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Rally 'Round the Circular Economy

Discarded plastics underscore both the problem and the opportunity

New facilities could create a $9.9-billion increase in U.S. economic output.

THE DEMAND for lifetime stewardship of products, including safe and appropriate end-of-life disposal, increasingly impacts the chemical industry. Today's growing call to maximize the use of resources and minimize the amount of waste — often termed the "circular economy" — adds a new twist and offers chemical makers a chance to reap rich rewards.

Careless and cavalier disposal of products has created severe environmental issues. Discarded plastics, such as single-use containers, shopping bags and drinking straws, exemplify the problem and provide what many see as its most visible and alarming manifestation. As our March cover story, "Industry Tackles Plastics Plague," http://bit.ly/2v6SfOT, pointed out, chemical makers and other firms are starting to address that issue, both through collaborative efforts and individually.

Initiatives include work to convert used plastics into feedstocks for new plastics and chemicals, other raw materials for manufacturing, as well as fuels for transportation and other uses. Researchers are exploring a broad variety of options; for instance, May's "Upcycling Promises to Pare Plastics Pollution," http://bit.ly/2Y4Qazm, describes a process that combines single-use polyethylene terephthalate (PET) beverage bottles with bio-based materials such as muconic acid to create fiber-reinforced plastics (FRP) with higher market value than the PET itself and better strength than conventional FRP.

"Advanced plastics recycling and recovery technologies have the potential to revolutionize the way we make, use and reuse our plastic resources," believes Steve Russell, vice president of plastics at the American Chemistry Council (ACC), Washington, D.C.

Success can lead to substantial economic benefits according to a report, "Economic Impact of Advanced Plastics Recycling and Recovery Facilities in the U.S.," that ACC issued in late March.

While 3.1 million tons of post-use plastics were mechanically recycled in the United States in 2015, 26 million tons of such material were sent to landfills that year, according to U.S. Environmental Protection Agency data, notes ACC.

The report uses what it calls a conservative assumption, i.e., recovery and processing of 25% of landfilled material. This material would support 260 new plastics recycling and recovery facilities, it states. To come up with that estimate, ACC developed a "model" representative facility. This relies upon pyrolysis and catalytic depolymerization and can handle comingled mixed plastics. However, ACC adds that other technologies such as gasification also may make sense.

The model facility requires a capital investment of $36 million and annually can process 25,000 tons of mixed plastics to make 82,500 bbl of diesel, 41,000 bbl of naphtha and 2,000 mt of waxes.

These facilities would result in 38,500 jobs — 9,400 at the sites themselves, 15,100 at supply chain partners, and the remainder spurred by the spending of those workers, the report estimates. This represents a $2.2 billion increase in annual payrolls, says ACC.

Moreover, U.S. economic output would rise by $9.9 billion, notes the report. Increased output at the new recycling and recovery facilities would account for $4.1 billion, with the rest of the gain stemming from the impact on suppliers and worker spending.

This added dimension to stewardship offers industry an opportunity to do well by doing good.

MARK ROSENZWEIG, Editor in Chief
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Examine Site Enhancements

Ongoing tweaks aim to improve your visits

We're always looking for ways to make your experience more meaningful.

YOU DON'T have to reinvent the wheel to make a better vehicle. Indeed, you just have to make enhancements in the right places. At ChemicalProcessing.com we're always poking around the site looking for ways to make it better for you.

In fact, late last year I wrote about the site's new navigation and color scheme (see: "Check Out Site Upgrades, Top Content on Chemical Processing" http://bit.ly/2W0eepQ). And currently I'm working with our development team to bring even more changes to the site — all aimed at helping you access all the tools and resources available on myriad topics.

We're rolling out changes as the design and programming team implements them; so, over the next several months you'll see a variety of upgrades. Currently, we've increased the spacing between lines of text to help you more easily read our award-winning content. And, soon, you'll see a new font style. Trust me when I say that picking new fonts stirs a lot of debate. Serif or sans serif? What font family size works best? What will special characters (mainly the Greek alphabet) look like? How will type render in a mobile version?

In addition to an airier look to the copy, we're also moving toward a one-column display. Right now, the main content appears in one column, and is flanked by what we call the "right rail" that houses advertisements and related reading among a few other things.

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All this information will reside in one column in the future. We've already repositioned "Related Content" below the article. We reckon that once you've finished a story, you well may want to check out similar content aimed at helping your site be as efficient, safe, environmentally friendly and economic as possible. Be on the lookout for updates to the Related Content and Most Popular sections (which also will reside after articles) — we're exploring adding images from the stories to these areas.

POWERFUL LINK

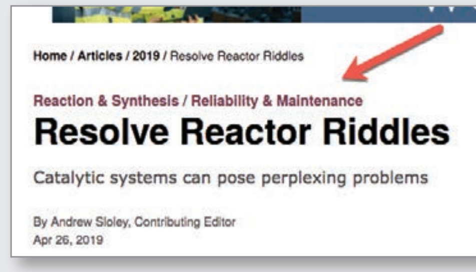

Figure 1. Clicking on "eyebrow" (indicated by arrow) takes you to content in that category.

We've already increased the size of headlines and decks (the brief descriptive text directly under the headlines). And we've moved the social media tools so they follow the articles. That way, after you've read the article and feel compelled to share it with friends and co-workers, you can do so with ease.

From a "why didn't we think of that sooner" perspective, we've also added what we call an "eyebrow" to our article pages. Eyebrows appear above the headline (see Figure 1) and give the relevant categories for the particular piece of content. So, for example, if you're reading the article "Resolve Reactor Riddles," (http://bit.ly/2W0PvRZ), simply clicking on the categories in the eyebrow will let you find oodles of other content in "reaction & synthesis" and "reliability & maintenance."

One thing we've eliminated from our site is the ability to comment on articles. Unfortunately, many of the inputs came from phishers, who often provided links to nefarious sites, or from people promoting commercial products or services. We certainly still want to hear from you. Email your comments to either me (tpurdum@putman.net) or editor Mark Rosenzweig (mrosenzweig@putman.net); we'll consider them for our sporadic Letters section in the magazine and online. In fact, I can add your comments directly to an article as an editor's note.

These next several months hold many small but mighty changes. I look forward to making the site an even better place to visit. I hope that's just what you will do. ●

TRACI PURDUM, Senior Digital Editor
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Come Up with Better Cost Estimates

Understand where significant errors can arise and how to combat them

Consider several actions to improve your estimates.

MY ESTIMATE wasn't even close. That surprised me because some accounting knowledge from my bookkeeper mother had rubbed off on me. So, I asked for a full breakdown from the bidder, something I had learned to do when managing projects in the Air Force. This revealed higher material costs than those I had used, which were based on old projects. However, that only accounted for part of the deficiency.

My estimate was completed in April. By that time of year, most constructors have a pretty full dance card. Therefore, they probably padded the estimate a little if they already had work lined up. Depending on the expertise needed, all the available labor in a geographical area may get signed up quickly once the ground thaws.

Material costs typically cycle up beginning in March. Starting sooner usually isn't really an option. Construction is difficult from November through March, sometimes even through May, in cold climates.

Then, there's the concrete. Once temperatures drop below 40°F, most foundation contractors charge more than double and the risk of failure increases. Freshly poured concrete that freezes can lose up to 50% of its 28-day strength during the critical first four days. Also, nobody really wants to dig a footing in frozen ground, especially because it's shrunk — what happens when spring comes?

Sometimes, though, work must take place in winter. I once was asked to come up with a way to clean oil tanks in February in Illinois. The cleaning professionals were impressed by my idea of using propylene glycol but they and I knew the cost would be high — about three times the tab of a summer cleanout with water alone.

Hence, when projects start up in March or April, demand can't keep up with supply and prices soar. Demand also can impact the price of materials like nickel, copper, palladium or tungsten. A single big project temporarily can corner the market for a material.

Plants in warmer climes also must contend with weather concerns. For instance, construction during hurricane season, which in the northern hemisphere runs from June to November, is a challenge. (For tips on getting ready for hurricanes, see: "Prepare Your Hazardous Waste For a Natural Disaster," p. 21, http://bit.ly/2KbvdiC). Also, refiners on the Gulf Coast and elsewhere avoid shutdowns in the summer because of the high demand for gasoline then, preferring to perform turnarounds in the fall or spring.

Now, let's consider shipping costs. These have gone up substantially in the past couple of decades. Using U.S. Department of Transportation data and 2.36% average annual inflation from 1990–2018, I found the cost of rail transportation, while pretty much flat during the 1990s, climbed steeply starting in 2005 — increasing by 171% from 2005 to 2018. Truck transportation cost information is spotty but, as of 2018, it cost 15.6¢/ton compared to 5.1¢/ton for rail. Trucking costs likely will rise, e.g., in response to a recent labor rule change reducing driver hours for safety reasons. Air shipment cost runs about 31.5 times that of rail using 2018 numbers.

Shipping during peak times can be expensive. The Christmas holiday season peak is mid-August to mid-October. Container ships are scarce and in demand during this period, which can impact boxed components. Pipe and heavy machinery often are shipped via traditional cargo ships, which costs more.

Given all these complications, let's consider actions you can take to improve your estimates. First, don't use material estimates that are older than a decade. Second, break out transportation and other costs to gain insight into them. Avoid factors that can increase costs, e.g., air or truck shipment, transport during peak times, etc.

Stage project items carefully. Maybe it's less expensive to clean tanks in the winter, despite the high cost, than to create a bottleneck in the spring that could delay a project into the fall. Organizing tie-points more effectively, such as by completing them a year or so ahead of an outage or at a time of year when labor costs are lower, could dramatically reduce project costs. One $800-billion-dollar project I worked on had more than 600 tie-points; imagine if these were done years earlier when the refiner first knew the regulations would come into effect instead of when funding was available. Decisions companies make years before often impact today's costs. ●

DIRK WILLARD, Contributing Editor
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New Class of Catalysts Emerges

Inexpensive metal oxides promise to enhance a variety of processes

MANY REACTIONS require the cleaving of C-O bonds. Now, a team of researchers from Oregon State University (OSU), Corvallis, Ore., and the University of Delaware (UDel), Newark, Del., has discovered a class of metal oxide catalysts that reportedly are more active than commonly used transition metal ones.

"This work was inspired by our research on the conversion of biomass, such as wood and agricultural residues, into fuels and commodity chemicals. We wanted to understand the principles of biomass conversion using oxide-based catalysts, which previous studies had suggested were selective catalysts," says Konstantinos Goulas, assistant professor of chemical engineering at OSU.

Because oxides are abundant and relatively inexpensive, the team compared how fast specific chemicals can be made on a variety of metal oxide catalysts. The results provided insight into what properties generate the best metal-oxide catalysts. The team found that substrate plays as important a role as the catalyst itself in C-O bond activation. Their findings appear in *Nature Catalysis.*

"We measured the activity of a series of oxides for the hydrodeoxygenation (HDO) reaction and found that this trends with Gibbs free energy of formation of the oxide (ΔGfo — a property tabulated in various databases)," notes Goulas. "This trend looks like a so-called volcano curve: it rises to an apex at approximately ΔGfo = -1 eV, corresponding to IrO_2, and then falls down as the oxides become completely reduced to the unselective metallic form due to the presence of hydrogen in the reaction. This tells us that if you want to run an HDO reaction efficiently, your catalyst needs to be an oxide that's reducible (i.e., has a ΔGfo that is not too negative), but not too reducible (so it does not become a metal during reaction)."

"Regarding the opportunities this offers us, one could think of many reactions," he adds. "One example could be methane and alkane oxidation in general (for miniature power devices). Another one is the oxidation of CO and volatile organic compounds in the context of pollution abatement from stationary and mobile sources. Last but not least, this could apply to systems like the oxidative dehydrogenation (ODH) of hydrocarbons, such as propane and propylene, for the production of propylene and acrolein, respectively. It all boils down to ease of removal of oxygen atoms from a catalyst surface!"

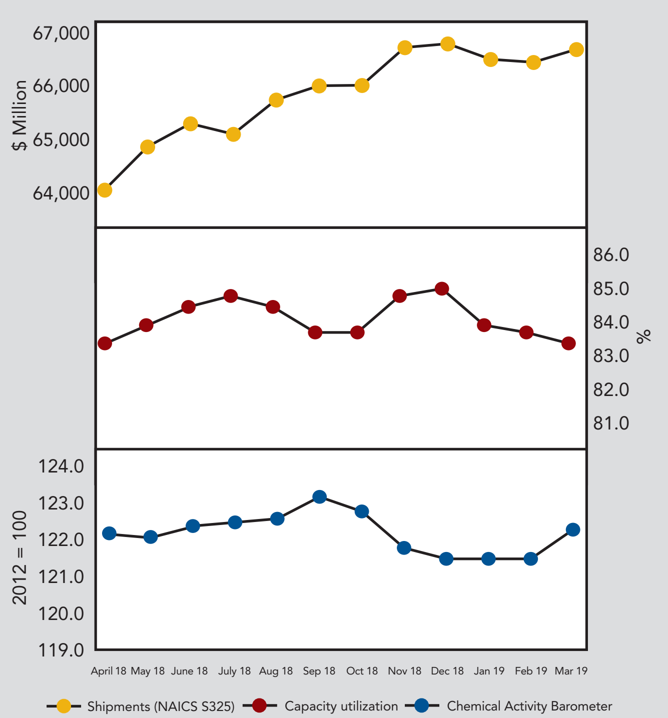
"When we started this investigation, we had a good understanding of the mechanism of the HDO reaction over RuO_2. However, we weren't sure if the mechanism would be the same over other oxides. Moreover, we wanted to discover new catalysts comprised from elements cheaper and more earth-abundant than Ru... Based on our investigations, our colleagues from University of Pennsylvania discovered that NiCu alloy catalysts are very selective and active for the HDO reaction. This was important, because Ni and Cu are both earth-abundant elements. Our subsequent investigations, using X-ray absorption spectroscopy, showed that this is due to the formation of an oxide!"

"While I would love to see this system commercialized, the techno-economic analysis questions are beyond my expertise. The ultimate goal of this process is the production of biomass-derived para-xylene (pX) and terephthalic acid," says Goulas.

Recently published papers by his colleagues indicate that production of pX from biomass compares favorably to its production from petroleum.

"Regarding the further development of these systems, I would say that answering questions related to reaction engineering and process intensification is the way to go right now," he says.

ECONOMIC SNAPSHOT



Shipments and the CAB rose but capacity utilization slipped. *Source: American Chemistry Council.*

Better Solid Refrigerants Beckon

A BREAKTHROUGH in refrigeration science by researchers in the U.K. and Spain promises to revolutionize the way the chemical industry carries out its expensive cooling processes. The team, at Cambridge University, Cambridge, U.K., Universitat Politècnica de Catalunya, Barcelona, Spain, and Universitat de Barcelona, Barcelona, achieved pressure-driven thermal changes — or barocaloric (BC) effects — at near room temperature that they call colossal and an order of magnitude better than those observed in any other BC materials.

At the heart of the breakthrough are highly malleable plastic crystals (PCs), also known as orientationally disordered crystals, which lie at the boundary between solids and liquids. This malleability allows PCs to undergo huge pressure-driven thermal changes as a result of molecular reconfigurations.

In this case, the researchers worked with commercially available samples of the PC neopentylglycol (NPG), which is made from cheap abundant elements and already widely used by the chemical industry in the synthesis of paints, lubricants and cosmetics. As the PCs of NPG transition to an ordered crystal structure under the applied pressure, they yield what the researchers describe as an enormous latent heat.

The temperature change achieved is comparable to that observed in standard commercial refrigerant R134a and other hydrofluorocarbons (HFCs) and hydrocarbons (HCs), the researchers say.

"Refrigerators and air conditioners based on HFCs and HCs are also relatively inefficient," notes Xavier Moya, a Royal Society Research fellow in Cambridge's department of materials science and metallurgy. Moya is also a leader in the field of solid refrigerant research.

Moya believes the demonstration of colossal BC effects in commercially available PCs should

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immediately open avenues for the development of safe and environmentally friendly solid-state refrigerants.

Following the filing of a priority patent application, Moya now is working with Cambridge Enterprise, the commercialization arm of the university, to obtain funding to develop demonstrations of the technology.

"We are now crossing the so-called 'valley of death' which stretches between promising materials and a working prototype ready for industry adoption. We are currently assessing the feasibility of developing an efficient barocaloric cooling cycle for light commercial refrigeration applications while providing zero greenhouse warming potential," notes Jennie Flint, senior commercialization associate at Cambridge Enterprise. The work already has attracted industrial interest from several sectors — demonstrating both the industry pull and the potential breadth of applications of the technology, she adds. "Industry collaboration is key to incorporating our barocaloric materials into future cooling devices," Flint stresses.

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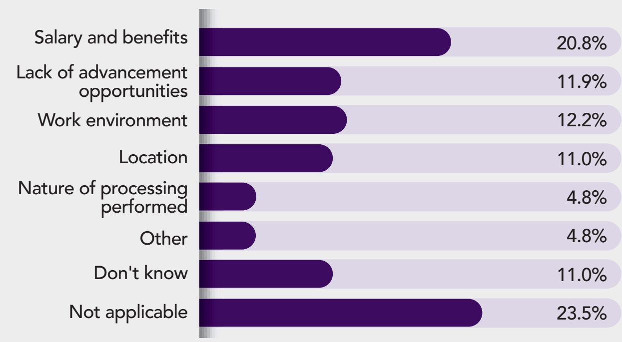
What factor most hinders your site's efforts to attract and retain technical staff?



"Salary and benefits" was cited most often as the key hindrance.

Tame your Workhorse

Properly sizing your centrifugal pump and providing the right flow control can save energy

Constant heavy throttling of control valves wastes a considerable amount of energy.

THE CENTRIFUGAL pump is a workhorse in the process industries. However, the way such pumps are used frequently undermines their efficiency. In particular, system designers typically oversize pumps during the design stage to ensure the pumps provide the needed flow. In addition, the methods used for flow control often are wasteful. In this column, we address this pervasive pair of problems.

Throttling valves. A valve on the discharge side of the pump controls the flow. This is the most common form of centrifugal pump control. Partially closing the control valve (or balancing valve in a static application) at the pump discharge is a convenient but inefficient way to reduce the flow of an oversized pump. As the control valve closes, it reduces the flow rate — but adds frictional resistance the pump must overcome.

Flow resistance due to throttling wastes a considerable amount of energy if the valve constantly stays heavily throttled (say, <60% open). The most common improvements are:

- Trim the pump impeller. This is a low-cost option and typically a good solution if the required flow always is less than design, the flow reduction isn't too large, and the required flow rate is fairly constant. (However, predicting resulting performance demands care; see: "Centrifugal Pumps: Avoid Surprises When Cutting Impellers," http://bit.ly/2DNd5rd.)
- Install a variable frequency drive (VFD). VFDs save energy as the pump's speed is reduced. They are an ideal solution if the pump's capacity varies widely. However, VFDs are comparatively expensive and can't always be justified. (For tips on applying VFDs effectively, see: "Consider VFDs for Centrifugal Pumps," http://bit.ly/2Yao7yF.)
- Install a right-sized, high-efficiency pump. If the pump is significantly oversized for its maximum flow requirement or if its hydraulic efficiency at the normal operating point is low, this may be the best option.

Recirculation. With recirculation, the pump produces a constant flow greater than the maximum process demand. Fluid required by the process goes to downstream equipment while the excess fluid flows, via a recirculation line with a control valve, directly back to the suction tank. The constant recirculation of excess fluid makes this the least efficient form of flow control.

However, recirculation can serve an important function by providing minimum flow protection. If the flow through a pump falls too low, pump damage can result from rapid heating of the fluid within the pump as well as induced pressure pulses originating within pump suction and discharge areas by recirculation vortices. Stopping the recirculation flow when it's not needed to protect the pump can achieve more-efficient minimum flow protection.

In addition, you can arrange automatic control valves for recirculation to open only when the system flow is below the pump's minimum flow requirement. A pressure sensor in the pump discharge line can control the valves and open them at a high pressure, or you can use a spring-controlled mechanism set to open automatically at a pre-defined pressure. This arrangement greatly improves the control system's energy efficiency.

Parallel pumping with throttling valves. Here, multiple pumps piped in parallel discharge into a common header. This arrangement usually relies on throttling control valves to regulate flow in different lines coming off of the main supply header.

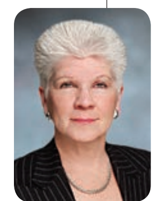
An opportunity to save energy often exists in constant-speed parallel pumping systems having more than three pumps. This is because the last pump started generally doesn't add a large amount of additional flow to the system. The fourth or fifth pump typically runs as an "insurance policy," in case one of the other pumps fails. However, this insurance policy can be expensive. Turning one pump off and installing automatic controls capable of starting an additional pump if the header pressure falls below a pre-determined level can ensure proper operation with fewer pumps and lower energy costs.

For further details and examples, see: Glenn T. Cunningham, "Rotating Equipment: Centrifugal Pumps and Fans," Chapter 15 in "Energy Management and Efficiency for the Process Industries," Alan P. Rossiter & Beth P. Jones, Wiley-AIChE, 2015, pp. 186-20.

ALAN ROSSITER, Energy Columnist,
with guest contributor Glenn Cunningham
arossiter@putman.net

Get Ready for South Korean Deadline

Register existing chemical substances by June 30



A company's global commerce can come to a dead stop.

GLOBAL CHEMICAL substance notification deadlines continue to populate the regulatory horizon. For companies active in worldwide markets, it's crucial to review and meet all important notification and registration deadlines in each country. This article focuses on South Korea's policy and explains why it's essential to meet these deadlines.

In 2006, when the European Union (EU) kicked off its Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) regulation, it sparked a seemingly unending series of country-specific chemical notification/registration regulatory requirements critically important as a prerequisite to engage in global commerce. Many countries, including the U.S., have since undertaken and updated their chemical notification programs. Presently, Asian countries, most notably South Korea, are updating their chemical programs.

The South Korea amended its Act on Registration and Evaluation, etc., of Chemical Substances (K-REACH) on January 1, 2019. All existing chemical substances (i.e., substances listed on South Korea's current chemical inventory) manufactured in or imported to South Korea at greater than or equal to one ton per year are now subject to registration. This means if you are manufacturing chemical substances in or exporting into the South Korean market, you need to be aware of these registration requirements.

Existing chemical substances must be pre-registered by June 30, 2019. Pre-registered substances benefit from registration grace periods that allow those substances to be imported without full registrations.

Who needs to pre-register? Any person manufacturing or importing existing chemical substances greater than or equal to one ton per year. Just as with the EU's REACH regulation, foreign manufacturers/producers who export existing chemicals to South Korea may appoint an "Only Representative," as the legal entity, to pre-register chemical substances on their behalf. This is an especially useful tool allowing companies without "boots on the ground" to work with a local entity to discharge their chemical registration obligations.

How do you determine if you have an existing chemical substance? Search the Korea Existing Chemicals List (http://ncis.nier.go.kr/en/main.do) for substance status. Substances not listed, designated priority existing chemicals (PEC), or considered exempt are not eligible for pre-registration.

What are the consequences if pre-registration isn't complete by deadline? If a substance isn't pre-registered by June 30, 2019, the registration grace period is inapplicable. Substances not pre-registered will require registration before manufacture or import. Substances not pre-registered or registered are subject to suspension of manufacture/import/use/sales. For commercial entities with business interests in South Korea, any suspension or cessation of business operations would have devastating consequences and could result in lost sales, contractual disputes and related misadventures.

What information is needed to pre-register? To pre-register an existing chemical, the following information is necessary:

- The name of the chemical substance;
- Expected annual manufacture/import quantity;
- Classification and labels of the substance;
- Use details;
- Name/contact information of the manufacturer or importer; and
- Any other information specified under the Ordinance of the Ministry of Environment.

Global commerce requires chemical accountability; chemical notification and registration requirements are here to stay and will proliferate over time. It's critically important for stakeholders to recognize this fact of business life, institutionalize this new reality, and monitor and comply with all such requirements. The consequences of failing to do so are significant. Global commerce can come to a dead stop for an entity that is ill-prepared to demonstrate compliance. Such failure can invite regulatory sanctions, commercial peril, and brand reputational damage, among other unpleasant and costly consequences. The good news is many opportunities exist to find and secure support for satisfying these requirements and thus ensure commercial continuity.

LYNN L. BERGESON, Regulatory Editor
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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.

WASTEWATER TAKES A NEW TURN

More sites now view it as a resource rather than residue

By Seán Ottewell, Editor at Large

WASTEWATER TREATMENT is becoming an integral part of processes at many plants as more and more chemical makers worldwide strive to achieve or at least approach zero liquid discharge (ZLD). At the same time, developments in technology are helping both to increase the percentage of usable water recovered and the capture of potentially valuable contaminants.

“The bottom line is that companies are trying to reuse and recover as much water as possible — whether it’s because of operating in a water-stressed area or because of local regulations regarding potable water use. The key is finding innovative ways to increase water recovery while at the same time preserving overall process reliability,” says Bill Heins, Bellevue, Wash.-based global leader for market development, Suez Water Technologies & Solutions.

For example, if a plant needs to go to ZLD, then Suez works to increase water recovery on the membrane side and so make evaporator/crystallizer equipment smaller (Figure 1) — with an associated decrease in operational cost (opex) and capital investment (capex). "There is a big drive to use this approach now," he notes.

Another approach involves very high recovery reverse osmosis (RO) systems. "The reject from these doesn't need an evaporation unit at all and can pass straight into a crystallizer. So, if you can increase RO-based water recovery, you can decrease size and, therefore, cost and energy consumption of the overall ZLD system," explains Heins.

Standardization and modularization of ZLD equipment are increasingly popular, too, because they can reduce expensive field rework and speed up construction, he observes. Suez began its modularization work 15 years ago and now is in its fifth generation of modular design, Heins adds. The company can modularize any required technology. "So, for example, in remote regions everything is fully containerized — RO, nanofiltration (NF), whatever technology is needed."

"We have a lot of interesting innovations, for example on tackling pressure limitations and temperature limitations. New materials and designs are certainly helping us to overcome these challenges," he says.

One example is with high temperature (100°C) RO. Inherently hot waste streams need cooling prior to processing in a membrane system. However, this often results in unwanted precipitation of organic compounds and increased fouling potential. "So, it many cases, it may be desirable to design membrane systems to operate at elevated temperatures," notes Heins.

Another example is on the thermal side, with the evaporators and crystallizers used in ZLD processes: "You can get very high concentrations of salt which can be very corrosive. So, we are working to operate processes at lower temperatures — which will also lower the cost of materials of construction."

High temperatures and pressures and extreme pH conditions remain challenges but the key, according to Heins, is integration of your wastewater treatment technologies.

Most of Suez's wastewater treatment projects fall into two categories: recovery and reuse of water from a wastewater stream to reduce demand for fresh water; and that plus resource recovery. In the latter category, the company is becoming a specialist in lithium recovery from its involvement in treating wastewater from both mining and plants.

POTENT PAIRING

DuPont Water Solutions (DWS), Edina, Minn., has found that teaming ultrafiltration (UF) and RO filtration technologies can purify up to 70% of wastewater for reuse.

"The contamination level of the wastewater entering these UF and RO systems is usually elevated compared to typical surface or well water treatment systems; therefore, we've focused on further developing UF and RO technology with fouling resistance to improve the operational reliability," explains DWS principal research scientist Tina Arrowood.

Companies in water-scarce regions now are pushing to recover up to 95% of their wastewater for operational reuse, she notes. However, that poses challenges

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DOWNSIZING

Figure 1. Making evaporator/crystallizer equipment smaller decreases opex and capex. *Source: Suez Water Technologies & Solutions.*

because the levels, e.g., of suspended solids, hardness, dissolved organics and salt, exceed those suitable for traditional RO recovery methods.

Here, DWS uses a minimal liquid discharge (MLD) approach that involves tailoring a core set of technologies — RO, UF, NF and ion exchange (IX) — to the specific application to maximize high-quality permeate for reuse. The company continually updates its technologies; five different filter elements and membranes were introduced fairly recently.

"By combining these technologies, the MLD process can convert wastewater into a reliable source of water for an industrial plant. Applying MLD tackles industrial water management on both ends and reduces dependency on freshwater withdrawal, while also lowering the industrial plant's discharge footprint in both liquid and solid waste," says Arrowood.

Successful operation requires the proper sequence of RO element types throughout a treatment train to meet specific water recovery and reuse targets.

Here, she cites the example of a textile mill whose wastewater contained 7,000 mg/L of total dissolved solids and 150 mg/L of COD after primary and secondary wastewater treatment. These values rose to 140,000 mg/L and 3,000 mg/L, respectively, after 95% of the water was recovered by an MLD process.

"Treating water over this range of composition requires more than one RO element type to optimize the energy, reliability and permeate quality throughout the pure water recovery process. The choice of RO element and the attributes that element provides must align with the changing treatment demands as the wastewater is concentrated," she stresses.

Employing an MLD approach in conjunction with ZLD can reduce costs by up to 60%, Arrowood asserts. MLD recovers with inexpensive membrane processes up to 95% of the wastewater for reuse and reduces the volume of water requiring final dewatering via expensive thermal ZLD methods.

As an example, she points to a chemical plant in China that was using RO elements in an MLD process to recover an additional 90% of purified water from the concentrate of its primary wastewater recovery system and, thus, decrease the wastewater volume needing thermal dewatering to achieve ZLD. A year later, the site upgraded its MLD process by adding a NF unit to treat the concentrated waste brine stream from the RO system and convert more than 60% of this water into a purified sodium chloride solution for reuse. This upgrade enabled reducing by half the nearly 40 t/d of solid ZLD waste destined for landfill.

Innovations such as these together with new product releases such as durable, fouling-resistant elements will fill critical gaps in cost/performance in a variety of water treatment and reuse applications, Arrowood believes.

BETTER BIOLOGICAL PROCESSING

Meanwhile, Microvi, Hayward, Calif., has developed a proprietary platform called MicroNiche Engineering (MNE). The company uses this to create novel biocatalysts that intensify biological processes by increasing the organism density by orders of magnitude while reducing reactor sizes and simplifying the process treatment train.

"We use MNE to re-create features of an organism's natural habitat, or microniche, which helps optimize the performance

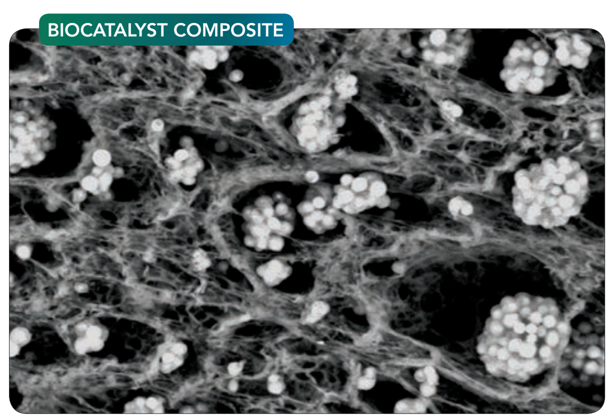

Figure 2. Scanning electron micrograph shows structure that underpins enhanced performance of organism. *Source: Microvi.*

of organisms in industrial bioprocesses. While the development process is complex, the outcome is remarkably simple: nearly any organism optimized for nearly any bioprocess — deployed in the versatile format of an MNE biocatalyst composite," explains Ameen Razavi, director of innovation research.

In many cases, users simply can drop MNE biocatalysts into their existing reactor or vessel. A composite (Figure 2) can come in a variety of forms and geometric configurations to suit particular process requirements.

The company has developed more than 6,000 different composites so far. If an application requires removal of NO_x, SO_x and volatile metals from flue gases, for example, up to 100 may get tested to identify the single best-performing biocatalyst to use.

Because the high-density organism population is so controlled, the reaction doesn't produce biosolids. Treatment generally involves a single pass with the biocatalyst retained in the reactor at all times. Microvi's first commercial system, at a site in Australia, has run for a number of years with no recycle, recharge or replenishment of the biocatalysts, says the firm.

"The key advantages of the Microvi technologies include: ease of use, minimal maintenance requirements, robustness across changing operating conditions, longevity, the ability to work across a range of temperatures (including some applications, such as wastewater treatment, at temperatures as low as 4°C), and a reduction in lifecycle costs on the order of 30–50%," says Razavi.

The company's latest move is a tie-up with Scottish Water, Dunfermline, Scotland. It has installed a fully automated, purpose-built wastewater treatment pilot plant in Bo'ness, Scotland, with the aim of developing catalysts capable of reducing ammonia and organic carbon pollutants.

Here, it is using an existing, safe species of organism rather than creating a specific one for this waste. If the trial is successful, the same biocatalyst could be applied across a broad spectrum of wastewater treatment plants.

"Our biggest engineering challenge is optimizing the integration of the biocatalyst into existing tanks and re-using mechanical equipment to minimize costs. As a result, we are testing different configurations to give us maximum flexibility, given the variability in asset types we would come across," he notes.

Razavi describes the results of phase one testing at the plant as

exceptional. Scottish water now has extended the trial until June to enable investigating different process configurations. If the extended run achieves the same level of success, a full-scale demonstration plant would be the logical next step, he believes.

Wastewater treatment isn't the company's only focus. The technology also can play a role in providing clean water from ground and surface water, recovering valuable nutrients such as phosphorus from wastewater, and converting a variety of solid and gaseous feedstocks into fuels, chemical intermediates, and specialty chemicals, it says.

TREATMENT AS A SERVICE

For its part, InOpSys, Mechelen, Belgium, manages typically non-recyclable process streams by recovering water, raw materials and valuable components such as zinc and lead with an on-site flexible modular mobile unit (FMMU) that uses an advanced oxidation process. The company primarily focuses on biopharmaceuticals and fine chemicals.

A plant doesn't incur any capex for the FMMU; instead, it pays based on the quantity of treated wastewater. That wastewater then can go to the site's own treatment facilities rather than to offsite incineration.

"We design, test, construct and operate the FMMUs on-site. The service is offered as an opex," explains CEO Steven De Laet.

Janssen Pharmaceutica, Beerse, Belgium, exemplifies this strategy in action, he says. Janssen manufactures over 30 products at Beerse, including ovarian and breast cancer treatment doxorubicin and Crohn's disease treatment ustekinumab.

The company is committed to closing the material loops in its manufacturing processes and turned to InOpSys in an effort to tackle a difficult-to-process waste stream containing zinc. Janssen has had to store that waste stream and then send it to an industrial incinerator.

The two companies worked together to develop a recycling process to remove and recover the zinc from the waste stream. The zinc essentially reacts with sodium sulfide to form zinc sulfide, which is extremely insoluble in water. This is removed as a zinc sludge and then used by metal specialist Nyrstar, Balen, Belgium, in its zinc production process. Because the wastewater stream now is devoid of zinc, it can go to Janssen's onsite wastewater treatment plant.

"We are now expanding our activities within Europe and perhaps also North America," notes De Laet. ●

PROPERLY PREPARE FOR A NATURAL DISASTER

Take some sensible steps now to avoid issues with hazardous wastes

By Wade Scheel, Stericycle Environmental Solutions

THE 2017 hurricane season was one of the most expensive in U.S. history. Combined, Hurricanes Harvey, Irma, Maria and Jose exceeded $200 billion in damages. In 2018, the world watched as Hurricanes Florence and Michael wreaked havoc in North Carolina and the Florida Panhandle. Hurricane Michael was recorded as the strongest storm to make landfall in the U.S. since Hurricane Andrew in 1992. So, as the 2019 hurricane season starts, operators of chemical plants should get ready.

Unfortunately, too many businesses focus more on how to address the aftermath of a hurricane — or other extreme weather, such as tornados and flooding, that also can lead to significant damage — than preparing for the next event.

Indeed, many facility operators aren't equipped to handle weather-related emergencies. One of the most dangerous and costly mistakes chemical plant managers can make is neglecting to prepare hazardous waste for the impact of natural disasters.

To reduce the risks of injury, environmental harm or regulatory penalties, a successful response to a disaster requires extensive expertise and knowledge of hazardous materials and waste management. Often, natural disaster response involves emergency response to one or more spills, e.g., of fuels, chemicals, U.S. Department of Transportation (DOT) hazardous materials and U.S. Environmental Protection Agency (EPA) hazardous wastes. This necessitates successfully performing critical tasks such as identifying unknown substances, spill containment, proper waste handling and cleanup.

Chemical industry leaders must place utmost importance on determining how to protect hazardous materials and wastes, as well as how to clean and dispose of them following a disaster. To avoid putting facilities, inventories and profitability at risk, they must take proper precautions so that operations are resilient in the event of a disaster, especially one resulting in high winds, heavy rainfall and flooding.

The following tips will help you better prepare to protect hazardous waste in chemical facilities before and during extreme weather emergencies.

IDENTIFY HAZARDOUS WASTE

Before any action steps can take place, it's necessary to understand what's considered hazardous waste. The EPA defines hazardous waste as "waste with properties that make it dangerous or capable of having a harmful effect on human health or the environment." Once an item with hazardous properties no longer is usable, it's deemed hazardous waste.

The EPA regulates hazardous waste under the Resource Conservation & Recovery Act (RCRA) to ensure these wastes are managed in a compliant manner. RCRA mandates that generators of hazardous waste are responsible for waste from

the time of generation to its final destruction, and sees that these wastes are managed in ways that protect human health and the environment.

Hazardous waste items have ignitable, corrosive, reactive or toxic characteristics. To determine whether a product is considered hazardous waste, review its safety data sheet (SDS), manufacturer information, label and ingredients. You also can check specific guidelines provided by hazardous management service providers.

CREATE AN EMERGENCY RESPONSE PLAN

A lack of diligent preparation can lead to increased destruction and financial loss in the aftermath of a weather-related disaster. When creating an emergency response plan for a natural disaster, you should consider several factors.

First, facilities must assess their risk for natural disaster incidents. For example, a business on the Pacific Coast has the greatest risk of being impacted by earthquakes, wildfires and mud slides. In contrast, a facility on the Atlantic Coast more likely may encounter hurricanes and flooding. By identifying the most probable hazards, sites can plan to handle hazardous waste properly.

Next, plant operators should determine emergency response roles. Consider who will make crucial decisions in the event of a disaster, who will be involved in managing hazardous waste, and who will assist in its removal.

Additionally, an appropriate emergency response plan should include proper communication protocol. One common mistake organizations make when preparing for a disaster is not putting a thorough communication plan in place. Particularly in the event of a disaster, a lack of communication or a breakdown in delivering important messages is problematic and can pose hurdles, especially after the incident reaches the public eye. Proactive planning with local emergency responders is key to obtaining the response and support needed when an emergency strikes.

Lastly, keep in mind that when an area has been hit by a major hurricane, roads and access points often are blocked from entry. So, you should identify your emergency response partner in your emergency response plan so that its staff can gain entry to the site when there are restricted access areas. An emergency response partner also can handle all contact with local law enforcement and response teams to find out when it's safe to travel to affected facilities and begin the hazardous waste cleanup process.

SAFEGUARD WASTE

Before disaster strikes, plant managers can take steps to prevent waste from releasing inside the facility and into neighboring communities. If possible, remove excess waste and hazardous materials from the facility before any inclement weather hits.

Most chemical processing facilities have an abundance of bulk waste. While larger containers often are secured and don't migrate in the event of a disaster, smaller containers run the risk of being lifted, carried or turned over, releasing hazardous materials into local communities and waterways. There's also a potential risk of release in storage areas with an overflow of materials. To prevent these issues, keep hazardous waste storage areas clear, and take steps to mitigate items from spreading. Containers should be closed, sealed and relocated to a reinforced area of the facility or to an off-site space. Elevating containers can help prevent a release, especially if flooding is a concern. In any case, clearly identify, segregate and don't block off storage areas.

Once extreme weather has subsided, teams should check the status of the materials on-hand and decide what's been compromised, what must be removed and what should be replaced. Pumping out sewage tanks and disposing of incomplete manufactured articles also is a good idea.

RESPOND TO CONTAINER LEAKS

In dealing with a container leak, the two most important steps are identifying the spilled material and securing the container for cleaning. For compliance and safety, you must monitor the entire process to ensure timely and accurate communication, proper documentation and appropriate procedures.

After identifying the leaking material and assessing any immediate threats to human health and the environment, expert technicians should secure both the container and the surrounding area while also ensuring that no additional material can escape. It may make sense to move the container to a secure area, with special attention paid to weather and wind direction to maximize safety. Technicians also may perform air monitoring to check oxygen levels.

Cleaning requires use of specialized equipment, which may include HEPA-filter vacuums, salvage drums and disposable cleaning products. Technicians will separate damaged or contaminated items from any items deemed safe. Upon completion, the facility operator should request a detailed action report that includes images, a call log and supporting documentation.

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IMPLEMENT A POST-INCIDENT RESPONSE PROCESS

Unfortunately, many facility managers don't take the necessary steps for managing hazardous waste until regulatory compliance dictates otherwise. However, ignoring regulatory mandates can severely undermine the organization's brand, the safety of its employees and the trust of the community.

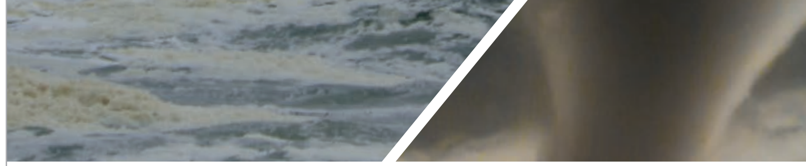
A post-incident response process and plan helps ensure the facility has taken the necessary steps to reduce further risk following a natural disaster. One important aspect is minimizing personnel exposure. So, when beginning the post-incident response process, it's important to restrict access only to key personnel.

Plant operators then must verify any impacted building's structural integrity to prevent catastrophic failure, which can result in injuries, severe damage and even death. City or government engineers must clear individuals to enter the building. Even after being allowed to enter, proceed with caution. Waste storage areas aren't necessarily the only problematic areas. The severe weather will have shifted many items: shelving may have collapsed; the roof may have blown off; and light fixtures may have fallen. During remedial efforts, team members will need to break down, identify and segregate all hazardous materials.

Examine all areas of the site to determine if products require replacement, to prevent chemicals from entering waterways and to dispose of incomplete articles that no longer are usable. Chemical processing facilities typically involve higher volumes of bulk waste, likely resulting in more significant damage during extreme weather.

UNDERSTAND THE IMPACT OF NON-COMPLIANCE

There are many repercussions of improperly handling hazardous waste at any given time, including in the event of a disaster. Organizations that don't understand federal, state and local regulations face environmental, health and safety risks, as well as chemical destruction. In addition, facilities may incur significant monetary penalties. While the financial burden of non-compliance is substantial, the negative impact these public fines have on brand perception can be even more damaging.



Because the public is showing growing concern for environmental issues, local and even national news outlets are quick to pick up on any perceived offenses by corporations. In addition, the proliferation of social media means negative news about environmental fines or improper disposal of hazardous waste spreads quickly and pervasively across those channels.

Common missteps that could result in fines include:

- lack of, or improper, labeling;
- open containers of hazardous waste onsite;
- dumping hazardous waste down the drain;
- having no or inadequate hazardous waste manifests;
- failing to properly train employees in hazardous waste management, handling and emergency preparedness;
- non-compliance with hazardous waste generator regulations; and
- not having hazardous waste determinations on file.

The average cost of a proactive environmental compliance program for hazardous waste varies but, with millions of dollars in potential fines at risk for non-compliant practices and consumer loyalty at stake, organizations must be well informed about changes from the EPA and update their hazardous waste management programs accordingly.

SEEK ASSISTANCE FROM EXPERTS

Even with a proper emergency response plan in place and great awareness of the importance of regulatory compliance, process plants should enlist the help of hazardous waste removal experts. Professional response is essential to several high-pressure tasks, such as identifying unknown substances, managing spill containment, handling hazardous waste and overseeing cleanup.

Substance identification is one of the most important responsibilities in any emergency response. Trained experts not only can identify numerous chemicals and compounds but also can assess any potential dangers. They can quickly and accurately identify an unknown substance and provide its SDS, which informs the on-site technicians of proper handling procedures, physical data, potential health hazards and equipment requirements for storage and disposal.

Without a pre-existing agreement in place, it could take more time for you to line up a third party to access and service your facility during a hurricane or other natural disaster, as its priority will be to tend to existing customers first. Therefore, it's important to find the best emergency response partner for your facility before a disaster rather than waiting until the damage has occurred.

In the aftermath of a natural disaster, waste and environmental concerns are only a part of a larger, complicated picture. Every hazardous waste emergency response situation must be managed with a commitment to safety and full compliance. When disaster strikes, follow all applicable regulations from the initial response to cleanup and ultimate closeout of all paperwork and reporting.

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IMPROVE YOUR COOLING TOWER TREATMENT

Environmentally friendly chemistry may offer better corrosion and fouling protection

By Brad Buecker and Ray Post, ChemTreat

COOLING WATER plays an essential role in process operations at many plants. For a majority of these facilities, the cooling system contains one or more cooling towers. The metals used in the tower, cooling water piping and heat exchangers may include carbon steel, galvanized steel, copper alloys and stainless steel. Protecting all these metals from corrosion and minimizing scaling and microbiological fouling in cooling systems pose ongoing challenges. Adding to the difficulty, operators face emerging restrictions on the discharge of a number of impurities in cooling tower blowdown, including phosphorus, zinc and other metals, biocide residuals, and dissolved and suspended solids. This article examines evolving chemistry that provides improved corrosion and fouling protection while also being more environmentally friendly than previous treatment methods.

MICROBIOLOGICAL FOULING

This often is the most problematic and severe issue in cooling water systems (Figure 1). Even with fresh water as the makeup source, such fouling can occur rapidly. The risk has gotten even worse at many plants that now have switched to alternative, lower quality water, e.g., secondary wastewater plant effluent, for plant makeup. Such supplies potentially can introduce large quantities both of nutrients (nitrogen species and phosphorus) and food (organic compounds) to cooling water, thereby increasing the potential for fouling.

For decades, plants have used some form of oxidizing biocide as the core treatment for microbiological control. Gaseous chlorine once was the common choice due to low cost but safety concerns influenced movement toward safer compounds, at first liquid bleach. However, many makeup water supplies are mildly alkaline, and the most common cooling tower treatment programs for the last four decades have relied on alkaline chemicals — and alkaline conditions can render chlorine compounds somewhat ineffective. Consider the reaction when chlorine is first injected into water:

$$Cl_2 + H_2O \Leftrightarrow HOCl_{aq} + HCl_{aq} \quad (1)$$

Hypochlorous acid, HOCl, is the killing agent. As pH rises, HOCl increasingly dissociates:

$$HOCl_{aq} \Leftrightarrow H^+_{aq} + OCl^-_{aq} \quad (2)$$

The hypochlorite ion, OCl^-, is a much less powerful killing agent than HOCl.

A common enhancement to this chemistry came from blending bleach and a bromine compound, usually sodium bromide (NaBr), to produce HOBr, the bromine analog to hypochlorous acid. It is an effective oxidizer and dissociation occurs at a higher pH than HOCl, producing more of the effective undissociated acid. Now, though, other alternatives are becoming more popular due to their ease of application and improved ability to kill microorganisms.

A key aspect of any program is to treat the water before organisms can settle on cooling system surfaces. Organisms that attach and multiply rapidly will form a slime layer for protection and, within this film, numerous microbial colonies will develop, including anaerobic bacteria like the sulfate reducers whose metabolic byproducts can induce severe corrosion (Figure 2).

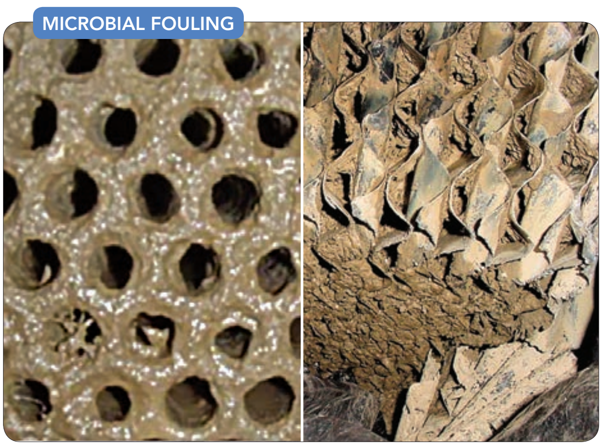

Figure 1. Severe fouling can afflict a heat exchanger (left) and tower fill (right) in a cooling water system.

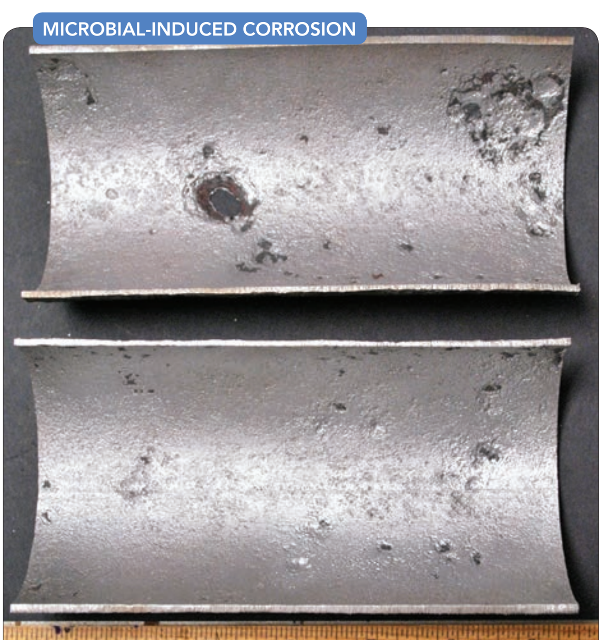

Figure 2. Metabolic byproducts of anaerobic bacteria such as sulfate reducers can cause pitting.

Compounds such as monochloramine (NH_2Cl) and monobromamine (NH_2Br) have exhibited strong results in attacking settled microbiological colonies. Their efficiency appears due to the compounds being weaker oxidizers than chlorine or bromine; they aren't consumed by the slime layer but rather penetrate to the microorganisms underneath to kill them. Production of the compounds must occur in situ by mixing bleach, dilution water and ammonium salts just prior to injection.

Meanwhile, hydantoins, a group of compounds known for a long time, now are being employed in new ways. Hydantoins are ring structures; a common product is 1-bromo-3-chloro-5,5-dimethylhydantoin.

When this compound dissolves in water, it releases chlorine and bromine that then serve as the biocide. The halogenated hydantoins typically are manufactured as granules or tablets. These commonly are loaded into a compartment connected to a side-stream loop on the cooling water system. The product slowly dissolves and is introduced to the main cooling water.

New chemistries have been developed where non-halogenated hydantoin molecules are in a liquid solution and are introduced separately from an oxidizer. The hydantoin then serves to stabilize the oxidizer and improve residence time in the cooling water. In contrast to ammonium salts that can react vigorously if contacted with bleach without adequate dilution, you can safely blend liquid hydantoin with bleach in the injection line. These formulations may include a biodispersant to break apart the protective slime layer to allow the biocide to better contact the underlying organisms.

Plant personnel often seem to overlook the use of non-oxidizing biocides to supplement the oxidizing compounds. These non-oxidizing products function either by damaging the cell wall of organisms or interfering with metabolic processes within the cells. Table 1 lists properties of some of the most common non-oxidizers.

Non-oxidizers are more persistent and typically are shot fed to the cooling system only two-to-three times per week in conjunction with oxidizers. Due to their persistence, they are more effective in dead legs, closed cooling systems and under layup conditions. However, you must carefully evaluate the microbial species in the cooling water to determine the most effective non-oxidizing biocides because their action targets specific metabolic functions. Always apply antimicrobial compounds, whether oxidizing or non-oxidizing, in accordance with the directions on the label. Where discharged to "waters of the state," you must incorporate them into the plant's National Pollutant Discharge Elimination System (NPDES) permit. Also, as with all chemicals, safety is an absolutely critical issue when handling biocides.

CORROSION AND SCALE CONTROL

A critical aspect of proper water treatment equipment design and chemistry program selection is obtaining

comprehensive and, ideally, historical raw water quality data. Often, plant owners and technical personnel underestimate the importance of complete raw water data and prepare project specifications with an incomplete water analysis (see: "Don't Foul Up Your Water Treatment Program," http://bit.ly/2IQvp6Y). Raw waters typically contain many impurities, a number of which can combine to form deposits or influence corrosion. Table 2 lists several common impurities and their potential consequences.

Additional deposition of silicate, sulfate and fluoride salts, and other compounds also is possible.

For the last four decades, the core of the most common cooling tower treatment method has been inorganic and organic phosphate (also known as phosphonate) chemistry to control both scale formation and corrosion. Supplemental zinc addition provided further corrosion protection. However, new developments are leading to a significant change.

Phosphate/phosphonate programs emerged as the preferred technology with the phase-out of chromate-based corrosion inhibitors in the 1980s due to environmental concerns. The chemistry can be effective but is much more complex than chromate treatment. Upsets in chemical feed or control, or changes in makeup water chemistry may lead to deposition and corrosion. Now, another factor —increasing restriction on discharge of phosphorus and zinc in cooling tower blowdown — is propelling a transition in treatment methods. Many areas of the country are controlling, at least from point sources, discharge of phosphorus to the environment because it's the limiting nutrient for toxic algae blooms (Figure 3), such as the severe on-going ones in Florida.

New non-phosphorus/non-zinc programs not only

NON-OXIDIZING BIOCIDES

Chemical	Advantages	Disadvantages
2,2-dibromo-3-nitrilopropionamide (DBNPA)	Fast acting, effective against bacteria, degrades quickly to non-hazardous byproducts.	Degrades quickly above pH 9, not very effective against fungi and algae. Degraded by reducing conditions.
Glutaraldehyde	Effective against sulfate-reducing bacteria (SRB).	Incompatible with ammonia and some amines. Weak on algae.
Isothiazoline	Effective against bacteria, particularly nitrifiers, and fungi. Works well with oxidizing biocides. Active over a wide pH range.	Skin sensitizer. Degraded by sulfide, sulfite and reducing conditions.
Quaternary amines	Effective against most microorganisms, particularly algae. Active over a wide pH range.	Can cause foaming. Efficacy reduced by hardness. Interacts with anionic dispersants and fluorescent tracers.

Table 1. These products either damage the cell wall of organisms or interfere with their metabolic processes.

COMMON RAW WATER IMPURITIES

Impurity	Potential Problems
Calcium ion (Ca^{2+})	Can react with alkalinity, sulfate, silica and other ions to form hard and insulating scales. Scaling most often occurs in systems with cooling towers, where the water "cycles up" in concentration due to evaporation.
Magnesium ion (Mg^{2+})	At alkaline pH, can react with silica to form a hard scale.
Silica (SiO_2)	The most complicated of all impurities. At acidic pH, can deposit homogeneously. As pH rises above 8, can combine with magnesium and calcium to form scale.
Chloride	A serious corrodent, particularly of stainless steel because the chloride ions penetrate the steel's protective oxide layer and induce pitting.
Sulfate	Can combine with calcium to form hard deposits. Also a corrosive agent, although not as problematic as chloride.
Dissolved oxygen	A primary corrodent of carbon steel.
pH	Metals such as carbon steel are most stable in mildly alkaline water. Corrosion rates increase with increasing acidity; however, in certain circumstances, significant corrosion will occur if the water becomes too alkaline. High pH also influences some scale formation mechanisms, particularly calcium carbonate.
Dissolved solids	The total dissolved solids (TDS) in the water contribute to its conductivity. Increased conductivity allows current in electrochemical cells to flow more easily, increasing the corrosion potential of the water.
Suspended solids	Materials such as dirt, metallic particles and other solid debris can contribute to fouling of cooling water systems.

Table 2. Raw water typically contains many impurities.

Figure 3. Phosphorus in cooling water blowdown is a key nutrient for blooms such as this one. *Source: Jesse Allen and Robert Simmon, NASA Earth Observatory.*

eliminate such discharges but also can provide an additional benefit. Some new chemistries, e.g., reactive polyhydroxy starch inhibitors (RPSIs) such as FlexPro, offer less potential for fouling and much better corrosion protection than the phosphate-phosphonate programs. Unlike the phosphate-phosphonate treatments, which rely on deposition of such products as calcium phosphate, iron phosphate and zinc hydroxide for corrosion inhibition, an RPSI, per the functional groups on the molecules, actually forms a surface barrier on metals.

On a pound-per-pound basis, RPSI currently is competitive with phosphate/phosphonate treatment methods. Moreover, it significantly improves corrosion protection, more than tipping the scales in favor of the new chemistry. However, its application, like that of any other new technology, requires careful evaluation of process conditions to ensure success. The product is sensitive to excessive sulfate concentrations in the water, although it shows excellent results in protecting metal surfaces from chlorides. Some users, in trimming feed rates to perceived ideal conditions, have reduced the concentration too far, which, in turn, allowed localized corrosion sites to develop. Difficulties have arisen in cooling waters with

high iron concentration (which can pose problems under many circumstances). Here, iron bacteria form black, unsightly colonies, particularly if the biocide feed is insufficient. These deposits provide a quite nasty example of the consequences of inadequate microbiological control.

Another important issue is the location of corrosion coupons for monitoring product performance. In general, corrosion rates increase with increasing temperature. Corrosion coupons placed in cool locations of the system may not accurately indicate performance at other spots, particularly the surfaces of heat exchanger tubes. Also, systems that previously have suffered corrosion and rusting likely will require a significantly higher dosage than necessary with new, clean systems.

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KEEP COOL

Many plants appreciate the need for proper treatment of cooling water. After all, fouling, scaling and corrosion in a cooling water system can cost a site millions of dollars in lost heat transfer and equipment damage. Today, additional factors such as the environmental impact of makeup and discharge chemistry heighten the stakes even more. So, facilities should keep up-to-date on treatment options and reconsider their programs. ●

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Effectively

Consider six tips for filtration that also minimize leakage

By Colter Marcks, Donaldson Co.

VIRTUALLY EVERY industrial chemical process requires compressed air. It is used to texturize products, dry sterilized equipment, form containers, move ingredients through lines, and serve as protective blankets around product stored in tanks. As essential as it is, compressed air also can be a prime source of contamination.

This problem is addressed by standards for clean, dry air — chiefly the International Organization for Standardization's ISO 8573-1, which defines contaminants and specifies a range of purity classes for particular processes. Meeting this standard requires careful treatment and filtration.

First, it's important to identify the probable contaminants in your facility. The impurity most prevalent in compressed air systems usually isn't rust or dirt, although equipment can shed solid particulates. The greater risk is liquid — a combination of condensate that forms as compressed air cools and lubricants that leach from oil-flooded compressors, which are the most common units at plants. Moisture itself is a threat, of course, but a water/oil mixture also is an ideal organic diet for bacteria, which multiply quickly in the warm crevices of compressed air lines.

Thus, keeping air dry and oil-free is critical to product quality and safety. This typically requires a series or "train" of filters and dryers. Although each facility is unique, appropriate treatment usually involves prefiltration in the utility room as well as point-of-use filtration before compressed air contacts a product.

Remove Contaminants from Compressed Air

Prefiltration in the utility room usually calls for:

- a coalescing filter (1–5 µm) to remove oil and protect the refrigerated dryer;
- a refrigerated dryer to condense and remove water content;
- a cyclone separator to mechanically drain remaining liquid condensate; and
- a coalescing filter (1–5 µm) to eliminate aerosols.

Point-of-use filtration before compressed air contacts a product typically requires:

- an adsorption dryer to remove water vapor; and
- point-of-use filters (0.2 µm) to take out contaminants potentially picked up in system lines.

Filtration removes a surprising volume of oily water from compressed air. At room temperature, a filtration system designed to handle air traveling at 500 std. ft^3/min from an air compressor operating at 100 psi will might handle about 30 gallons of condensed water every 8 hours, notes the "Compressed Air and Gas Handbook." This volume varies from one climate to another and fluctuates daily with temperature and humidity changes around a plant.

COMMON MYTHS

Managing moisture content and contamination while keeping compressed air from leaking is a challenge in filtration. Unfortunately, six common myths often undermine efforts. So, let's look at them as well as tips for better results.

Myth 1 — The smaller the micron size the better. Truth: Focus on actual contaminants.

Carefully examine technical data sheets before selecting a filter. Not all filter manufacturers observe industry standards and their micron rating can give a misleading sense of filter performance. For instance, filters labeled 99.999% effective at an extremely small particle size, such as 0.01 µm, can seem impressive. However, that particulate size, which is 5,000 times smaller than the diameter of a human hair, actually is easier to catch than a 0.1-µm particle. More importantly, it's too small to be of any practical significance as a contaminant.

Instead, pay attention to *actual* contamination threats in your compressed air system and the micron sizes they represent. Aerosolized oil, for example, ranges from approximately 0.1 to 1.0 µm, depending on turbulence from elbows and bends in a system. Use the purity classes in ISO 8573-1 as a point of reference and specify filters validated for efficiency at the particle sizes of interest.

Also, look for equipment verified by a third party using internationally accepted filter test methods. For example, the Institute of Energy and

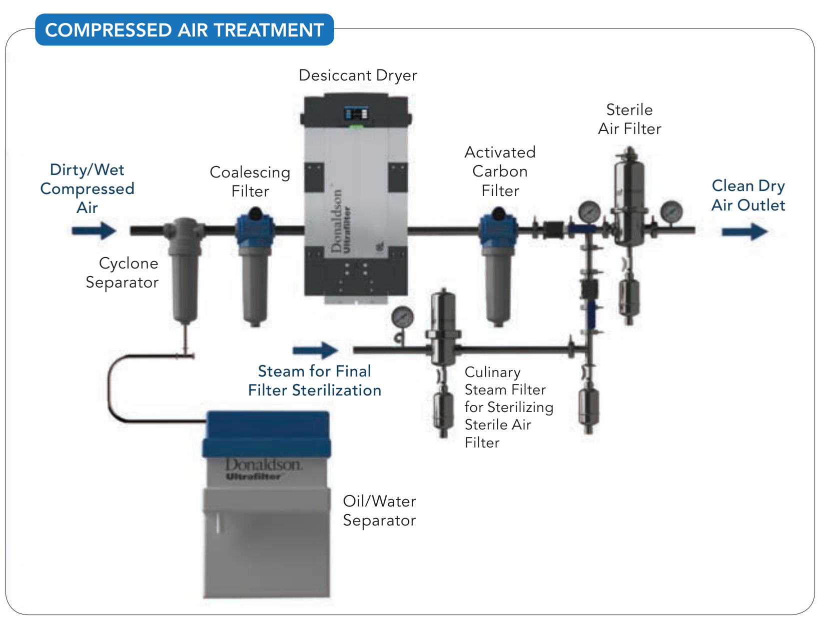

Figure 1. Proper treatment typically requires a train consisting of filters, dryers and separators.

Environmental Technology in Germany validates Donaldson filters using test method ISO 12500 to measure the removal of aerosols, vapors, water and particulates.

Myth 2 — All pressure drop data are equally valid. Tip: Insist on filters tested in a wet condition.

Because of higher pressure drop, it takes more energy to push compressed air through a restrictive filter. This is why it's important to specify filters tested in a wet condition. Compressed air filters remove water and oil aerosols, creating a liquid surface tension that restricts airflow. Reputable filter manufacturers will report wet pressure drop performance — the test method specified by ISO testing standards — on their technical data sheets. All else being equal, a higher performing filter will have a lower wet pressure drop.

Myth 3 — Filter media composition doesn't matter. Tip: Hydrophobic/oleophobic media can lower operating costs.

Cheap filters may appeal to the cost conscious. However, if their media is restrictive, they can make a compressor work harder, consuming energy that outweighs their lower price.

On just one filter designed for airflow of 1,000 ft^3/min, every additional psi of pressure to overcome restrictions adds energy costs of more than $1,000/yr (based on an estimate of 8,000 hr/yr at 10¢/kWh). Over a ten-year system life, extra energy costs for one filter could add up to $10,000 due to airflow restrictions over the life of the installation (Figure 2).

Both the material and configuration of filter media drive this airflow requirement. The best elements should catch liquid from the stream and immediately drain it away. This requires oleophobic and hydrophobic fibers, which shed oil and water and maintain a drier state. The media also should be free of binding resins, which block airflow.

In addition, composition is important for retentive filtration for biological processes. When propagating a desired micro-organism is crucial, protecting its cultures from being out-competed by harmful bacteria or viruses in compressed air is essential. So, if your process makes a microbial product or otherwise has a strong focus on purity, specify a bacterial-retentive compressed air filter designed for this purpose. General coalescing air filters are designed to remove oil and water, and don't have microbial contaminants factored into their design.

Myth 4 — Visual inspections will tell me to replace a filter. Tip: Monitoring and preventive maintenance are more reliable.

Replacing or regenerating filters at the right time is important. If you act too late, you risk contamination; too soon, you waste resources. "Walk-around" inspections aren't reliable. Instead, start with the manufacturer's recommendations and then evaluate the wear-and-tear patterns specific to your process.

You can do this by monitoring pressure drop across the filter with gauges upstream and downstream of the element. A drop in differential pressure (DP) beyond a prescribed level can spur attention. While some filter housings come with DP indicators, keep in mind these are sensitive devices that can malfunction with age. If a filter decomposes or is damaged, the increased airflow actually may register a false pass.

IMPACT OF PRESSURE DROP

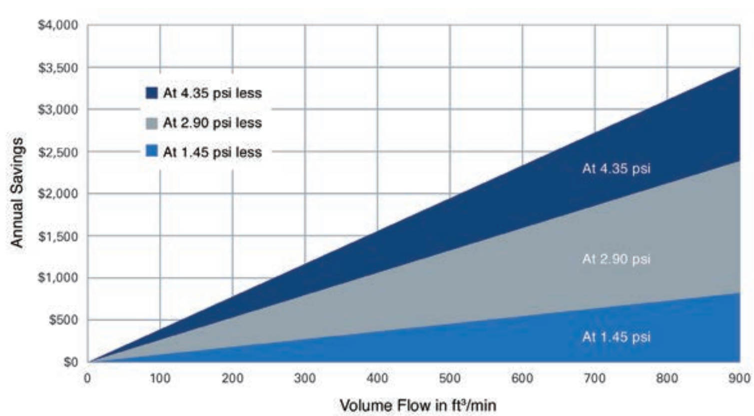

Figure 2. Even a modest decrease can lead to significant energy savings.

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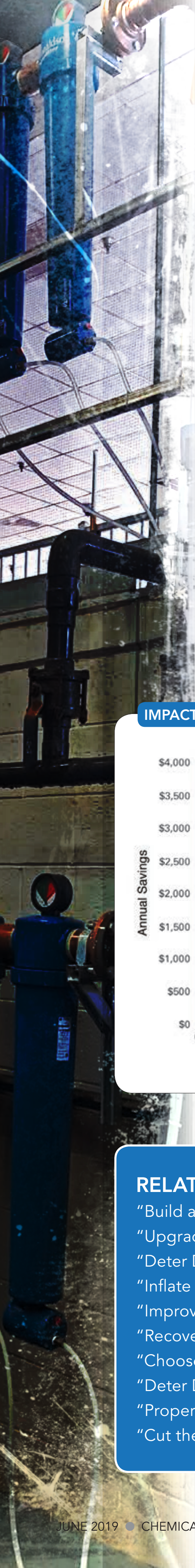

The Industrial Internet of Things (IIoT) undoubtedly will improve the accuracy of DP monitoring. Sensors and connectivity on filtration components will help make detection more precise. However, filtration still is a relatively new application for the IIoT, and installation costs can be quite steep across an entire facility. In the meantime, be on the safe side and schedule filter changes proactively and at conservative intervals. Regular replacements can improve system reliability and reduce the potential for energy loss or production downtime.

Myth 5 — Captured liquid can be manually drained. Tip: A zero-loss drain will prevent compressed air loss.

Water and oil extracted from compressed air lines require periodic emptying. As already noted, system lines can generate tens of gallons of oily condensate per day. Some technologies are better than others at draining this byproduct without wasting compressed air.

Older plants may use a ball valve on the bottom of the filter housing, which is manually opened to release condensate. Fluctuating temperatures and condensate load hamper predicting when to drain, though, and the manual draining can allow compressed air to escape. An alternative is an internal float drain in the housing, which opens when liquid accumulates. However, the float drain's valve often can plug with unsanitary sediment or jam open or closed, releasing air or failing to drain.

For these reasons, using a zero-loss (i.e., of compressed air) drain is a better option. Using electronic controls, such a drain (Figure 3) senses the liquid level and opens at a predetermined level. The valve closes before the liquid drains completely, thus retaining compressed air in the system. While these electronic drains represent a higher capital expense, they provide demonstrable net savings.

Myth 6 — Condensate can be dumped down the drain. Tip: An oil/water mixture requires proper disposal.

The oil/water emulsion collected from compressed air systems is classified as hazardous waste even if the proportion of oil is small. Environmental regulations prohibit the disposal of this mixture in any manner

that could contaminate a well, municipal water supply or groundwater. Overlooking this requirement potentially can subject a processor to fines.

You can pass your condensate through an oil/water separator to extract the oil from the condensate stream. The oil stream then can be put into a hazardous waste container and properly handled. The remaining water is clean enough to pour down a drain. Oil/water separators reduce the volume of waste a chemical processor must dispose of and comply better with environmental regulations.

ZERO-LOSS DRAIN

Figure 3. Such a unit drains automatically without loss of compressed air.

DON'T ERR WITH COMPRESSED AIR

As this article has highlighted, proper design and maintenance of filtration systems for compressed air are critical. Compare materials and data offered by filter manufacturers and consider return on investment rather than only initial capital costs. Obtaining a comprehensive evaluation of your system by a qualified process filtration consultant can be helpful. Work with suppliers that are knowledgeable about filter operation and maintenance needs from end-to-end and that offer equipment validated to meet objective standards. ●

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Get Smart About Control Valve Positioners

Advances in technology improve performance and foster predictive maintenance

By Jim Braxton, Badger Meter

THE QUEST by process plants to optimize efficiency and production capacity is leading to a greater focus on preventive maintenance. This, in turn, calls for maintenance preplanning and more active asset management.

Such efforts certainly should extend to control valves. After all, they play a critical role in most operations. A poorly performing control valve can cause significant losses because of shutdowns, lost production, reduced efficiency and unsafe events.

The positioners that maintain and control the valve setpoints can provide crucial insights. That's why plants increasingly are turning to smart valve positioners. These devices not only position the valve actuator highly accurately but also monitor and record data, and offer robust diagnostic functions as well as other features. Devices with integrated digital communications can give plant operators greater visibility and control over critical production assets, resulting in improved plant performance and greater operational efficiencies.

VALVE POSITIONER BASICS

A valve positioner is a device mounted on the actuator that exerts or reduces air pressure as necessary to ensure the valve achieves the correct position. When there's no positioner, the pneumatic (air) control signal goes directly to the actuator. Once installed, the positioner intercepts the analog/digital signal and outputs a pneumatic signal proportional to the bench range of the actuator.

A valve positioner acts as an interpreter between the control valve assembly and the control system. Its job is to translate output signals from the control system and adjust the air to the actuator that moves the valve to the desired position. The positioner also may take position feedback from the valve stem/shaft and send it back to the control system.

Generally speaking, control valve positioners come in three types:

- *Pneumatic positioners.* These receive a pneumatic signal from the controller and output a pneumatic signal to the actuator.
- *Analog (or electro-pneumatic) positioners.* Here, the input signal generally is 4–20 mA rather than pneumatic. These devices, which are mounted directly and axially to the actuator stem, suit quarter-turn rotary actuator applications.
- *Digital (or smart) positioners.* Such units also receive an analog signal or a communication protocol such as HART, Foundation Fieldbus or Profibus but their built-in microprocessors convert the analog signal to a digital signal for more precise control. Digital positioners also can offer diagnostic data, e.g., on valve position and friction as well as response history, that are invaluable for setting predictive maintenance schedules. Modern positioners not only collect data about the valve/actuator but also automatically let users know how the instru-

ment and its assembly are performing and assist with troubleshooting and maintenance.

Smart control valve positioners allow tighter control over the process variable by increasing the speed and accuracy of the actuator response. The positioner, by ensuring the valve is in the right place, helps in overcoming factors such as friction that affect performance as well as problems like non-linearity and deadband. In addition, positioners can amplify or reverse an input signal as needed.

DESIGN EVOLUTION

Control valve technology doesn't change as quickly as other areas of automation. Instead, valve products gradually evolve over time to keep pace with the changing user requirements and industry standards.

For example, while most valve positioners are side-mounted, new top-mounted designs use a linear connection that mitigates hysteresis between the positioner and actuator by feeding back the actual position of the actuator in a faster, more consistent manner. This approach provides significantly improved flow control.

Other recent developments enable smart digital valve positioners to deliver data regarding valve stroke and thrust, output pressure to the actuator, positioner temperature, valve seat/plug wear, high/low friction and valve performance.

Many users now are demanding that valve positioners provide predictive diagnostics — because it's critical to predict failures in the valve, control signal and positioner before they impede operations. Improvements in diagnostics play an important role by enabling the move from traditional corrective maintenance to predictive maintenance. Diagnostics with valve positioners also offer the ability to test valves to determine if maintenance or replacement is required.

Valve equipment manufacturers have developed positioner technology that provides real-time performance statistics. Their objective is to support methods for evaluation of valve health, operation and configuration. These capabilities, in turn, allow for predictive maintenance, intelligent alarm management, self-surveillance in accordance with NAMUR NE107 recommendations, and service management.

Some digital positioners come with valve diagnostic software as a Device Type Manager (DTM) for integration into control systems based on Field Device Tool technology. The positioner DTM enables the user to edit a complete "health" report on the valve with all data of configuration and diagnostics. In addition, it can control a partial stroke test that

PRECISION BATCHING

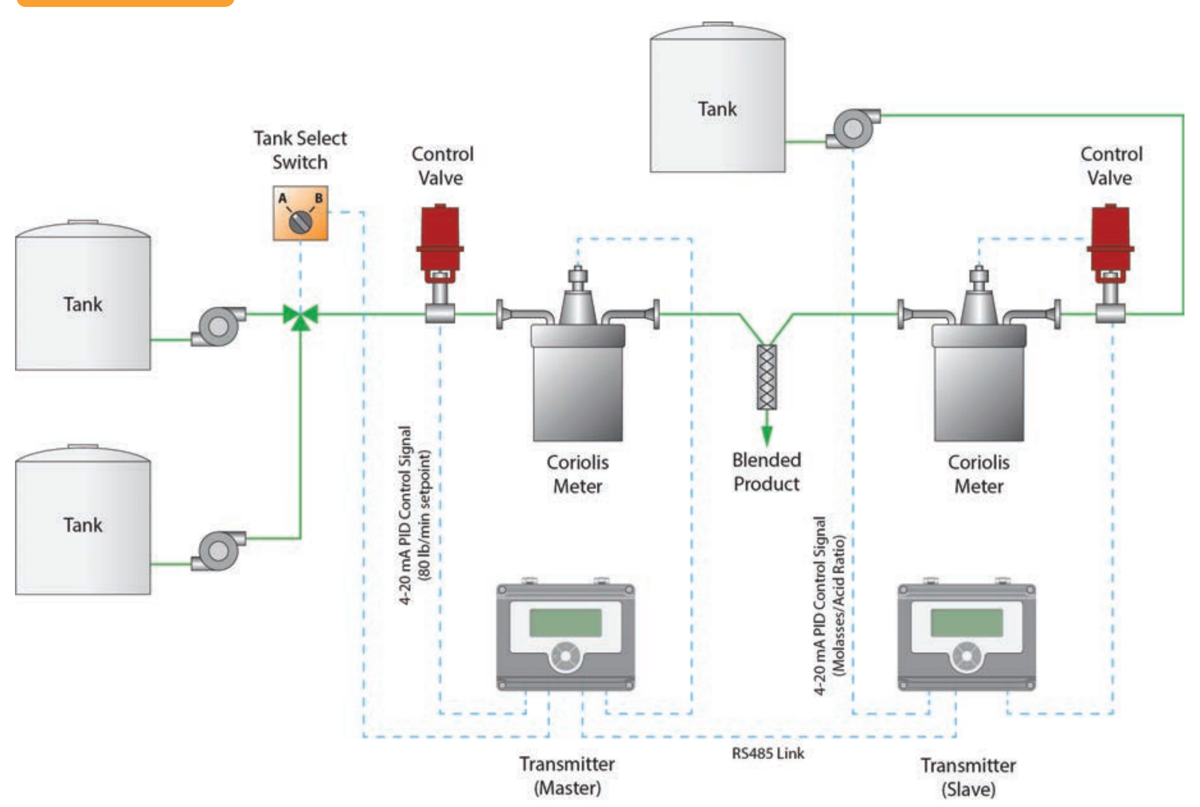

Figure 1. Successful and trouble-free operation depends upon careful equipment selection.

offers operators a tool to check the trouble-free function of emergency shutdown valves.

FUGITIVE EMISSIONS

Plants strive to minimize their fugitive emissions to keep employees and communities safe, lessen environmental impact, comply with stringent air-quality regulations, optimize energy consumption and maximize operating efficiency. Early detection of fugitive emissions via leak monitoring enables facilities to promptly schedule maintenance to curb potential air pollution and avoid fines.

There's no clear indication of just how much control valves contribute to overall gas and vapor leaks. Nevertheless, monitoring valves for fugitive emissions certainly is prudent. Fortunately, some digital positioners for pneumatically actuated valves feature comprehensive diagnostics tools that continuously check for fugitive emissions to help process plants meet the ANSI/FCI 91-1 standard and comply with regulators' emissions guidelines. Equipped with integrated network communication and utilizing specialized valve packing and pressure switch gauges, these devices — in the event of a leak — will trigger an immediate alarm, alerting system controls through a standard industrial communications protocol such as Profibus PA, Foundation Fieldbus or HART through ordinary discrete outputs; such positioners can be configured to close the valve without any external communication.

PROPER SELECTION

Control valves can play a huge role in helping a process plant improve productivity and efficiency. In most cases, ensuring an efficient and successful operation such as batching (Figure 1) requires a precise combination of valves, meters, sensors and other equipment.

You must consider several essential aspects to choose the correct valve positioner:

1. *Understand the technology.* The smart valve positioner has become the standard at process plants. However, too many end users aren't taking full advantage of its functionality. Doing so offers important operational benefits that can help a facility do more on a tight budget.

Using a smart positioner on control valves with rotary or linear actuators enables a plant to:

- implement precise control over operations;
- increase the speed of response to changes in the process;
- minimize valve stem packing friction and the resulting hysteresis;
- negate flow-induced reactions to higher pressure drops; and
- compensate for internal force imbalances.

The first step in leveraging the capabilities of digital valve positioners is to understand how to most effectively implement them in a process operation. It's essential to invest in

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tools such as plant asset management software and valve self-diagnostics applications, which can capture, consolidate and present information in an actionable format.

The latest generation of positioners allows for collection of the control valve assembly's performance while the process plant is running, and also stores information in the positioner memory for analysis. For instance, through continuous self-diagnostics such a positioner can check every aspect of its operation — as well as the health of the valve itself. This could include an indication that plugs or seats have worn out, supply air pressure is high or low, or high or low friction exists. Operators can view the alarm list to see a description and categorization of all failures, determine when the failures occurred and review instructions for addressing the problems.

In addition, equipment designers are eliminating the need for handheld devices for valve configuration by enabling users to set up the device using push button controls at the positioner itself. A consistent auto-start procedure maintains trims, gains, etc., at the optimal settings for control and speed; keeps the valve from over-shoot; and avoids the common problem of "chatter mode."

2. *Compare the alternatives.* When thinking about moving from analog to smart digital valve positioners, keep in mind that smart positioners actually can be less expensive than their older analog counterparts. Indeed, due to all the analog accessories built into smart devices, sizeable cost savings are possible.

In addition, newer smart digital positioners are more reliable and have more installation options than analog positioners. They are microprocessor-based and can provide valuable fieldbus communications and diagnostic information.

Digital positioners also have a significant edge because they have fewer moving parts than analog positioners and are designed to automatically self-calibrate. They monitor critical variables such as valve travel and thrust, air pressures, temperature and valve friction, and provide real-time data so users can identify and fix any performance problems before they escalate into emergencies.

Finally, it's much easier to set up and install digital valve positioners than analog ones because digital devices can be

Figure 2. Electronic calibration and configuration speeds set up.

calibrated and configured electronically (Figure 2). This not only means that control loops can get up and running faster during the commissioning process but also greatly decreases the risk of human error.

3. *Consult with the experts.* Few operating companies today have specialists who are knowledgeable and up-to-date on the latest designs and features in valve technology. So, to make the best technical and economical choice, seek outside help, particularly from experts at vendors. They know the factors most important for the selection of positioners and can offer guidance for picking the right positioner for a specific application and environment. In addition, most valve positioner manufacturers offer training to help end users learn how to mount and set up a digital positioner and to perform commissioning and troubleshooting.

4. *Review all considerations.* Every technology, including the current breed of smart control valve positioners, has overlooked advantages as well as potential limitations.

Most process plants under-utilize several capabilities of digital positioners. For example, opting for the same type of smart device for both linear and rotary valves can significantly reduce the time, effort and cost for training instrumentation technicians and other personnel. The advent of advanced diagnostics also provides a real-time evaluation tool for valve health and operating parameters — helping to manage both the overall wellbeing of crucial equipment assets and the plant itself.

Modern digital positioners do have a few noteworthy drawbacks and aren't always the optimum solution for a particular application or environment. This is the case for applications lacking a digital control signal or power. Also, avoid digital positioners when there's no compressed air or gas source and in environments with temperatures that are excessively high (above 212°F) or low (below -40°F).

In addition, users with simpler applications may save money by opting for pure pneumatics (3–15 psi) or a current-to-pressure (I/P) converter. Hysteresis also is possible with some linkage kits.

Some of the under-appreciated issues that could complicate a digital positioner's successful implementation include

incorrect mounting kits, loose and worn linkages, and insufficient pressure from a compressed air source. Excessive vibration on integral-mounted positioners could require the use of a remote-mounted positioner.

In addition, plant personnel deploying smart positioners must become familiar with a digital environment and, if necessary, acquire additional software and computer skills. The set-up and commissioning of a digital positioner differs markedly from that of a familiar analog or hybrid device because the user encounters many more parameters and choices.

It's important to understand that digital positioning technology can't resolve all the issues associated with traditional types of positioners. So, perform due diligence to verify the chosen option really offers the stated advantages and, especially, to ensure it has the correct diagnostic capabilities to alert operators of potential problems.

A COMPELLING CASE

By upgrading control valve positioners from analog to digital, process plants can maximize productivity and improve their competitiveness in today's marketplace. The specific benefits of this approach include:

- minimizing environmental, asset and worker safety risks;
- improving compliance with fugitive emissions regulations;
- maintaining operational efficiency and reliability;
- enhancing product quality;
- increasing plant productivity;
- shortening maintenance time; and
- reducing capital costs.

Adding smart positioners with digital communication and diagnostic capabilities also assists plants in contending with the loss of experienced personnel and optimizing staff productivity. The latest generation of smart positioners helps operators do more diagnostics locally and better understand overall valve performance at a lower cost. Moreover, they enable a single operator to monitor the performance of hundreds of devices. Control room personnel can access and analyze data supplied by smart instruments to determine what valves are malfunctioning and identify the root causes of problems. ●

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Cloudburst Creates Commissioning Confusion

Delving deeper into performance and corrosion issues is essential

THIS MONTH'S PUZZLER

Our plant decided to make some repairs to the top trays in the main fractionating tower above the light cycle oil (LCO) stripper in our fluid catalytic cracker. We suspected trays were leaking based on the temperature profile and high level in the LCO stripper below the trays. We scheduled repairs during an outage. During that shutdown, we found corrosion of stainless-steel/carbon-steel welds affecting four trays. When we got inside, I noticed several weld repairs that didn't appear in the maintenance files. I then talked to people about past weld repair work on the system and recorded what I could find (see figure online at http://bit.ly/2HqBio5).

A severe thunderstorm caused the power to fail for half a day during the hydrostatic test, delaying the startup. So, staff rushed commissioning to meet the turnaround window. Although tower performance has improved, it's still not quite where it should be. The liquid level in the LCO stripper seems high and the pump-away motor amps seem low. The temperature elements in the middle-bottom of the column don't seem right because the difference between the trays is small. The pressure transmitter above the reboiler isn't working correctly.

In fact, when reviewing the commissioning records, I noticed that many transmitters weren't checked in an effort to cut startup time. I'd like to run a simulation but don't have any reliable data above the feed tray for comparison.

The unit superintendent blames the corrosion on the wash procedure that maintenance uses. Maintenance says corrosion from periodic washing is impossible. Our process group says the concentration of caustic used for washing is high and the wash temperatures are too hot. (We use 10-psig steam reduced from a 450-psig system.) However, they agree with maintenance that the washing isn't the culprit.

This is as far as I've gotten in my investigation. Have I missed anything? What else should I look for? Is there room for improvement in the wash procedure? Should I worry about corrosion reported at the bottom of the tower? (Maintenance says this is normal.)

REFER TO API 571

It is likely that your problem is with the process and not so much maintenance wash procedures. I recommend looking into the stream components, particularly chloride concentrations. You may have a very-well-known damage mechanism, called ammonium chloride corrosion, at work in your main fractionator tower. I have included a couple of snippets from [the American Petroleum Institute's Recommended Practice] API 571 — Damage Mechanisms Affecting Fixed Equipment in the Refining Industry that may be helpful:

5.1.1.3 Ammonia Chloride Corrosion

5.1.1.3.1 Description of Damage

General or localized corrosion, often pitting, normally occurring under ammonia chloride or amine salt deposits, often in the absence of a free water phase.

5.1.1.3.2 Affected Materials

All commonly used materials are susceptible, in order of increasing resistance: carbon steel, low alloy steels, 300 Series SS, Alloys 400, duplex SS, 800, and 825. Alloys 625 and C276 and titanium.

5.1.1.3.3 Critical Factors

a) Concentration (NH_3, HCl, H_2O or amine salts), temperature and water availability are critical factors.

b) Ammonium chloride salts may precipitate from high temperature streams as they are cooled, depending upon the concentration of NH_3 and HCl, and may corrode piping and equipment at temperatures well above the water dewpoint [>300°F (149°C)].

c) Ammonia chloride salts are hygroscopic, and readily absorb water. A small amount of water can lead to very aggressive corrosion [>100 mpy (>2.5 mm/y].

d) Ammonium chloride and amine hydrochloride salts are highly water soluble, highly corrosive and form an acidic solution when mixed with water. Some neutralizing amines react with chlorides to form amine hydrochlorides that can act in a similar fashion.

e) Corrosion rates increase with increasing temperature.

f) When they deposit above the water dewpoint, a water wash injection may be required to dissolve the salts.

5.1.1.3.4 Affected Units of Equipment

a) Crude Tower Overheads

1) Tower tops, top trays, overhead piping and exchangers may be subject to fouling and corrosion. Deposits may occur in low flow zones due to ammonia and/or amine chloride salts condensing from the vapor phase.

2) Top pumparound streams may be affected if ammonia or amine chloride salts are present.

5.1.1.3.5 Appearance or Morphology of Damage

a) The salts have a whitish, greenish or brownish appearance. Water washing and/or steamout will remove deposits so that evidence of fouling may not be evident during an internal visual inspection.

b) Corrosion underneath the salts is typically very localized and results in pitting.

c) Corrosion rates can be extremely high.

5.1.1.3.6 Prevention/Mitigation

Alloys that are more pitting resistant will have improved resistance to ammonium chloride salts but even the most corrosion resistant nickel alloys and titanium alloys may suffer pitting corrosion.

a) Crude Units

1) Limit salts by limiting chlorides in the tower feed through desalting and/or the addition of caustic to the desalted crude.

2) A water wash may be required in the crude tower overhead line to flush the salt deposits.

3) Filming amine inhibitors are often added to control corrosion.

Kelley VanLoon,
mechanical integrity technical manager
Provenance Consulting, LLC, Lubbock, Texas

LOOK THROUGH THE FOG

You should have focused on the top of the tower from the sour water pump to the feed tray. The key to successful troubleshooting is to use methods that pinpoint problems related to the root cause. When you cast a wide net, you confuse yourself in a wash of minor faults. My materials science professor said look at the small items, like fasteners, not the vessel they're attached to for signs of severe corrosion.

Unrecorded repairs were common before the advent of management of change procedures. This was especially true during outages when hours are long and everyone's driving towards the common goal of getting the refinery up and running.

Poor instrumentation support during commissioning is common because this work usually is the last item on a checklist and everyone else has burned up the clock. Good planning and backup support can ameliorate this rush. You should check the performance of each instrument against past readings and decide if a radioactive scan is necessary to spot additional leaks not detected and repaired in the trays or leaks that were improperly repaired.

It seems like the stripper is showing lighter than normal liquids, which could indicate a leak in trays above. I wouldn't put much stock in the low amp reading by the pump but I would call out the level indicator high reading as significant if a diaphragm instrument was used.

Operations could have a point as far as the caustic wash and temperature. It's not unusual to push the limit on concentration or temperature in maintenance to get the desired results more quickly; if this happens enough, caustic can cause severe pitting in stainless steel and erosion in carbon steel. This could contribute to additional forms of corrosion if present.

Dirk Willard, consultant
Wooster, Ohio

AUGUST'S PUZZLER

An engineering firm we hired disagrees with me about pressure relief on a methanol/water/formaldehyde column (Figure 1). The company is adamant that we must size and install a relief valve for two-phase flow.

The distillation tower operates at about 15 psig and has a design pressure of 45 psig. The tower recovers at the condenser about 99% of the methanol along with a few percent of formaldehyde and water. The methanol gets recycled back to the formaldehyde plant. Some trace vapor travels through 110 ft of 1-in. pipe before passing into a 16-in. vent to a thermal oxidizer (TOX).

After I heard from the firm's engineer whose analysis indicated the relief valve was necessary, I did a fire-sizing calculation myself and then computed the choked flow for the 1-in. vent from the receiver to the TOX knockout drum. I found the choked flow capacity far exceeds that required for fire sizing. My engineering report disparaged the loss of methanol to the TOX but concluded that no relief valve is needed.

The firm's relief expert counters that I can't take a reduction for four inches of fiberglass insulation in a stainless steel jacket; he says fiberglass may burn. Without that reduction, the flow capacity is much greater than the choked flow. Besides, he contends, two-phase flow, not vapor, will exist in the 1-in. vent. He also notes that he must look at other scenarios. Initially, he challenged my engineering report by mentioning the vent line could have an isolation valve — thus, necessitating a relief device. However, the line to the knockout drum doesn't have a valve. He also stated the relief must be on the tower, not the receiver.

In addition, the expert says the vent system might not be capable of handling the flow of all the vessels connected to it if a site-wide fire occurred. I told him we don't assume the entire site is on fire to size a vent for a relief flow.

What do you think? Do we need a relief valve on this distillation tower? Is the 1-in. vent adequate? Are there any other scenarios worse than a pool fire that could result in a large relief flow? Is two-phase flow in the vent likely or is it just something the expert wants to consider to reinforce his argument?

Send us your comments, suggestions or solutions for this question by July 12, 2019. We'll include as many of them as possible in the August 2019 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.

METHANOL/WATER/FORMALDEHYDE TOWER

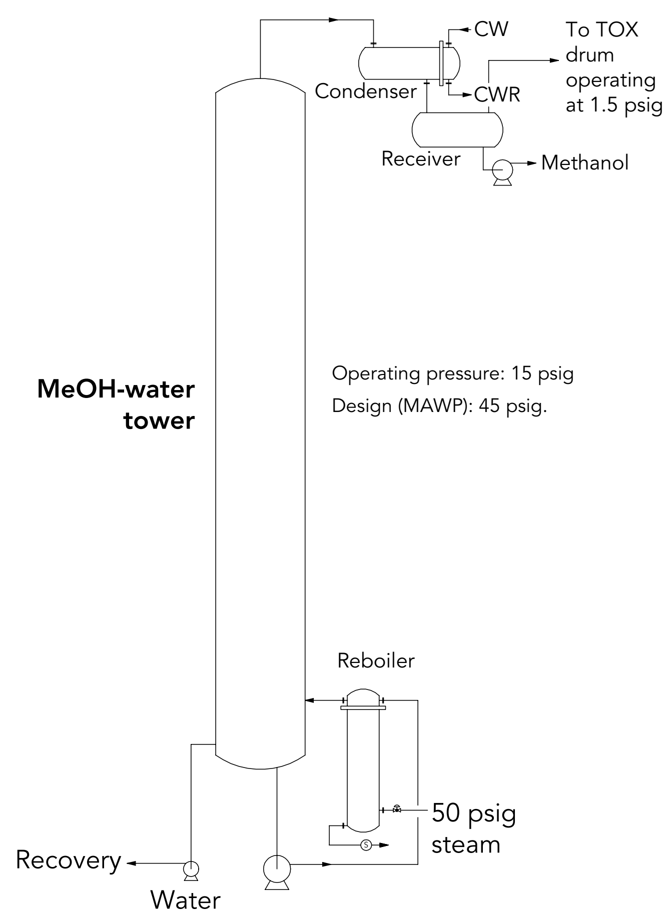

Figure 1. The need for a relief valve is a bone of contention.

Orifice Calculations Can Put You in a Hole

Significant mistakes can occur even for such a simple device

The right calculation method for orifices depends on the system.

ARE RESULTS reasonable? That's a question that engineers should pose for all calculations. However, defining what's reasonable can be difficult. Determining that requires both understanding the basic principles of the process as well as experience in application, as three recent orifice calculations demonstrate. All three had errors that could have caused problems. Fortunately, the mistakes were caught and then corrected. A look at these examples illustrates several elements of arriving at a reasonable result.

In our first case, piping attached to a high-pressure vapor/liquid separator had a design pressure that couldn't handle the full pressure in the drum. If the control valve feeding the line failed open, it was possible that high flow could cause the line pressure to be exceeded. One standard approach to prevent this from happening is to put a restriction orifice in the line (upstream of the specification change to the lower pressure) that restricts the flow rate.

Orifice calculations for single-phase flow are relatively straightforward. So, after a quick chat, orifice specification was handed off to a junior engineer. The engineer came back with an orifice size of 1.65 in. The orifice was going to be installed in a 2-in. NPS schedule 160 line. The line diameter is 1.687 in.

This isn't a reasonable result. How did the calculation go wrong? The culprit could be one of a number of factors: misunderstanding of the situation, a calculation error, use of an inappropriate method, or a poorly defined task set. Some questioning identified the cause. No one had made clear that the purpose of the orifice was to restrict flow. The junior engineer hadn't understood that and, so, made the calculation assuming the entire flow rate after the control valve failure would go down the line. This completely contradicts the actual intent of the orifice. Here, the objective of the orifice — to restrict flow — wasn't communicated well, if at all.

For orifices, the wrong calculation method also can lead to unreasonable results, as occurred in our second example. The right calculation method for orifices depends on the system. Is it liquid flow, gas flow or flashing flow? Will the fluid attain sonic velocity? Methods are available for each situation. Many commercial software packages will calculate orifice pressure drops and sizing as needed.

Much of the software for orifice sizing comes from flow instrument vendors. These vendors are most interested in the pressure drop at the location of the tap for the pressure drop reading to get a flow rate. The pressure tap is located at the vena contracta. This is the point downstream of the orifice where the flow velocity is the greatest and pressure drop is the highest. Downstream from this point, the pressure rises again as the fluid slows down to the bulk velocity in the piping.

When using control element sizing software for orifices, it's important to know if you need the pressure drop for an instrument (with a tap located at the vena contracta) or the permanent pressure drop downstream. When putting in an orifice as a flow restrictor, the downstream pressure drop is what's important. Using the vena contracta pressure drop instead of the permanent pressure drop results in an over-sized orifice. Flow rates will be higher than expected at the flow restriction conditions. If the flow restriction is in place for safety reasons, this may have serious consequences.

The third recent example with restriction orifices illustrates software misuse. Rather than doing an orifice calculation, an engineer sized orifices with a conventional process flowsheet simulator. The flow was handled as feed through a pipe element in the simulation. The engineer specified a short pipe segment with a restricted diameter as the pipe element. The software adjusted the diameter until it reached a target flow rate and pressure drop. That final diameter of the pipe segment was used as the orifice diameter. How close the result is to a proper orifice calculation depends upon the Reynolds number in the pipe segment, the length used and the diameter. All three must be taken into account to make this approach work. It's simpler, easier and more accurate to use the orifice equations or the correct software.

Orifices may appear simple. In fact, they are simple. But even simple things require understanding and experience to get right.

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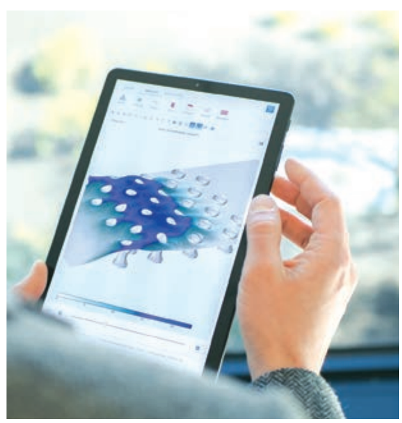

take simulation applications on the road, without being limited by device hardware. Providing field technicians with Comsol Multiphysics directly on their Android devices allows them to bring the R&D work on site. Administrators continue to have full control over who can access and run the apps by using Comsol Server.

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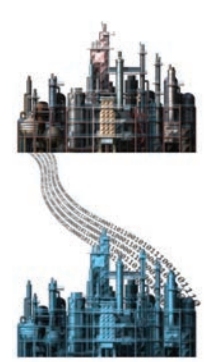

their operational risk in real time on SpheraCloud. An included early warning system makes all risk exposure visible, prominent and available in real time. This is designed to help reduce organizations' vulnerability to high-potential near-misses and major hazards. The technology also allows companies to improve their risk management capabilities while improving productivity and managing costs.

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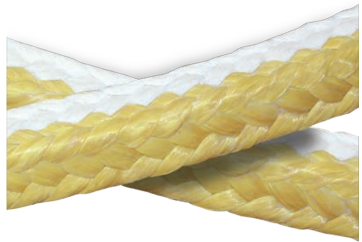

fewer gland adjustments than conventional packing. The product combines a burn-resistant material (white) on the sealing side, with a highly resilient outer fiber (yellow). The burn-resistant material conforms to the pump shaft for a strong seal, while the fiber resists extrusion and transfers radial load to the sealing side of the packing. The result is a packing that utilizes the gland load more efficiently and achieves a reliable and quicker break-in period, says the company. It can be used as end-ring or seal-ring by simply reorienting the packing during its installation, saving time and money in pump operations.

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The HUB-40EX hazardous area-rated flow sensor comes with a choice of either sinking or sourcing digital output in either a 316 stainless steel or aluminum junction box; or for areas with limited space, a version with no junction box at all. Compatible

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aspenONE Version 11 software release enables users to leverage analytics to streamline operations and boost profitability. The release includes enhancements to aspenONE asset performance management (APM), engineering, manufacturing and supply chain software suites and introduces Aspen GDOT dynamic optimization software, which unifies production optimization for energy and bulk chemical companies in complex industrial environments. The software suite incorporates prescriptive maintenance into planning and scheduling to warn of future equipment condition issues and plan interventions for asset failures and quality issues. It improves operational analytics for continuous and batch operations to accurately identify sources of process and quality variability and to improve asset utilization.

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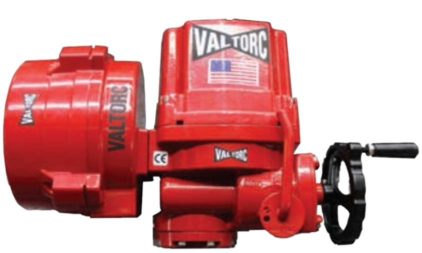

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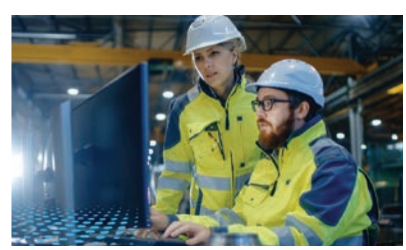

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Europe Eyes Endocrine Disrupting Chemicals

Whole-mixture approach to assessment points to health concerns

Several new approaches can help define acceptable exposure levels based on epidemiological data.

A FOUR-YEAR, European Union (EU)-funded project has concluded that the health risks associated with mixtures of man-made chemicals are underestimated. In 2015, the EU's Horizon 2020 R&D program initiated the EDC-MixRisk project to investigate how to study the effects of these real-life relevant mixtures.

The project brought together a research consortium consisting of epidemiologists, chemists, biostatisticians, medical doctors, molecular biologists, and experimental and regulatory toxicologists from 12 European universities and Mount Sinai School of Medicine, New York.

Their starting point was that man-made chemicals can create combinations of chemical mixtures to which we all are exposed during our lifespan. However, current risk assessment and management practices focus mainly on exposure to single substances. Exposure to hazardous substances, especially endocrine disrupting chemicals (EDCs), during the fetal period is of particular concern as it can lead to irreversible changes in organ and tissue development and increased susceptibility to diseases later in life.

Together, the researchers developed a novel approach based on identifying and testing EDC mixtures associated with adverse health outcomes in humans. Using epidemiology data from a Swedish cohort study of more than 2,300 pregnant women, they created reference mixtures to mimic real-life exposures at concentrations found in the women. These mixtures were then tested in various cell and animal experimental models. The toxicological data from these tests helped establish new methods and strategies for mixture risk assessment to better account for complex environmental exposures.

"The novel whole-mixture approach has allowed us to assess the number of mothers in the cohort that are at risk for effects in their children, effects related to growth and metabolism, neurodevelopment and sexual development," explains Åke Bergman of the department of environmental science and analytical chemistry and coordinator of the EDC-MixRisk project at the Karolinska Institute, Stockholm.

Other research led by Giuseppe Testa at the European Institute of Oncology, Milan, used human brain organoids to directly assess the impact of such mixtures on the closest available model of the developing human brain. The work uncovered that real-life concentrations of EDCs interfere with the same regulatory networks already involved in the genetic forms of autism spectrum disorder and intellectual disability.

"This new method enables investigation of relevant chemical exposures on equally relevant windows of sensitivity during human brain development," says Testa.

Meanwhile, at the Centre National de la Recherche Scientifique, Paris, endocrinology expert Barbara Demeneix and her team investigated whether the mixtures interfered with brain development and growth through modulation of thyroid hormone signalling.

"Thyroid hormone is essential for brain development and children born to mothers that have insufficient thyroid hormone also have increased risk of autism spectrum disorder and IQ loss. Thyroid hormone signalling and numerous thyroid hormone dependent genes were disrupted by the mixture in the different models tested. These findings reveal a mechanism whereby brain development is affected by exposure to the chemicals at relevant human exposure levels," she notes.

The researchers concluded these new approaches can be used to define acceptable exposure levels based on epidemiological data, or the integration of human and experimental data. They also may provide empirical support for estimating the size of a potential additional mixture assessment factor that could then be used in a chemical risk assessment. "Our whole-mixture approaches can only be used retrospectively for chemicals for which epidemiological data are available. For 'new chemicals' a prospective risk assessment is required," they note.

The EDC-MixRisk project launch coincided with the results of a 2015 study from environmental and public health organizations in Europe and the United States that estimated that exposure to EDCs likely costs the EU €157 billion ($172 billion) every year in healthcare expenses and loss of earnings.

The results of that study, published in the March 2015 issue of the *Journal of Clinical Endocrinology and Metabolism*, concluded that exposure to EDCs is in part responsible for a range of conditions including infertility and male reproductive dysfunctions, birth defects, obesity, diabetes, cardiovascular disease, and neurobehavioral and learning disorders.

At the time, the authors believed their €157-billion estimate to be conservative as it represented 1.23% of Europe's gross domestic product (GDP). These costs may actually be as high as €270 billion ($294 billion), or 2% of GDP, they said. In today's prices that's €370 billion ($414 billion).

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