

# CHEMICAL PROCESSING

LEADERSHIP | EXPERTISE | INNOVATION

Pollution Control eHandbook

## PRECLUDE POLLUTION PROBLEMS



# Table of Contents

<b>2016 Presents Regulation Challenges</b>	<b>3</b>
Legislation will focus on unfinished business, work plan chemicals and green chemistry efforts	
<b>Plants Plug Away at Leaks</b>	<b>5</b>
The quest for improved safety, sustainability and cost savings drives efforts to reduce fugitive emissions	
<b>Select the Right VOC Abatement Method</b>	<b>10</b>
There's no one-size-fits-all approach and use varies greatly by application	
<b>Increase Sustainability with Thermal Oxidation</b>	<b>14</b>
The right emission control system can help meet compliance and reduce energy costs	
<b>Additional Resources</b>	<b>20</b>

# Ad Index

<b>Anguil</b>	<b>4</b>
<a href="http://www.anguil.com">www.anguil.com</a>	
<b>Dürr</b>	<b>9</b>
<a href="http://www.durr-cleantechnology.com">www.durr-cleantechnology.com</a>	



# 2016 Presents Regulation Challenges

Legislation will focus on unfinished business, work plan chemicals and green chemistry efforts

By Lynn Bergeson, Regulatory Editor

**WITH ONE** year to go in the Obama Administration, the Office of Pollution Prevention and Toxics (OPPT) continues to make progress on its agenda, although a number of significant and difficult challenges are teed up for 2016. The biggest wild card is the enactment of Toxic Substances Control Act (TSCA) reform legislation and its impact on U.S. Environmental Protection Agency (EPA) leadership and OPPT staff in potentially undertaking the hard work of implementing TSCA reform legislation.

## UNFINISHED BUSINESS

Aside from possible TSCA reform implementation, OPPT will have its hands full. Unfinished business before OPPT in 2016, particularly regarding significant new use rules (SNUR), includes promulgating final SNURs on the long-chain perfluoroalkyl carboxylate (PFAC) and perfluoroalkyl sulfonate (PFAS) chemicals and toluene diisocyanates. In addition, there are yet-to-be-final SNURs on certain nonylphenols/nonylphenol ethoxylates and polybrominated diphenyl ethers (PBDE), including decaBDE (this action, proposed in April 2012, also includes a TSCA Section 4 test rule). Many of these rules present complex issues; OPPT is likely to struggle as it reconciles the many comments it received and determines its approach in the final rules. Several of these SNURs also include that pesky issue of including imported articles within the rule's scope. We look to further evolution of OPPT's approach to this issue in 2016 (relevant expected actions include the SNURs on long-chain PFAC/PFAS and PBDE chemicals). Another open item is an expected proposed rule for Sections 8(a)/8(d) reporting on oil and gas production (i.e., fracking) chemicals (this was the subject of a citizens' petition filed in 2011 under TSCA Section 21).

In 2016, we also will see the second iteration of reporting under the updated TSCA Section 8(a) chemical data reporting rule. The rule contains some important changes from the requirements in 2012, including reducing the reporting threshold from 25,000 lbs/year at a site to 2,500 lbs/year at a site for chemicals subject to any of several TSCA actions (e.g., test rules, pending or final SNURs, and Section 5(e) consent orders, among others) and requiring if a chemical triggers reporting between 2012 and 2015, the reporting must include data for each of the four years.

## WORK PLAN CHEMICALS

The work plan, updated in 2014, contains approximately 90 existing chemical entries; to date, OPPT has initiated

assessments on 14 chemicals/clusters. Progress includes completed risk assessments on five chemicals (three proceeded to risk management and two were dropped from further review — antimony trioxide and the fragrance ingredient 1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[*y*]-2-benzopyran (HHCB)); four with ongoing risk assessments; one with a data needs assessment; and four cases in the initial assessment stage. Chemicals proceeding to risk management include paint removers N-methyl pyrrolidone and methylene chloride, and the chlorinated solvent trichloroethylene when used as a degreaser, stain remover in dry cleaning and spray fixative. The EPA is considering both voluntary and regulatory actions, including using TSCA Section 6(a) to manage the identified risks. We expect the EPA will propose Section 6 regulations on one or more of these chemicals this year, given that the Administration will change in 2017. It's also likely the EPA will release risk assessment documents this year for one or more of these chemicals/clusters as part of an effort to demonstrate it can conduct and complete such assessments (and deal with problem formulation comments) in a timely way.

## GREEN CHEMISTRY

The EPA has emphasized the need for greater progress in green chemistry and Design for the Environment (DfE). Tangible progress was realized when, in February 2015, the new Safer Choice label was unveiled to generally but not universally positive reviews. OPPT also announced the inaugural Safer Choice Partner of the Year Awards in 2015; 2016 winners will be announced in the spring. The DfE Safer Choice program also aims to add hundreds of chemicals to the Safer Chemical Ingredient List. Efforts to increase visibility and market adoption of award-winning green chemistry technologies remains a priority of OPPT management, although limited resources have hampered activity. We expect these efforts to continue to grow in 2016 and encourage clients and friends to look carefully into these opportunities. ●

**LYNN BERGESON**, Regulatory Editor  
lbergeson@putman.net

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.

**ANGUIL**<sup>TM</sup>

**EPA**

OBJECTS IN MIRROR ARE CLOSER THAN  
THEY APPEAR WITHOUT ANGUIL

**Air Pollution Control Technologies for Volatile Organic  
Compounds, Hazardous Air Pollutants and Odors.**

**Thermal and Catalytic Oxidizer Design, Manufacturing  
and Service Since 1978!**

**[www.anguil.com](http://www.anguil.com)    (414) 365-6400**



# Plants Plug Away at Leaks

The quest for improved safety, sustainability and cost savings drives efforts to reduce fugitive emissions

By Sean Ottewell, Editor at Large

**CHEMICAL COMPANIES** such as BASF and Dow are working hard both to identify and deal with the sources of their fugitive emissions. Meanwhile, vendors such as Garlock and Honeywell Process Systems are developing technologies and procedures to make the job faster and more cost-effective.

Fugitive emissions may pose significant hazards to people and the environment as well as sizable economic penalties from loss of materials. “Fugitive emissions cause losses during production, transport and storage. Many of the substances concerned are toxic and it requires know-how and state-of-the-art technology to contain their release,” notes Christoph Moritz, coordinator air quality, BASF, Ludwigshafen, Germany.

To reduce fugitive — also known by BASF as diffuse — emissions, the company implements strategies at its sites that meet local, national and international standards. At the heart of these strategies are three basic rules.

First is avoidance. “Here, we use state-of-the-art equipment such as low-emission seals that have been designed for use with critical chemicals. We also run quality assurance programs for mechanics and operators, who are properly trained in special courses according to latest standards, for example, VDI 2290 in Germany,” he adds. (The VDI 2290 guideline deals with flange connections for liquid and gaseous media to meet emission control requirements; it covers various metals and applies to services with a maximum operating temperature of 400°C.)

“Besides regular inspection and maintenance, our plants are controlled by means of pressure drop sensors. Seals and flanges are replaced at defined intervals,” says Moritz.

The second basic rule is detection of emissions and leaks (Figure 1). Typically, plants rely on a conventional flame ionization detector (FID) that is sensitive to organic substances. Analysis of the substance begins at a pre-set threshold concentration, for example, 500 ppm. If such a concentration is exceeded, operating staff takes immediate action.

An infrared (IR) camera often serves as a preliminary detection device (Figure 2). Set in a “fume sensitive” mode, it can spot an increased concentration of a substance; a more precise check with an FID immediately follows.

## TANK INSPECTION



Figure 1. Plant technician uses a flame ionization detector to check seals and flanges on a set schedule. Source: BASF.

## IR CAMERA



Figure 2. Readings from a camera can provide the first warning of a leak, and spur follow-up checks with a flame ionization detector. Source: Sage Environmental.



“All plants are equipped with such sensors and any leaks detected are instantly repaired. The detection procedures themselves may vary from country to country depending on local regulations and the requirements of the respective authorities,” he explains.

The final basic rule is calculation of emissions; the methods used depend upon the relevant standards (EPA, DIN, etc.). To create a proper comparison between the different standards, BASF has carried out internal studies and sponsored several postgraduate research theses. “These have revealed valuable information about the correlation between ‘sniffed’ concentrations of organics and the corresponding leakages in g/h — i.e., mass flow. Moreover different methods of calculation for diffuse emissions were compared and quantified,” Moritz says.

#### LINK TO SUSTAINABILITY

For Dow Chemical, Midland, Mich., reducing process spills from equipment and decreasing fugitive emissions are part of its overall sustainability strategy. Launched last year, its 2025 sustainability goals commit the company to maintaining world-leading operations performance in natural resource efficiency, environmental protection, health and safety.

To this end, Dow has set a goal to reduce severe process safety and containment events by 70% by 2025, a target the American Chemistry Council, Washington, D.C., suggests for its members. The company’s fugitive emissions strategy covers small emissions of gases or vapors from equipment flanges, seals and packing components that are difficult to detect without specialized equipment.

“Our current focus on reducing fugitive emissions centers on improving Dow’s leak detection and repair (LDAR) management system. This includes improvements to LDAR training, work processes, tracking tools, quality assurance and control and self-assessments. Additional improvements will focus on the technology used by contract providers,” notes a spokesperson.

Dow’s site in Lauterbourg, France, provides a prime example of this work in action: the plant has reduced process

spills and associated emissions by 75% over the past four years.

The key driver of this change was an improvement project that focused on three main actions.

The first was having plant leadership set clear expectations about the reporting of actual and potential leaks and spills of any size. All such events require a root cause investigation and the assignment of corrective actions.

The second was creating an improvement team to lead overall efforts and implement projects identified. These projects included rearranging equipment, using color-coded caps to distinguish hazardous from non-hazardous chemicals, labeling valves to indicate those that only should be opened in exceptional circumstances, and implementing checklists and double-checking by a second operator to ensure proper valve resealing.

The third action was ensuring that all operations team members — plant operators, engineers, maintenance and leadership — contribute to the reporting of leaks. This involved setting individual goals, measuring performance against these goals, and factoring participation in leak-reduction efforts into team member recognition and performance management.

To support the initiative, the site also upgraded its assets, e.g., replacing circle pumps with screw flasks, introducing valves that only can be opened by key, and installing leak detectors that can shut down equipment automatically.

#### IMPROVING TECHNOLOGY

Advances in technology are helping chemical companies both to better identify the sources of their fugitive emissions and meet evolving legislative demands, says Jim Drago, principal applications engineer, Garlock, Palmyra, N.Y.

Identifying sources is critical, he notes, citing a 1997 study “Analysis of Refinery Screening Data” (Publication 310 of the American Petroleum Institute, Washington, D.C.) that found 90% of all such emissions coming from fewer than 5% of the 50,000 components subject to fugitive emissions compliance. This 5% included components with high magnitude leaks, typically greater than 10,000 ppm. “Consider the fact that the threshold for categorizing a component as leaking is usually



#### VOC MEASUREMENT



Figure 3. Current sniffing technologies for monitoring volatile organic compounds rely on a probe with a small diameter. Source: Team Industrial Services.

500 ppm and one asks the questions: ‘Why are we monitoring all these components that are not leaking or are small leaks? How can we identify the components with large leaks and eliminate 90% of our emissions?’”

One emerging technology is high-flow sampling. The current sampling techniques, designated in EPA Method 21, measure volatile organic compound (VOC) concentration at the probe’s end, which is fairly small — about ¼-in. in diameter (Figure 3). With high-flow sampling, the size of the probe end is 1½–2-in. in diameter (similar to that of the hose of a household vacuum cleaner) and so the probe takes in a much larger volume of sample of the ambient atmosphere around the equipment of interest. “This is accepted as being a full sampling of the entire leak, so it can be an easy leap to quantifying the leak in kg/h,” notes Drago.

IR camera technology also taken a big leap forward, he says. Originally the cameras just were used to “see” leaks and were go/no-go instruments heavily dependent on factors such as the ambient atmosphere and wind conditions. They

#### GAS CLOUD IMAGING



Figure 4. Camera can identify specific hydrocarbons and also generate a leak rate. Source: Rebellion Photonics.

often were not accurate with leaks below around 2,500–5,000 ppm and sometimes weren’t even useful below 10,000 ppm, Drago explains.

“Companies such as Rebellion Photonics, Houston, Texas, have changed all that with gas cloud imaging (GCI) camera technology. This now gives you the ability [to] carry out continuous or mobile monitoring with a camera and immediately get a leak rate,” he says. The GCI camera (Figure 4) detects gases’ unique spectral signal, which enables advanced algorithms to identify specific hydrocarbon fingerprints within an emission; operators are immediately alerted to potential hazards on a site.

Meanwhile, seal manufacturers, including Garlock, are focusing on installation techniques. “We’re not seeing ‘OMG that’s new’ products for, for example, valve stem seals, which are the primary emission source on any plant. Rather, we are refining and tweaking what we do. At conferences and in discussions with customers, we are really stressing the importance of good installation practices and the quality of the installers themselves and the people who oversee them.”



Valve manufacturers and seal makers are engaging in much greater review of valve designs, says Drago. Both are becoming much more serious about getting certification to API 624 — a standard that specifies the requirements and acceptance criteria for fugitive-emission-type testing of valves.

Finally, he expects much of the open forum discussions and conferences this year to focus on what the next generation of LDAR regulation from the U.S. Environmental Protection Agency (EPA) will look like. “It seems they will be very much in line with its NextGen strategy,” he notes.

Running from 2014–2017, NextGen, which is the EPA’s plan to improve the effectiveness of its compliance program, brings together five interconnected components: easier-to-implement design regulations and permits; promotion of advanced emissions/pollutant detection technology; greater use of electronic reporting; increased transparency, making information more accessible to the public; and development and use of innovative enforcement approaches such as data analytics and targeting to achieve more-widespread compliance.

#### WIDER ROLE FOR WIRELESS

Development of robust, cost-effective wireless technologies is helping companies achieve their goal of zero incidents, says Diederik Mols, global business leader industrial wireless solutions, Honeywell Process Solutions, Amsterdam, The Netherlands. “Every leak could lead to an incident; look what happened at Buncefield,” he stresses. (For details on the explosion at the Buncefield fuel depot in the U.K., see “It’s Time to Tank Complacency,” <http://goo.gl/kCa0xw>.)

Since the incident at Buncefield, liquid leak detection has gotten much greater priority because of the dangers posed by explosive vapor clouds formed by fugitive emissions via evaporation from such spills, notes Mols. Tank roof monitoring also has become more a priority, firstly to avoid overfills and secondly to ensure that floating roofs are kept even to avoid gas vapor leaks, he adds.

In addition, he has noticed that companies are getting much more stringent in their detection-to-alarm time demands. Here, he cites a customer in Qatar that runs one of the world’s largest integrated liquefied-natural-gas complexes. The company wanted a warning system to alert personnel in the administration area of any toxic gas leakage. One of the critical requirements was to generate audio and visual alarms within three seconds of detecting a gas leak — a demand that had proved the stumbling block for another vendor who could not meet the required latency period. Honeywell’s success lay in the use of its OneWireless infrastructure and the XYR 6000 Universal I/O wireless transmitter, which together enabled the rapid audio and visual alarming required.

Advances in personal gas detectors also are bolstering the protection of personnel from the danger of leaks. For instance, later this year, Honeywell plans to introduce new technology specifically designed to reduce the risks for operators working on their own in remote areas of the plant, such as tank farms or wastewater treatment facilities, or even outside the perimeter. It monitors vital functions, hazardous gas levels and whether or not an operator is down. Any alarms from the detector will be displayed and triggered in real time in the control room. “Not only do you get better gas-detection information, but also the system can be the difference between life and death for a field operator,” says Mols.

The future of emissions detection technology lies in further miniaturization and improved cost-effectiveness of sensors — along with closer tailoring of the technology to the demands of regional legislation, he believes. ●

#### RELATED CONTENT ON CHEMICALPROCESSING.COM

“Wireless Network Improves Leak Detection,” <http://goo.gl/oMEVkk>

“Leaks Don’t Lie,” <http://goo.gl/SedMKy>

“Plants Look Harder for Leaks,” <http://goo.gl/c6VzTH>

“Prepare to Clamp Down Tighter on Leaks,” <http://goo.gl/jw9xHH>

“Understand All the Costs of Gas Leaks,” <http://goo.gl/G4RiJz>



LEADING IN PRODUCTION EFFICIENCY

# ECOPURE® OXIDIZERS

FOR THE MOST PROVEN, EFFECTIVE,  
AND EFFICIENT REMOVAL OF  
EXHAUST GAS AND LIQUIDS

Dürr **Ecopure®** systems offer the most options for environmental compliance in the chemical processing industry. Dürr conducts the necessary engineering studies and analyses which result in the right environmental system design for your company's compliance and energy needs.



[www.durr-cleantechnology.com](http://www.durr-cleantechnology.com)



# Select the Right VOC Abatement Method

There's no one-size-fits-all approach and use varies greatly by application

By Jason Schueler, Anguil Environmental Systems

**THE REQUIREMENTS** for clean air standards continue to increase in tandem with the concern over greenhouse gas (GHG) emissions and their impact on the planet's atmosphere. This drives new and better-suited technologies in manufacturing and throughout industry.

Manufacturers that can adapt to the new air pollution control landscape, realize the environmental and economic benefits of these new technologies. Yet, many questions still remain: Is there a best-suited abatement device for a specific industrial process? How does each technology compare in terms of operational costs and abatement efficiency? What is being done to adapt these technologies to the ever changing GHG standards? Most manufacturers worldwide in the chemical processing industry (CPI) are required to comply with regulations such as the United States' National Emission Standards for Hazardous Air Pollutants (NESHAP) for chemical manufacturing. Similar regulations are being adapted around the world as environmental awareness and air pollution issues continue to increase.

The primary emissions from CPI processes include volatile organic compounds (VOCs) as well as hazardous air pollutants (HAPs). Except for carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), carbonic acid, carbonates, metallic carbides and methane, VOCs are any organic chemical compound that contains the element carbon. When left untreated, these compounds degrade in the presence of sunlight, converting to ozone or visible pollution such as smog.

Worse, HAPs are VOCs that have additional harmful properties beyond their detrimental effects to the atmosphere, such as contributing to the causes of cancer, respiratory ailments, heart conditions, birth defects and nervous system damage to those exposed.

## ENTER OXIDATION

As awareness of these harmful properties gained traction in the 1970s, the concept of oxidation for emission abatement

began as a way to mitigate these effects. At that time, many developed countries put new regulations in place. Oxidation is the process of converting hydrocarbons to CO<sub>2</sub> and water vapor (H<sub>2</sub>O). To achieve proper oxidation, three conditions first must be met, referred to as the "three Ts": time, temperature and turbulence.

Each VOC has an auto-ignition temperature (AIT) at which it combusts in oxygen's presence. By elevating the temperature of a VOC-laden process stream to above the AIT of the pollutants within, oxidation occurs. However, to ensure all emissions in the stream are oxidized properly, the stream must be maintained at that elevated temperature for a minimum amount of time.

Further, turbulent mixing of the stream occurs such that all compounds are in contact with the oxygen that is present. The mixing is promoted within the equipment through the oxidation chamber's design. The specific compounds in the process stream and the desired destruction rate efficiency will determine the temperature and residence time required.

Regardless of the oxidizer size or type, all require supplemental fuel to support emission combustion. This typically is achieved with a natural gas-fired burner, which will produce CO<sub>2</sub> and nitrogen oxides (NO<sub>x</sub>). Knowing the detrimental effects of increasing GHGs into our atmosphere, reducing CO<sub>2</sub> and NO<sub>x</sub> emissions has become a critical part of oxidizer design. Systems with higher thermal efficiency require less supplemental natural gas for operation and therefore produce fewer GHGs.

Many processes involve batch and continuous chemical manufacturing applications, and they all vary greatly in volume and composition. Some of these include phenol production, ethylene oxide sterilization, pure terephthalic acid (PTA) production, formaldehyde production, organic chemical manufacturing, phthalic anhydride (PA) production, polyethylene terephthalate (PET) production and specialty chemical manufacturing.



No single type of oxidizer will be the best fit for every application, so a variety of abatement technologies have been applied in the CPI. Many chemical producers have used technologies such as flares, vapor combustors (VCs), catalytic and thermal oxidizers — each with its own pros and cons for any specific application. The catalytic and regenerative thermal oxidizers (RTOs) have been the most widely applied emission abatement technologies, though VCs fill a niche for certain applications.

#### CATALYTIC OXIDATION

Using catalyst in VOC oxidation lowers the temperature needed for destruction, reducing the fuel usage when compared to a thermal system. Catalytic oxidation has been a popular and familiar choice in the CPI for many years (Figure 1). During operation the VOC- and HAP-laden process stream is sent through a metal air-to-air heat exchanger via the system fan, either forced or induced through the equipment.

Within the heat exchanger, the process gas is preheated before entering the unit's combustion chamber to reduce fuel usage further. Within the combustion chamber, the gas is heated further, if required, by the oxidizer burner, raising it to the necessary catalyst activation temperature.

Next, the gas passes through the catalyst, causing the exothermic (heat-releasing) oxidation reaction to occur. The pollutants thus are converted to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The cleaned, hot process gas then is sent back through the heat exchanger to transfer heat back to the incoming dirty process stream. The heat exchanger reduces fuel requirements and saves

operating costs. In fact, with a process stream consisting of only 8–12% lower explosive limit (LEL), the oxidizers can be self-sustaining, requiring no additional fuel. Finally, the cooler, clean, process gas is released to atmosphere through the oxidizer stack.

*Catalyst categories and forms.* Catalysts come in two major categories: precious/noble metals and base metals. The former consists of platinum, palladium, rhodium and iridium. The latter consists of manganese dioxide, copper oxide and chromium oxide. Additionally, catalyst can come in two different forms: monolith and random packing. The monolith form typically is ceramic or stainless steel extruded blocks and then coated with the catalyst. The random packed form can be pellets, beads or spheres.

*Best applications for catalytic oxidizers.* Catalytic oxidizers are particularly suited for emission streams containing carbon monoxide, aromatic compounds and alkenes, as they easily are oxidized when passing over heated catalyst. Another example is formaldehyde emissions, which can be destroyed to a very high degree. Catalyst will continue to perform at high levels of removal efficiency for many years with minimal operational issues, assuming the process streams are free of damaging compounds and particles. Free of these, catalyst life theoretically is unlimited, but once in the field the lifetime typically ranges from three to eight years.

*Reduced lifetime causes.* The specific causes of reduced lifetime are poisoning, masking and sintering. The precious metal catalysts can be deactivated when exposed to certain chemicals, called poisons in this context. With platinum as a substrate, heavy metals such as mercury, lead and cadmium can bond with the precious metal and form inactive alloys. Catalyst sites also can be covered up or masked by particulates such as dirt, the phosphorous in lube oils or inorganic scale.

Furthermore, if the catalyst temperatures get too high, then sintering can occur. This is a process in which catalyst particles and the catalyst substrate bunch together to form larger crystals, reducing active surface area and decreasing the catalyst's destruction efficiency. As the most expensive part of the precious metal catalyst is the metal itself, it can be quite costly when deactivation occurs, as replacement is necessary. This can occur multiple times over a system's life.



Figure 1. This catalytic oxidation system controls emissions from a batch chemical process.



#### RTO SCHEMATIC

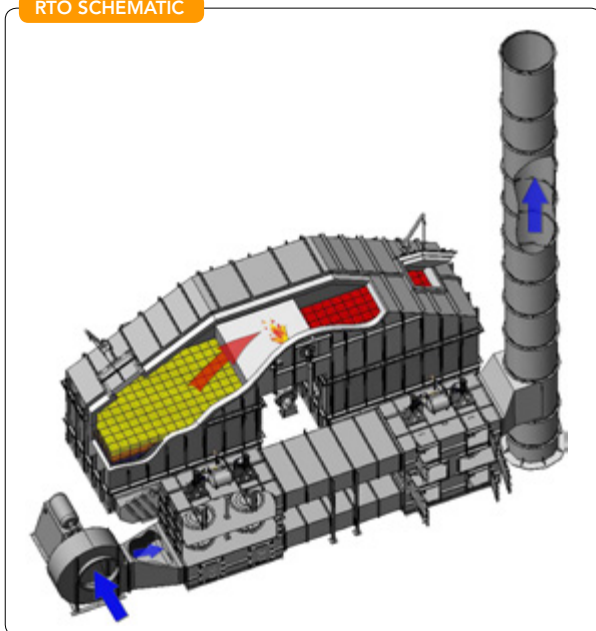


Figure 2. This schematic shows how flow and heat is transferred in a regenerative thermal oxidizer.

Despite the benefits that come with being able to oxidize at lower temperatures, catalytic systems can come with a hefty price tag. Integrated heat exchangers of 50%–70% efficiency typically are used to reduce the auxiliary fuel needed to maintain the minimum 570°F temperature needed for the catalyst. However, burners and fuel trains still are required to ensure sufficient heat is available to achieve the required destruction efficiency.

Often, a second heat exchange bundle is used to reduce fuel requirements further or to heat a second source of air for other uses in the facility. Still, supplemental fuel almost always is required. The heat exchangers usually are built with stainless steel to combat the high temperatures, as well as to prevent corrosion. All of these design requirements escalate the cost of the equipment quickly, making catalytic systems an expensive investment with potential risks and still a significant source of CO<sub>2</sub> gas emissions.

For those wary of the high capital cost, maintenance requirements and potential high operating costs and GHG emissions, a regenerative thermal oxidizer (RTO) may be an alternative.

#### REGENERATIVE THERMAL OXIDATION

The RTO is a thermal-style oxidizer that uses internal ceramic heat exchange media to reach upwards of 97% thermal efficiency, compared to ~70% of catalytic systems. Upon RTO startup, the media within is “charged” with heat by the system’s natural gas burner. During operation VOC-laden air first enters one of the RTO energy recovery chambers that is filled with ceramic heat transfer media. This high-temperature media transfers the heat stored within to the process as the gas passes up through the media blocks (Figure 2). By the time the gas enters the combustion chamber, its temperature has been raised significantly such that only minimal amounts of supplemental fuel are required to maintain the necessary destruction temperature.

In fact, with process streams in concentration of as little as 2–3% of the LEL, the RTO can operate with zero supplemental fuel. After oxidation, the hot, clean gas then passes down through the remaining energy recovery bed, where it transfers its heat back into the ceramic media. To maintain optimal heat recovery efficiency in the beds, the process gas’ flow direction is switched at regular intervals via the RTO’s automatic diverter valves, which are controlled by the system’s programmable logic controller (PLC).

*Hot gas bypass.* Early RTO designs could handle only low-concentration process streams. More modern systems can be equipped with a hot gas bypass (HGB) for processing waste streams with significantly greater concentrations, up to 25% LEL (Figure 3). Without an HGB, too much

#### HOT GAS BYPASS



Figure 3. This RTO uses a hot gas bypass damper for high-emission loading conditions.



#### VAPOR COMBUSTER



Figure 4. This robust device can handle varying emission flow rates and concentration changes.

VOC loading will result in a high-temperature shutdown of the unit because of the high thermal efficiency and the extreme heat released from the oxidizing VOCs.

However, with an HGB, the excess heat can be routed around the outlet media bed, effectively reducing the thermal efficiency as needed to allow greater VOC loads to be processed. The high-concentration process streams successfully are oxidized in an RTO without risking damage to the media or insulation within the unit. Early designs also were limited to only 90–95% destruction rate efficiencies (DRE), but improvements to the RTO structure and operating logic have allowed DREs of 99% in a two-bed unit. Even higher DREs are available with custom-engineered multiple-bed RTOs.

*Lower RTO-related costs.* Not only do RTOs offer lower operating expenses over their catalytic counterparts, but the capital equipment cost often is cheaper for similar-sized systems due to the absence of catalyst and metal heat exchange-

ers. Destruction efficiencies also are more consistent over the RTO system's life as no catalyst is degrading as it ages.

The RTO provides some benefits over a traditional catalytic system while also eliminating some of the concerns. However, the RTO is not the one-stop solution for all process streams. Streams with high-VOC concentration and low volume flow often can be processed through a VC for a fraction of the capital cost of the RTO or catalytic system.

#### VAPOR COMBUSTORS

The VC is similar to a traditional flare but is enclosed and uses more sophisticated controls. When regulations regarding visible emissions, noise and GHG emissions prevent the use of a flare, the VC can shine (Figure 4). With the right process, the system can be as simple as a burner, fuel train, reactor and controls, while still achieving 99+% DRE.

Combustion air can be provided via natural draft, and with a pressurized process a booster fan is not needed. The lack of heat recovery makes these systems simple, cost-effective and small. However, they also can require significant amounts of supplemental fuel, so they typically are best used as a solution for upset conditions that the RTO cannot process.

#### CHOOSING THE APPROPRIATE SYSTEM

Before beginning any abatement project, it is imperative to identify the air stream characteristics and constituents properly. Process emissions from batch and continuous applications can vary greatly in volume and composition. In addition, green business practices don't always coincide with energy reduction strategies, which often is the case with emission abatement products. Therefore, it is important to consult with a professional to ensure the correct abatement technology for your process conditions, budget constraints, energy demands and compliance objectives. Very few processes are identical, and not one specific technology choice can be applied on all applications. ●

**JASON SCHUELER** is a senior application engineer for Anguil Environmental Systems. He can be reached at [Jason.schueler@anguil.com](mailto:Jason.schueler@anguil.com).

# Increase Sustainability with Thermal Oxidation

The right emission control system can help meet compliance and reduce energy costs

Jon Hommes, Engineer, Dürr Systems, Inc.

**INSTALLING NEW** production processes or upgrading and expanding existing lines requires a review of the expected emissions. The right emission control system for Hazardous Air Pollutants (HAPs) and Volatile Organic Compounds (VOCs) can help efficiently and economically dispose of these environmentally hazardous wastes. Over the last 20 years, as emission limits have tightened and authorities have taken a more “holistic” plant-wide approach to air permits, the trend in the chemical processing industry has been to collect multiple waste streams plant-wide for

control in a single thermal oxidation system, despite the required additional source ducting and piping. This trend has been driven by an array of factors, including:

- Rising fossil fuel prices
- Tightening of emission limits for VOCs, HAPs, NO<sub>x</sub> and CO
- Goals for the reduction of a plant’s carbon footprint
- Increasing cost for disposal of organic waste liquids
- Minimizing the number of control systems to be maintained and points of emission monitoring and testing.

## WASTE LIQUIDS

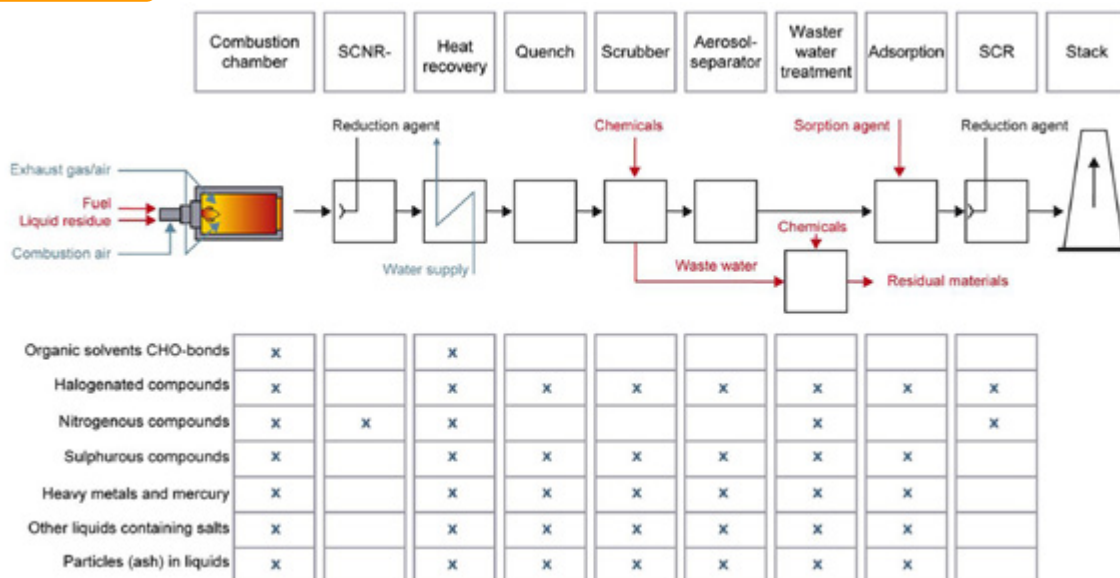


Table 1. Components in a modular direct-fired thermal oxidizer system can be selected based upon the waste stream contaminants.



CONTROL TRAIN



Figure 1. The thermal oxidizer system controls six process off gas streams, each handled by multiple skid-mounted off gas piping control trains.

All of these are key for companies increasingly committed to energy efficient, sustainable production. The benefits of a single, centralized thermal oxidation system can be best illustrated with a case study on the experience of a plant that recently added emission controls to many existing production processes.

Two types of thermal oxidizers are most frequently applied in the chemical processing industry: regenerative thermal oxidizers (RTOs) and direct fired thermal oxidizers (DFTOs), also known as afterburners. RTOs offer high thermal efficiency and very low fuel requirements for plants that generate dilute air streams contaminated with low concentrations of VOCs and HAPs. However, a DFTO is the best choice when:

- Production processes demand steam energy
- Required destruction efficiency is greater than 99.5%
- Highly caloric off gases with low oxygen must be handled
- High loading of halogenated or sulfurous compounds are expected (acid generators)
- Destruction of waste liquids is needed.

Many excellent guides and articles address the selec-

tion process between different types of oxidizers. This paper focuses on the DFTO exclusively.

A company manufacturing organic intermediates for the pharmaceutical and fertilizer industry decided to install a direct fired thermal oxidizer system to handle all liquid and gaseous waste streams from their many small to mid-size process reactors and storage tank vents. The DFTO is designed to handle a wide range of wastes including organic compounds containing halogens, sulfur and nitrogen.

The system consists of the required liquid pipe trains and storage tanks, process off gas pipe trains including explosion protection equipment, oxidation chamber, fire tube waste heat steam boiler, economizer, scrubber for acid gas removal, selective catalytic reduction (SCR) system for  $\text{NO}_x$  removal, an induced draft system fan and stack including emission monitoring system.

#### WASTE LIQUIDS AND OFF GAS SOURCES

The liquid wastes are accumulated from a number of sources across the plant and collected in a storage tank. The small storage tank was sized to accommodate the effluents from periodic tank cleaning processes. At this particular plant, all of the waste liquids are purely organic and have a consistent high caloric value which allows them to be fired directly through the thermal oxidizer's dual fuel burner system. After start-up, these systems can run entirely on the waste liquid fuel. Although not needed at this facility, a second system is sometimes used to collect liquid wastes with low or inconsistent caloric value or high water content. These wastes are atomized into the oxidation chamber adjacent to the burner through secondary injection lances.

In addition to the liquid wastes, a total of six process off gas streams are controlled by the thermal oxidizer system. Each off gas is handled by an independent control train and injected separately into the oxidation chamber (Figure 1). One stream is drawn from nitrogen-blanketed storage tanks using a blower, designed to handle potentially explosive gases, to maintain a slight negative pressure. The remaining streams



come from process reactors under pressure and can be routed to the oxidation chamber without blowers. The volume of off gas and VOC caloric content of each stream is highly variable, especially for several batch reactors and for the storage tanks which vent the most VOC during filling operations. These large variations of flow and loading lead to the first major benefit of a single, centralized DFTO system.

During preliminary engineering of the emission controls, consideration was given to multiple, smaller DFTO systems installed local to each process gas source. This arrangement has the advantage of minimizing the cost of the off gas collection system duct work and keeping each process fully independent. However, as the off gas sources were analyzed, it was determined that each DFTO would need to be designed for the peak off gas volume and caloric content required for that source under startup or upset conditions resulting in large oxidizer size. Furthermore, the much lower “normal” off gas flow is then difficult to handle efficiently in the large oxidizer. Designing for this high turndown is especially challenging for the several batch reactor processes.

Bringing all of these off gas streams to a single, centralized DFTO makes it possible to design for the peak VOC loading on several, but not necessarily all, processes simultaneously. This reduces overall system size *and capital cost*, while improving turndown and DFTO efficiency under normal operation. The availability of the organic waste liquids to the centralized DFTO also has a stabilizing effect on operation as the storage tank allows injection of liquids to cease during periods of maximum off gas loading (while collection in the tank continues) and to resume providing supplemental heat during periods of low off gas loading. The overall impact of the centralized DFTO is a significant reduction in natural gas (or other supplemental fuel) usage and thus the plant’s utility budget. By minimizing supplemental fuel usage, a corresponding reduction in the plant’s carbon footprint is achieved. Whether greenhouse gas (GHG) emission reductions are mandated, as they are in Europe, or whether they are voluntary, this is an increasingly important consideration for many companies.

### PROCESS STEAM

Many chemical plants generate and use steam on site for various process and heating requirements. The flue gas from a DFTO oxidation chamber is a source of high quality waste heat at 1,600 to 2,200°F that is easily convertible to saturated or superheated steam to supplement the facility’s gas, oil or coal-fired boilers and reduce their fossil fuel usage. To do this, the refractory lined oxidation chamber of the DFTO is simply transitioned to mate with the boiler inlet. Numerous considerations affect the boiler design and selection including:

- The desired steam pressure
- Requirement for superheated steam
- Presence of halogens or sulfur that generate acid gases
- The presence of silicon, phosphorous, metals and other dust-forming compounds.

In this case, the system includes a fire tube waste heat boiler to generate medium pressure-saturated steam, followed by a super-heater and an economizer for preheat of boiler feed water (Figure 2). High concentrations of hydrochloric



Figure 2. The system includes a fire tube, single pass waste heat boiler to generate medium pressure saturated steam.



and hydrobromic acid in the oxidizer flue gas result in a design that limits the heat recovery in the economizer to keep the outlet temperature above acid dew point under all operating scenarios. In addition, due to the distance from the facility's main boiler house, the system included a boiler feed water tank with redundant pumps and a deaerator for returning condensate.

Once again, a single, centralized DFTO when compared to multiple local units is significantly more beneficial. To achieve the same steam production, the capital cost is much lower for a single waste heat boiler system with high utilization than for multiple boilers connected to localized DFTOs. Waste heat boilers for localized DFTOs must be designed and sized for the peak flow and heat load from each oxidizer but will normally operate at just a fraction of that design capacity. It is obvious that the boilers themselves are capital intensive, but a single centralized waste heat boiler also minimizes installation costs associated with piping for boiler feed water, steam supply and blow down. The number of boiler startup and shutdown cycles is reduced, increasing the longevity of the equipment, and minimizing the time demands on boiler operators. The net effect is an improvement in the pay back that justifies waste heat recovery as steam. By choosing to recover waste heat, the plant further reduced their overall fossil fuel consumption and carbon footprint.

#### ACID SCRUBBER

After exiting the economizer, the flue gas is directed to a quench and acid scrubber (Figure 3). The quench cools and saturates the flue gas stream with water spray nozzles and flooded walls. The quench discharges the flue gas and water into the base of a vertical flow, packed column scrubber where HCl, Cl<sub>2</sub>, HBr, Br<sub>2</sub>, HF and SO<sub>2</sub> are absorbed and neutralized with NaOH solution. The scrubber removes over 99% of these contaminants; however, taller columns and multiple stages can be used to achieve



Figure 3. After exiting the economizer, the flue gas is directed to a quench and acid scrubber, much like this one.

greater than 99.9% removal. 50% NaOH is available as a utility at this facility and feeds a day-tank from which redundant pumps dose it into the recirculated scrubber wash water to control the pH.

The waste liquid and three of the six off gas streams currently contain halogens requiring scrubbing downstream of the oxidizer with the vast majority coming from methylene chloride in the waste liquid. Prior to installation of the new DFTO system, these halogenated liquids were transferred to tanker trucks and disposed of off site at significant expense (\$0.20 to \$0.50 per gallon). As with the waste heat boiler, adding a scrubber to the single centralized DFTO system has a significant capital cost advantage over scrubbing on multiple smaller units.

#### SELECTIVE CATALYTIC REDUCTION

In recent years, regulatory authorities have focused more and more on reducing NO<sub>x</sub> emissions from combustion



processes, and oxidizers are no exception. In the case of a boiler or process heater, the majority of  $\text{NO}_x$  emissions form as “thermal  $\text{NO}_x$ ” from  $\text{N}_2$  in the flame front of gas and oil-fired burners. In the case under study here, the vast majority of the expected  $\text{NO}_x$  comes from the oxidation of amines and other VOCs containing nitrogen in the plants off gases and waste liquids. Several alternative approaches for  $\text{NO}_x$  reduction were evaluated, including non-catalytic reduction in the oxidation chamber, before selective catalytic reduction (SCR) was chosen based on the high conversion efficiency required to meet the very low emission targets. SCR also offers the advantage that the catalyst used to reduce  $\text{NO}_x$  also favors the destruction of trace dioxins and furans formed during the oxidation of chlorinated compounds.

Because the flue gas exiting the scrubber is saturated and contains trace acids, the SCR system begins with a pre-heater module to raise the flue gas temperature above its dew point by mixing a small volume of hot air recirculated from downstream. This module is constructed in alloys resistant to chloride corrosion. The DFTO system’s redundant draft fans follow the pre-heater and are operated on variable frequency drives to maintain a pressure in the oxidation chamber slightly negative to atmosphere. The flue gas then enters

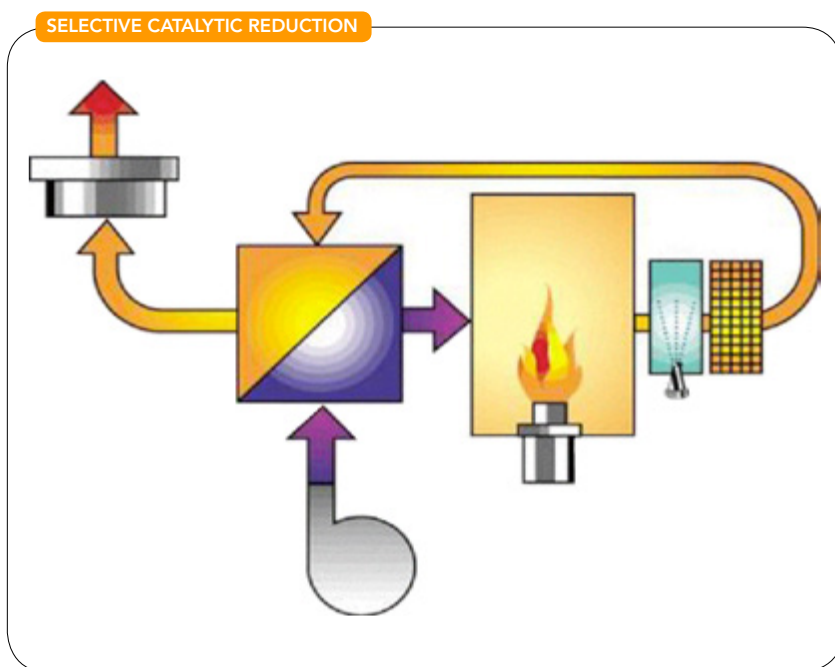


Figure 4. This diagram highlights the process flue gas takes in a selective catalytic reduction (SCR) system for  $\text{NO}_x$  control.

a recuperative heat exchanger that recovers heat from the SCR outlet (the reduction process is exothermic) to bring the flue gas up to reduction temperature. Finally, an aqueous ammonia reducing agent is sprayed into the stream, metered precisely to match the measured incoming  $\text{NO}_x$ , before the flue gas enters the catalyst beds where greater than 95% of the  $\text{NO}_x$  is converted to  $\text{N}_2$  and  $\text{H}_2\text{O}$ . The flue gas then passes through the other side of the heat exchanger on its way to the system stack where

it exhausts to atmosphere at about  $200^\circ\text{F}$  (Figure 4). Continuous emissions monitoring equipment in the stack, as required by the plant’s air permit, tracks exhaust concentrations of total hydrocarbon, hydrochloric acid and  $\text{NO}_x$  to confirm proper operation of the system.

The low  $\text{NO}_x$  emission required for this system was another factor in the selection of a single, centralized DFTO system over multiple systems. The SCR system is capital intensive, including expensive precious metal



catalyst, heat exchanger, and flue gas analyzers and strongly favored installing just one.

#### MEETING COMPLIANCE

For this manufacturer of organic chemicals operating many smaller processes, a single centralized thermal oxidizer system was the most cost-effective path to expand production while meeting new emission controls requirements. The resulting DFTO system benefited them by:

- Maximizing the destruction efficiency of VOCs and HAPs
- Reducing NO<sub>x</sub> emissions well below their permit limits
- Eliminating operating expenses for offsite waste liquid disposal
- Reducing plant-wide fossil fuel demand by using the caloric value of their wastes to generate steam
- Minimizing maintenance costs by installing just one system.

Taken all together, the plant's annual savings by reducing fossil fuel use in their boilers and by eliminating off site waste disposal costs actually exceed the operating costs

#### COMPLETE DFTO SYSTEM VIEW



Figure 5. This DFTO system helped reduce fossil fuel use in boilers and eliminated offsite waste disposal costs.

of their new emission control system. Over its design life, the DFTO system (Figure 5) provides a net pay back to the plant, proving that “being green” does not have to come at the expense of the bottom line. ●

**JON HOMMES** is an Engineer in the Clean Technology Systems business unit of Dürr Systems, Inc in Plymouth, Mich. He holds a B.S Ch.E. from the University of Michigan in Ann Arbor. For more information, contact [ctssales@durrusa.com](mailto:ctssales@durrusa.com).

# CHEMICAL PROCESSING

LEADERSHIP | EXPERTISE | INNOVATION

## ADDITIONAL RESOURCES

### eHandbooks

Check out our vast library of past eHandbooks that offer a wealth of information on a single topic, aimed at providing best practices, key trends, developments and successful applications to help make your facilities as efficient, safe, environmentally friendly and economically competitive as possible.

### Upcoming and On Demand Webinars

Tap into expert knowledge. *Chemical Processing* editors and industry experts delve into hot topics challenging the chemical processing industry today while providing insights and practical guidance. Each of these free webinars feature a live Q&A session and lasts 60 minutes.

### White Papers

Check out our library of white papers covering myriad topics and offering valuable insight into products and solutions important to chemical processing professionals. From automation to fluid handling, separations technologies and utilities, this white paper library has it all.

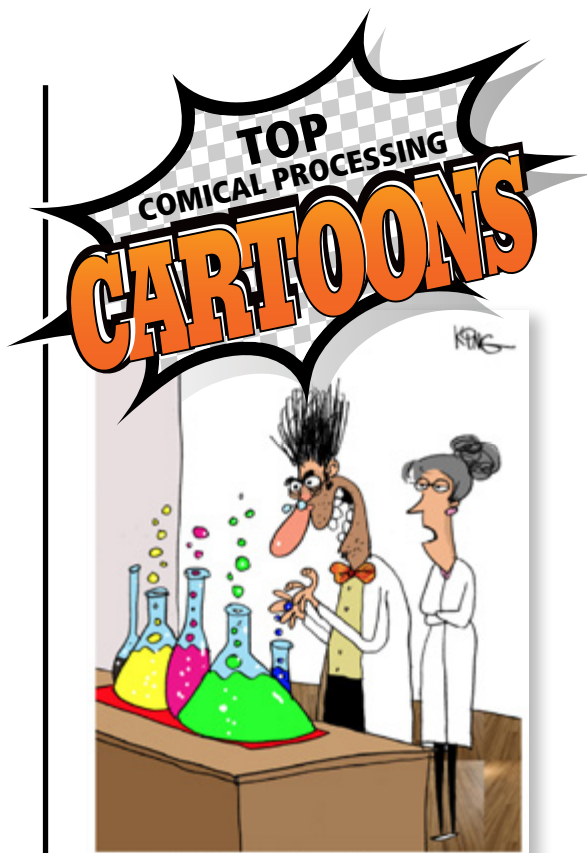
### Minute Clinic

*Chemical Processing's* Minute Clinic podcast series is designed to tackle one critical issue at a time — giving you hard-hitting information in just minutes.

### Ask the Experts

Have a question on a technical issue that needs to be addressed? Visit our Ask the Experts forum. Covering topics from combustion to steam systems, our roster of leading subject matter experts, as well as other forum members, can help you tackle plant issues.

JOIN US ON  
SOCIAL MEDIA!



Visit the lighter side, featuring drawings by award-winning cartoonist Jerry King. Click on an image and you will arrive at a page with the winning caption and all submissions for that particular cartoon.