more but reduced piping for the tower-exchanger connections make the overall installation cheaper.

As the exchanger becomes larger and heavier, the difficulty and cost of removing the exchanger bundle for maintenance or repair increase. Large vertical exchangers require pulling the bundle up a long distance; so the extra expense incurred by a vertical exchanger climbs. Also, as the tower becomes bigger, the position of the exchanger rises with the greater size of the tower bottoms section.

Services and industries such as petroleum refining that have a history of large units with high maintenance requirements tend to choose horizontal exchangers because they provide lower maintenance costs and quicker maintenance work. Nearly all thermosyphon exchangers in petroleum refining are horizontal. The time and cost required, e.g., to pull a 30-ft-long, 5-ft-dia. exchanger vertically up 30 feet are prohibitive.

Conversely, for units with low maintenance requirements and small exchangers, vertical installation offers worthwhile savings. Thus, many smaller chemical plants have nothing but vertical thermosyphon reboilers.

Vacuum operation also can affect the choice. Vertical reboilers under vacuum tend to have a subcooled zone in the bottom that doesn't do any boiling heat transfer. The static liquid head in the exchanger increases the pressure at the exchanger surface. The static head really won't change the boiling temperature very much for systems under pressure. However, in systems under vacuum, this static head can significantly raise the boiling temperature above the temperature of the bottom stage in the tower. This reduces the heat transfer in the bottom section of the exchanger. Heat-sensitive systems under vacuum sometimes use horizontal reboilers to keep the reboiler temperature lower.

For exchanger thermal design, vertical thermosyphons have relatively few issues. The exchanger flow patterns are straightforward and velocities are high. The only significant flow problem is geysering, i.e., liquid accumulating in slugs if the velocity drops too low; avoiding this may require adding pressure drop to the exchanger inlet.

Horizontal thermosyphons often are much larger and have low vaporization-side (shell-side) velocities. This can lead to liquid recirculation in the exchanger and accumulation of heavy components. Good practice with large horizontal thermosyphons is to have two or more inlets to prevent horizontal flow gradients and reduce internal recirculation.

You can make both types of thermosyphons work. The biggest selection criteria are size and weight. Larger exchangers shift the choice toward the horizontal thermosyphon. ●

ANDREW SLOLEY, Contributing Editor
ASloley@putman.net

Wafer Ball Valves Support Skid Systems

The direct-mount ASME/ANSI Class 150 wafer ball valves are designed to make skid systems more compact, lighter, and to improve efficiency and cost. The 723/724 Skid Series valve body uses less steel which means a lower cost per valve than other wafers on the market, says the company. A low-torque design allows for use of more compact and efficient actuators. This saves space while reducing materials, such as pipe supports, and labor costs. Available in stainless or carbon steel, the series comes in 30–60°, 60° and 90° V-port configurations. The valves are available in pneumatic and electric actuated packages and in "deadman" spring return handle assemblies.

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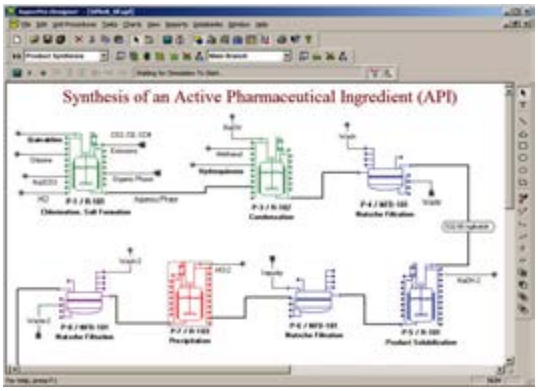

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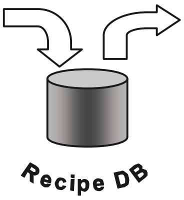

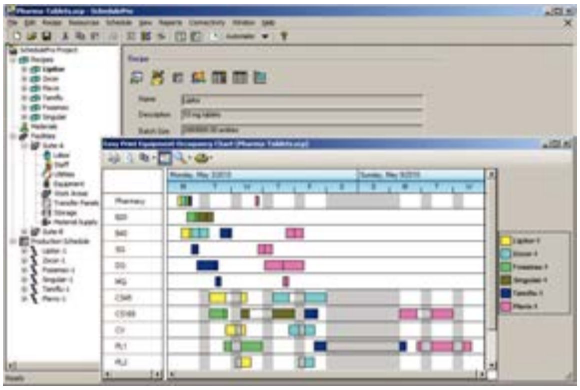

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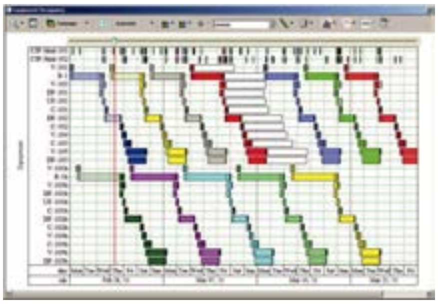

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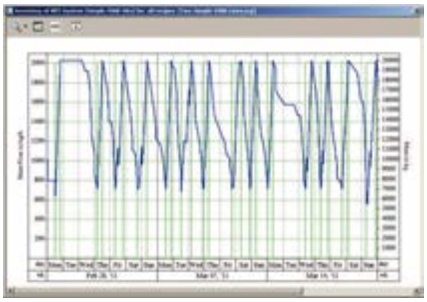

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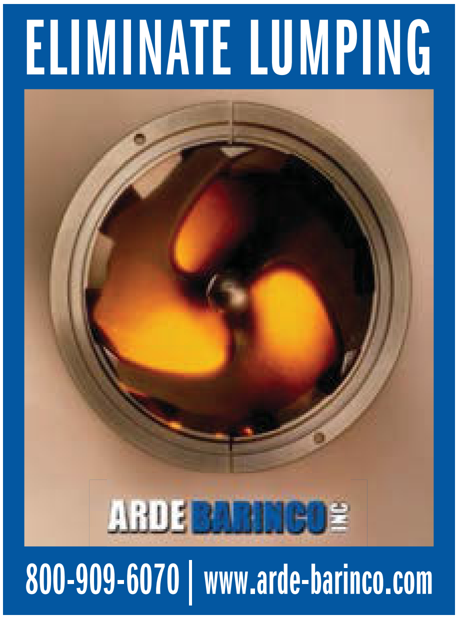
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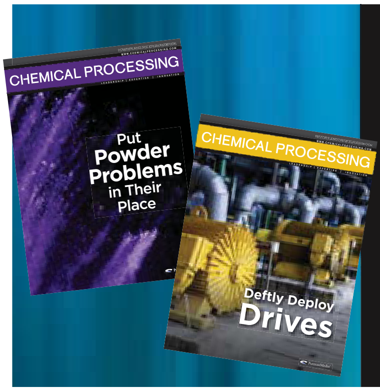
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DAC Technologies Ramp Up Capacity

Several joint projects aim to improve direct air capture and storage of carbon dioxide

The facility will be located in the U.S. Permian Basin.

INDUSTRIAL QUANTITIES of CO_2 from the atmosphere using direct air capture (DAC) technologies are a step closer in the United States following a licensing agreement signed between 1PointFive, Houston, and Carbon Engineering, Squamish, B.C.

1PointFive — a company formed by Oxy Low Carbon Ventures, LLC, a subsidiary of Occidental, and Rusheen Capital Management — will finance and deploy Carbon Engineering's DAC technology.

This continuous process captures CO_2 from the air and delivers it as a purified, compressed gas — using only air, water and energy as inputs.

Consisting of four major pieces of equipment, the process starts with an air contactor modelled on industrial cooling towers. A fan pulls air into this structure, where it passes over thin plastic surfaces that have potassium hydroxide solution flowing over them. This chemically binds with the CO_2 molecules, removing them from the air and trapping them in liquid solution as a carbonate salt.

The CO_2 contained in this carbonate solution is then put through a series of chemical processes to increase its concentration, purify it, and compress it for delivery in gas form, ready for use or storage.

A pellet reactor separates the salt from the solution to form small pellets. In the third step, a calciner heats the pellets to release the CO_2 in pure gas form. Also in this step, a slaker hydrates the processed pellets and recycles them back into the system to reproduce the original capture chemical.

The new facility will be located in the Permian Basin area of the United States on approximately 100 acres. Carbon Engineering, Oxy Low Carbon Ventures, and its contractors have completed more than 25,000 hours of design and development work so far.

The final front-end engineering design for the facility is slated to begin in the first quarter of 2021, with construction to start in 2022.

Occident will permanently and securely store the CO_2 captured at the facility deep underground in geological formations. The company has over 40 years of experience storing CO_2, sequestering nearly 20 million mt/y from its operations.

Meanwhile, Climeworks, Zurich, Switzerland, has signed an agreement with carbon storage specialist Carbfix, Reykjavik, Iceland, and Icelandic geothermal energy provider ON Power to lay the foundation for a new DAC plant that will significantly scale-up carbon removal and storage in Iceland.

Under the agreement, Climeworks will use its DAC technology to capture 4,000 mt/y of CO_2 from the air at ON Power's Hellisheidi geothermal facility.

Powered by renewable energy from the facility, the DAC technology involves a two-step process. First, air is drawn into modular CO_2 collectors. The CO_2 is then captured by adsorption on the surface of a highly selective filter material that sits inside the collectors.

Second, after the filter material is saturated with carbon dioxide, the collector is closed. The temperature inside the collector rises to between 80°C and 100°C, which releases the carbon dioxide at a purity of over 99%.

The gas is then cooled to 45°C and collected. Each individual CO_2 collector can capture approximately 50 mt/y of the gas.

The modular collectors, powered solely by renewable energy or energy from waste, can be stacked to build machines of any size, says the company. Grey emissions are below 10%, meaning that out of 100 mt of CO_2 captured from the air, at least 90 mt are permanently removed with only up to 10 mt re-emitted.

Carbfix will then use its technology to mix the carbon dioxide with water and pump it deep underground. Through natural mineralization, the carbon dioxide reacts with basalt rock and turns into stone within a few years.

Climeworks and Carbfix currently plan to expand DAC applications by further developing their technologies to the mineralization of atmospheric CO_2.

However, mineralization is not the only application open to Climeworks; the company is involved in three other research projects in which it uses CO_2 to produce renewable, carbon-neutral fuels and materials.

One, known as Celbicon (cost-effective CO_2 conversion into chemicals via combination of capture, electrochemical and biochemical conversion technologies), aims to develop new low-cost, small-scale, robust CO_2-to-chemicals technologies that operate at moderate temperatures with high efficiency/yield and low maintenance costs. The European Union-funded project involves 12 other research organizations and chemical companies. ●

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