WWW.CHEMICALPROCESSING.COM

CHEMICAL PROCESSING

LEADERSHIP | EXPERTISE | INNOVATION

Special Report

EFFECTIVELY DEAL WITH WASTE GAS

Start ▶

SPONSORED BY

DÜRR

PutmanMedia®

TABLE OF CONTENTS

AD INDEX

Cut the Cost of Waste Gas Incineration

An RTO often can offer an effective and fuel-efficient option

By Dan Banks, Banks Engineering, Inc.

A REGENERATIVE thermal oxidizer (RTO) burns very lean waste gases without using much fuel. If an RTO can be used, it's always more fuel-efficient than any other type of oxidizer. Operating temperature is about the same as a normal thermal oxidizer (say, 1,600°F) but the hot flue gas passes through a heat exchange module before reaching the stack.

The module is an insulated box full of heat exchange media, usually ceramic packing. At least two modules are used — one absorbs heat from the flue gas while the other sheds heat into the waste gas (Figure 1). When a box has absorbed all the heat it can, it's taken offline; waste gas then passes through it backwards until the box is cool again. Once cooled, it's returned to handling hot flue gas. Two boxes are needed so the flue gas always has a path to the exhaust stack — specialized valves set on a timer switch each box from heating to cooling every 5 minutes or so.

In this way, if one pound of waste gas enters at 70°F, one pound of flue gas exits at 200°F. With other thermal oxidizer designs, the pound of flue gas may exit at 500°F or 1,600°F — a lot more heat is lost up the stack. If the waste gas is lean, most of this heat comes from firing auxiliary fuel. The popularity of RTO units stems from the desire to cut such fuel costs.

THE BASICS

Waste gas incinerators react oxygen with waste hydrocarbons at high temperature to produce a clean flue gas. A perfect incinerator would have a destruction and removal efficiency (DRE) of 100%, zero fuel usage and zero emission of carbon monoxide and nitrogen oxides. A small amount of the original hydrocarbons always remains, though. If 1% is left, the DRE is 99%. Some CO and NO_x always are produced, too. However, NO_x emissions are lower for an RTO than for almost any other type of thermal oxidizer. Table 1 compares various options.

The U.S. Environmental Protection Agency and local air boards require DRE values from 95% upward, and CO and NO_x emissions measured in the "tons per year" range. Fuel usage is up to the operator but more fuel means higher operating cost and more greenhouse gases, so lower is better.

For good DRE values, furnace temperature must be high enough, residence time of the flue gas in the furnace must be long enough and 2% to 3% O_2 must remain in the flue gas leaving the stack. Stack temperature doesn't matter — furnace temperature is all that's important.

For most incinerators, furnace temperature is 1,400°F to 1,600°F. Higher temperatures require more expensive refractory to avoid heat damage. Furnace residence time typically is 0.5–1 seconds. Hydrocarbons that are hard to burn, like pesticides, may require more time. Oxygen content usually is about 3% or more by volume; as low as 2% O_2 might be OK. If the waste gas is "dirty air," it will contain all the oxygen needed. Otherwise outside air has to be added.

If the waste gas is relatively rich with hydrocarbons, a

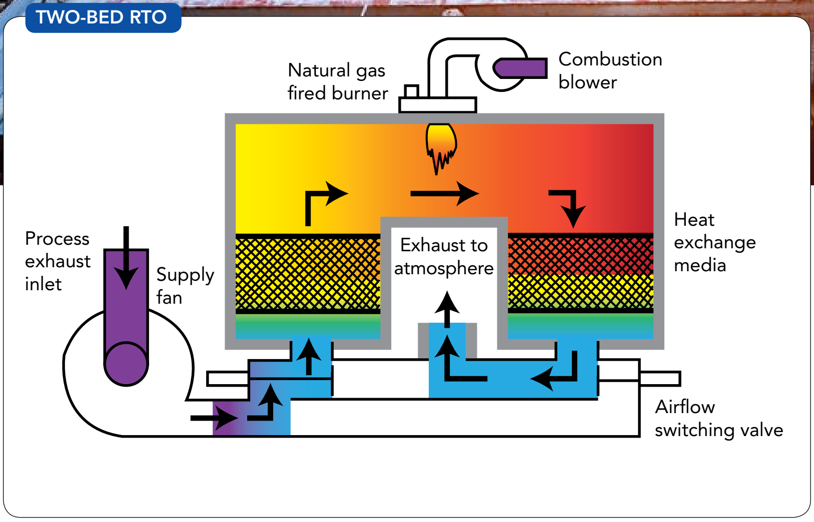


Figure 1. Heat exchange media alternate between heating and cooling. *Source: CMM Group.*

simple "direct fired" thermal oxidizer with a small burner will do the job. In this case, heat recovery is unnecessary but you can add a boiler if you need steam for process heating or to generate electricity.

Lean waste gas, in this situation, may require a large burner. That means some sort of heat recovery will make sense, because the cooler your stack gas, the lower your net operating costs. An RTO recovers heat very efficiently.

LIMITATIONS

While an RTO is the most fuel-efficient oxidizer, it doesn't suit all applications:

- A waste gas with entrained particles or droplets may cause fouling of the heat exchange media. In-place cleaning of the media is difficult or impossible. Fouled media means pressure-drop and efficiency problems. A direct fired oxidizer would be better.
- An intermittent waste gas requires idling or shutting down the RTO when waste isn't flowing. It can take several hours to heat an RTO system for operation. A direct fired oxidizer probably would be better.
- Too rich a waste gas may lead the RTO to be too efficient, resulting in furnace temperatures that can cause refractory damage. If the waste-gas heating value significantly exceeds 20 Btu/ft^3, an RTO is a bad choice. Most RTO designers want waste gas no richer than 25% of the lower explosive limit.
- A waste gas containing chlorinated hydrocarbons, like methyl chloride, or sulfur bearing compounds, like hydrogen sulfide, will form a stack gas that might produce acid droplets if cooled enough — keep in mind that an RTO provides cooler stack gas than other types of oxidizer. If acid droplets are expected, you may need special construction, driving up cost.

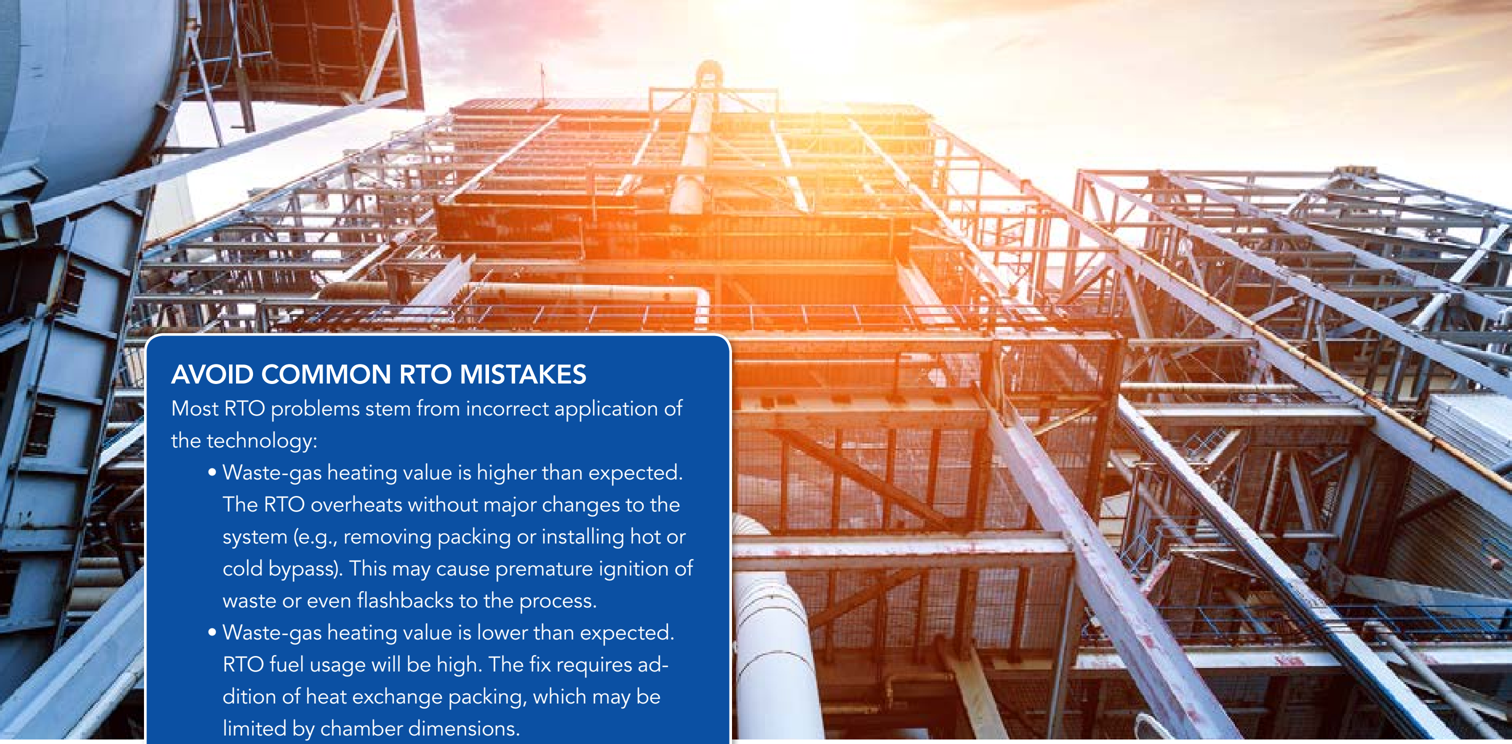
The sidebar summarizes some common mistakes in RTO selection and operation.

THE ROLE OF PACKING

Directing the lean waste gas through a packed bed enables its temperature to be brought close to the target furnace temperature using only residual heat left in the bed by the hot flue gas. Sometimes this results in the waste gas hydrocarbons igniting on their own, achieving a further rise in temperature. While an RTO furnace always has a fuel gas burner, with good design fuel gas consumption might be zero during normal operation.

Without heat exchange packing, an operating RTO would perform like an ordinary incinerator — fuel usage to reach the needed furnace temperature would be high with a lean waste gas. More bed packing lowers fuel gas needed or raises furnace temperature reached.

If the beds were never switched, an RTO would perform like an ordinary incinerator — the hot flue gas would heat the bed it's flowing through to the flue gas temperature and the lean waste gas would draw all of the heat out of the



AVOID COMMON RTO MISTAKES

Most RTO problems stem from incorrect application of the technology:

- Waste-gas heating value is higher than expected. The RTO overheats without major changes to the system (e.g., removing packing or installing hot or cold bypass). This may cause premature ignition of waste or even flashbacks to the process.
- Waste-gas heating value is lower than expected. RTO fuel usage will be high. The fix requires addition of heat exchange packing, which may be limited by chamber dimensions.
- Waste gas has unexpected particulate matter. Simple dusts will block gas passage through the heat exchange medium but can be vacuumed off. Reactive particles can bond to the medium, ruining it and, thus, requiring bed replacement. Combustible particles may collect in the medium and light off, causing thermal damage. Waste gas filters might be needed.
- Waste gas flow is greater than expected. Pressure drops through the RTO system may require larger blowers or different heat exchange medium.
- Waste gas flow is intermittent, with rapid startups required. From a standing start an RTO system can require several hours of heat-up. Abrupt flow or heating value changes cause temperature excursions and higher stack emissions.

Other RTO problems involve operating and maintenance practices:

- Nuisance shutdowns tempt operations to use automatic restart logic. Stay with manual restarts to catch potential safety problems and avoid disaster.
- Maintenance takes shortcuts. Using the wrong type of replacement thermocouple, leaving access doors loose (leaky) and other casual mistakes can result in elevated emissions, thermal damage or worse.
- Staff doesn't pay due care with the waste-gas gathering system. Spilling solvent under a process vent collection hood can convert the low-Btu waste gas into a high-Btu hazard for the RTO.
- Seasonal plant operating changes are ignored. Fuel usage can creep up. So, review RTO bed switching times. They affect heat recovery and fuel usage.
- The refractory lining is neglected. It doesn't last forever. Look for developing hot spots so you can schedule repairs to avoid unplanned shutdowns.

other bed. Fuel consumption would be high with a lean waste gas. Shorter bed switching time reduces fuel gas needed or increases furnace temperature reached.

The flow and composition of the waste gas determine bed size and packing type. You must use enough packing to absorb the heat from the full flow of stack gas — once a layer of packing is heated to combustion chamber temperature, it can't pick up any more energy so another layer must be added. The designer sets the pounds of packing in each bed according to the rate of stack gas flow and the time the bed is absorbing heat before it's switched. The type of packing used is an economic decision — random packing is cheaper but structured packing (Figure 2) takes up less room for the same amount of heat transfer.

TYPICAL CERAMIC BLOCK

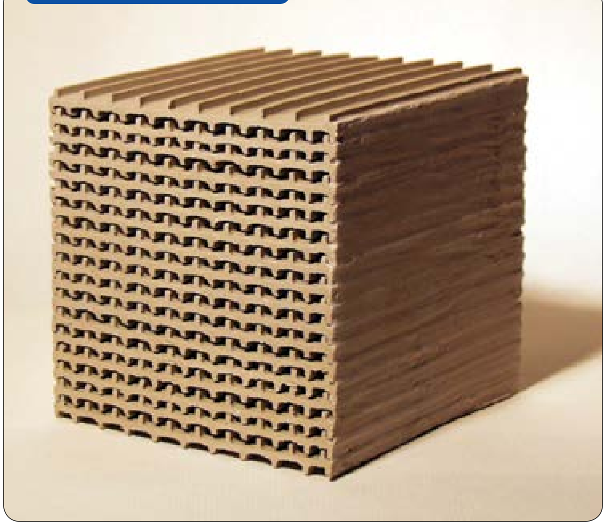


Figure 2. Structured packing requires smaller volume than random packing for the same heat transfer. *Source: Lantec.*

TYPE	WASTE TYPES	HEAT RECOVERED?	STACK TEMPERATURE, °F	MAXIMUM DRE, %	HEAT RECOVERY METHOD
Direct fired	Any gas or liquid	No	1,200–2,200	98–99.99+	None
Catalytic	Lean waste gases	Yes	≈500	95–99+	Metal gas/gas heat exchanger
Recuperative	Lean waste gases	Yes	≈500	95–99.9+	Metal gas/gas heat exchanger
Boiler	Any gas or liquid	Yes	350+	98–99.99+	Boiler and economizer
RTO	Lean waste gases	Yes	200–300	95–99+	Packed beds

Table 1. An RTO provides the lowest stack temperature.

Bed construction and the flow and composition of the waste gas dictate bed switching time. For greater heat-transfer efficiency, switching time needs to be shorter. But with larger beds switching time can be extended because there's more packing to absorb the heat. Every time the beds switch, a small burst of unburned waste gas flows to the stack; a high required DRE mandates longer switching times, which results in larger packed beds.

VARYING QUALITY GAS

A waste gas that usually is lean but occasionally can be richer demands special attention, as waste gas with more hydrocarbons requires less heat recovery to maintain low fuel-gas consumption. To reduce the heat recovery efficiency of the system, you can remove bed packing — but this is difficult. So, in such situations, units generally rely on either cold gas bypass (CGB) or hot gas bypass (HGB) to divert some gas around the heat recovery section of the RTO. With CGB, part of the cold waste gas is ducted directly to the furnace; with HGB, part of the hot furnace exhaust is ducted directly to the stack.

CGB and HGB also are used to keep the furnace from reaching an excessive temperature, which could cause permanent refractory damage or require specification of a different refractory grade. A typical high-temperature-shutdown set point might be 1,800°F.

HGB gives a higher stack temperature than that for most RTO designs. Special stack construction (stainless or refractory-lined carbon steel) may be required to avoid damage.

During normal operation RTO furnace and stack temperatures vary over a narrow range. This is because when the beds switch the waste gas entering the furnace (and the furnace gas entering the stack), they now are flowing through the alternate bed. The waste gas suddenly is hotter because it's flowing through the bed recently in contact with the hot flue gas. The flue gas suddenly is colder because it's flowing through the bed recently cooled by the incoming waste gas. If the beds switch every 5 minutes, the flue gas and combustion chamber reach their "average" temperatures approximately 2.5 minutes after the switch.

DIFFERENT DYNAMICS

In a direct fired incinerator increasing the fuel flow results in hotter stack gas within 5 seconds to 10 seconds. In an RTO increasing the fuel flow to the burner immediately heats the furnace — but the stack gas temperature rise is delayed by the heat absorbed in the packed beds. The higher RTO furnace temperature puts more heat in the packed bed receiving the

flue gas. At the end of the cycle that bed is hotter than at the end of the previous cycle; when the waste gas is switched back into it the waste gas temperature entering the furnace will be higher than in the previous cycle. The stack temperature as well as the furnace temperature will swing around an average value as the bed switching proceeds. In fact, a step change in fuel flow may require several cycles of bed switching to reach stable average stack and furnace temperatures.

This type of delayed response happens with any variation in RTO operation, including changes to waste gas flow, waste gas hydrocarbon content, burner fuel or air flow, and CGB or HGB flow.

DESIGN CONSIDERATIONS

As we all know, every pound of waste gas, air or fuel gas entering must be matched by a pound of flue gas out the stack and every Btu entering the RTO (as sensible heat due to a heated waste gas or as hydrocarbon heat release) must show up as a Btu in the stack gas or as heat loss through the vessel shell. What happens in the packed beds or the switching valves is important for saving fuel but, taken as a whole, "what goes in has to equal what comes out." So, for instance:

- If it's impossible to feed enough air to produce around 3% oxygen in the stack gas, then the RTO can't operate as intended.
- If the measured stack temperature is higher or lower than predicted by the Btu balance, then some other input isn't being considered — maybe the waste gas is richer or leaner than expected.

Given a specific waste gas, air flow, fuel gas flow and heat loss through the vessel refractory and insulation, you can calculate the stack gas flow, composition and temperature even if nothing is known about the bed packing, switching times, bypass flow or any other detail.

RTO design involves eight steps:

1. Perform a heat and material balance on the waste stream, including minimum/maximum flow, minimum/maximum hydrocarbon load, etc. Determine if any of the cases excludes use of an RTO — for instance, is the waste-gas hydrocarbon load so high that a different type of incinerator would make more sense?
2. Specify the packing types and amounts, along with the bed switching times to achieve the heat recovery efficiency needed for all operating cases. Packing vendors can provide these calculations for their products.
3. Size the combustion chamber, stack, inlet ducting, any bypass ducting, etc.
4. Size and specify the waste gas blower, fuel gas burner and combustion air blower.
5. Specify the type and amounts of refractory lining and external insulation.
6. Prepare the process and instrumentation diagram and process flow diagram(s).
7. Put together specification sheets for purchase of blowers, burners, instruments, etc.
8. Prepare fabrication drawings, parts lists, operating instructions and other documentation.

AN ATTRACTIVE ALTERNATIVE

An RTO provides the highest fuel efficiency of any type of waste-gas thermal oxidizer and, thus, may allow you to cut costs for incineration. However, it isn't best for all services, so you must understand its limitations. When an RTO is the right choice, you must then consider its particular design and operational issues. ●

DAN BANKS is principal consultant for Banks Engineering, Inc., Tulsa, Okla. E-mail him at dan@banksengineering.com.

Ecopure OXIDIZERS

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

Dürr **Ecopure** systems offer leading technologies 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.

CO$_2$ Gets a New Fizz

Technologies transform greenhouse gas into a feedstock for chemicals

By Seán Ottewell, Editor at Large

EFFORTS TO exploit waste carbon dioxide as a raw material to manufacture chemical products are advancing, driven by economics and the quest for sustainability. Companies such as Novomer, Oakbio and Liquid Light in North America, plus the Solar-Jet project in Europe are at various stages of developing technology to use the greenhouse gas. Such work is prompting interest and investment from major chemical companies including Saudi Aramco, DSM, BP and Shell.

For example, on May 21, Novomer, Waltham, Mass., announced the commercial introduction of its Converge polypropylene carbonate polyols for use in polyurethane formulations targeted at coatings, adhesive, sealant, elastomers (CASE) products, as well as rigid and flexible foams.

The move is an important step for the company, which has developed two technology platforms — one for carbon dioxide and the other for carbon monoxide — based on proprietary catalysts to transform propylene oxide or ethylene oxide into economically competitive, high-performance industrial products.

Converge polyols are designed to replace conventional petroleum-based polyether, polyester and polycarbonate polyols. The products, which are based on the co-polymerization of carbon dioxide and epoxides, contain more than 40% by weight carbon dioxide (Figure 1). Novomer says the use of waste carbon dioxide as a significant raw material gives the product an extremely low carbon footprint. In addition, because waste carbon dioxide is markedly lower in cost than conventional petroleum-based raw materials, production at full commercial scale is said to offer favorable economics compared to those of making conventional polyols.

The initial product offerings — 1,000- and 2,000-molecular-weight grades — are manufactured at a multi-thousand-ton commercial-scale toll facility in Houston. They currently are being tested by users and at the company's internal development center at Waltham.

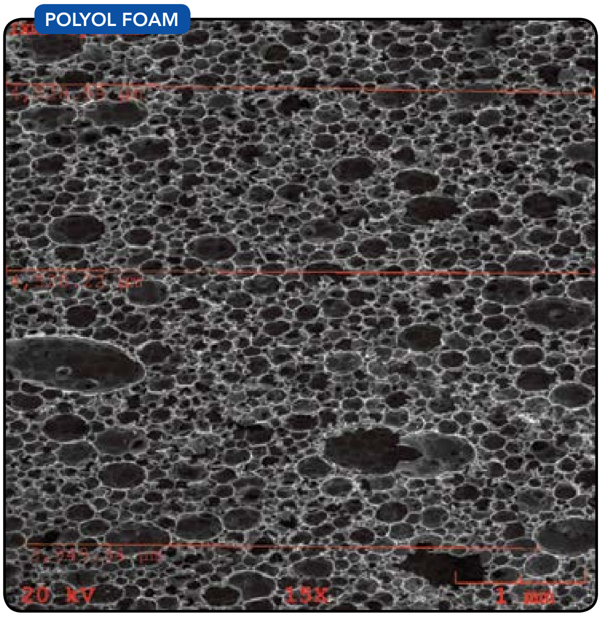


Figure 1. Foam contains more than 40 wt. % carbon dioxide and has an average cell size of about 150 microns. *Source: Novomer.*

"I can't name names yet but in June our first customer started buying one of our products in commercial quantities," says Peter H. Shepard, Novomer's chief business officer. "It's one thing to have the technology but a whole other thing to have someone else discover the value in a product and pay for it. That's a huge step forward. Once one customer starts using the product and getting good performance, it will help to springboard interest," he adds.

Interestingly, much of the interest in the technology is from companies that currently aren't in the CASE market but want to gain a foothold in it.

Figure 2. Vertical pipes provide laboratory (blue container) with flue gas directly from stack. *Source: Oakbio.*

The success of Novomer's technology has attracted investment from Saudi Aramco Energy Ventures (SAEV), the corporate venturing subsidiary of Saudi Aramco, Dhahran, Saudi Arabia.

SAEV's investment will fund ongoing development of the technology platforms as well as construction of a market-development plant to manufacture carbon-dioxide–based polyols, and the enhancement of Novomer's sales and marketing organization.

Shepard will not reveal the scale of SAEV's investment but does admit that it gives the company a good solid three years of operations. "Aramco are definitely into being a strategic partner, especially in the area of manufacturing. So if we meet certain targets, they would be very interested in housing a commercial plant." DSM also is involved but in a traditional venture capitalist role, he notes.

Novomer currently is developing a continuous production process at the Texas plant — an effort that will take about three years, he says — and working to make its catalysts less costly to use and more productive.

ALBERTA-BACKED INITIATIVES

Meanwhile Oakbio, Sunnyvale, Calif., and Liquid Light, Monmouth Junction, N.J., are among 24 groups that each will receive C$500,000 ($454,000) from the Climate Change and Emissions Management Corp. (CCEMC), Sherwood Park, Alberta, as part of its C$35-million (U.S.$31.8-million) international competition for technology to markedly cut greenhouse gas (GHG) emissions by creating new carbon-based products and markets. (For more details, see: "Carbon Competition Names First Round Winners," http://goo.gl/0bclv3).

Oakbio has created a technology that uses chemoautotrophic microbes to produce a number of chemicals from industrial waste, carbon dioxide and energy. Currently the company's main products are polyhydroxyalkanoate (PHA) polymers and n-butanol.

"Because we run a co-located flue-gas test laboratory at Lehigh Southwest Cement (Figure 2), Tehachapi, Calif., we were able to develop flue-gas-resistant strains using actual unadulterated flue gas and achieve up to 70% dry-weight yield of PHAs," says Brian Sefton, Oakbio's president and chief scientist.

The Lehigh project is significant because cement production currently accounts for 5–8% of global carbon dioxide release, according to Sefton. Lehigh itself produces 1 million t/y of the greenhouse gas.

Capture and conversion of carbon dioxide from the plant would yield over $1 billion/y of PHA or other products, Sefton notes. It also would increase the value of the cement produced there because builders could claim credits for achieving green building standards by using it, he adds. On a broader note, capturing and converting the 2 billion t/y of carbon dioxide emitted by the worldwide cement industry could supply the

entire global plastics market, he says.

Oakbio's n-butanol is the newer of the two products. "This is an important chemical feedstock as well as a drop-in biofuel with an octane rating similar to gasoline. This model is also capable of producing thousands of other compounds, many of which we have made in small amounts already such as diacids, ketones, esters, fatty acids and organic acids," notes Sefton.

The company currently uses bioreactors that vary in volume from 250 ml to 20 L. Oakbio is raising funds to take this program to pilot scale of 1,000–5,000 L.

The process has a number of advantages, says Sefton. First, it requires no costly extra ingredients such as promotors or antibiotics. This means the process water is very clean and can be re-used easily. "In addition, the process can uptake organic acids, acetone, benzene, diesel fuel and many other chemical compounds which are considered waste, including even dioxin, and break these down into energy and feedstocks for our target compounds."

Oakbio is working closely with Ohio State University, Columbus, Ohio, to leverage the school's molecular biology and enzymology expertise to increase n-butanol production to commercial levels. Sefton expects to achieve this in two years.

The PHA process is cost competitive and projected to be profitable at scale, he notes, while the n-butanol business is projected to be profitable once production levels reach the company target. Several chemical companies and fuel producers are watching developments closely, Sefton adds.

SOLAR SYNGAS

Figure 3. Process uses concentrated sunlight to convert carbon dioxide and water into a syngas that then is used to make kerosene. *Source: ETH Zurich.*

Meanwhile, Liquid Light has developed technology based on low-energy catalytic electrochemistry to use carbon dioxide to produce chemicals. By adjusting the catalyst design and combining hydrogenation and purification operations, the technology can make a range of commercially important multi-carbon chemicals including glycols, alcohols, olefins and organic acids.

The company believes that by using other feedstocks alongside carbon dioxide, a future plant would be able to manufacture multiple products simultaneously. "We are working on other catalysts to expand the list of possible products too," adds Kyle Teamey, Liquid Light's CEO.

A major chemical company is partnering in the work. This partner already has a variety of heterogeneous, homogenous and hybrid catalysts for the electrochemical reduction of carbon dioxide and also has developed catalysts for downstream processes, he notes.

In March, Liquid Light unveiled its first process — for the manufacture of monoethylene glycol (MEG). In lab-scale test runs, the demonstration electrocatalytic reaction cell met targets for energy needed per unit of output, rate of production, yield and stability/longevity of cell components.

Its process requires $125 or less of carbon dioxide to make a ton of MEG versus an estimated $617 to $1,113 of feedstocks derived from oil, natural gas or corn needed by other processes, claims the firm. These differences are especially significant because MEG sells for between $700 and $1,400 per metric ton.

The company says that current estimates indicate that licensees would gain more than $250 in added project value by opting for its process instead

of the best currently available technology for a 400,000-t/y MEG plant. A 625,000-t/y plant would have a 15-year net present value of over $850 million to a licensee, it adds.

An added bonus is that intermittently available renewable energy sources such as solar and wind can power the process. The result is that chemicals can be made directly from renewable energy sources and carbon dioxide, boasts the firm.

The plan now is to build a pilot plant in Canada to produce a ton of products per day and help to further validate the technical and economic feasibility of the technology.

SEEKING A SOLAR SOLUTION

In Europe, a joint research/industry project has demonstrated the production path for so-called "solar" kerosene. Known as Solar-Jet, the project uses concentrated sunlight to convert carbon dioxide and water into a syngas via a redox cycle with metal-oxide-based materials at high temperatures (Figure 3). The syngas, a mixture of hydrogen and carbon monoxide, then is converted into kerosene using commercial Fischer-Tropsch technology.

ETH Zurich, Zurich, Switzerland; Bauhaus Luftfahrt (a research institute funded by four aerospace companies), Munich, Germany; the German Center for Aerospace, Cologne, Germany; research and technology development consultancy ARTTIC, Paris, France; and Shell Global Solutions, Amsterdam, The Netherlands, are pioneering the development of the new pathway.

The Swiss university is working on the solar splitting of water and carbon dioxide to produce solar syngas, while Shell is addressing the syngas-to-solar-kerosene step.

The solar reactor consists of a cavity receiver with a 4-cm-diameter aperture through which concentrated solar radiation can pass; the aperture incorporates a compound parabolic concentrator to further boost the concentration. A 24-cm-diameter, 3-mm-thick clear fused-quartz disk window seals the reactor front. Sunlight comes from ETH's high-flux solar simulator.

The solar cavity receiver contains a reticulated porous ceramic foam made of pure cerium oxide. (The oxides of cerium have emerged as attractive redox active materials because of their ability to conduct oxygen ions faster than either ferrite-based oxides or other non-volatile metal oxides.)

This two-step thermochemical reaction's big advantage is its elimination of the gas separation steps needed after traditional thermolysis.

"Increasing environmental and supply security issues are leading the aviation sector to seek alternative fuels which can be used interchangeably with today's jet fuel, so-called 'drop-in' solutions," states Andreas Sizmann, the project coordinator at Bauhaus Luftfahrt. "With this first-ever proof-of-concept for 'solar' kerosene, the Solar-Jet project has made a major step towards truly sustainable fuels with virtually unlimited feedstocks in the future."

"The solar reactor technology features enhanced radiative heat transfer and fast reaction kinetics, which are crucial for maximizing the solar-to-fuel energy conversion efficiency," adds Aldo Steinfeld, who leads fundamental research and development of the solar reactor at ETH Zurich.

Although the solar-driven redox cycle for syngas production still is at an early stage of development, a number of companies including Shell already are processing syngas to kerosene on a global scale. "This is potentially a very interesting, novel pathway to liquid hydrocarbon fuels using focused solar power," says Hans Geerlings, principal research scientist at the Shell Technology Center in Amsterdam. "Although the individual steps of the process have previously been demonstrated at various scales, no attempt had been made previously to integrate the end-to-end system. We look forward to working with the project partners to drive forward research and development in the next phase of the project on such an ambitious emerging technology."

Within four years 50-kW solar reactor technology will be available but the first commercial, MW-scale application won't appear for 15 years, believes Steinfeld.

"Commercial scale-up will take place in a region of rich solar irradiation, where there is at least 2,000 kWh per square meter annually. The technical challenges involved in such a scale-up include efficient heat transfer and rapid reaction kinetics for maximum solar-to-fuel energy conversion efficiency," he adds. ●

Increase Sustainability with Thermal Oxidation

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

Jon Hommes, Engineer, Dürr Systems, Inc.

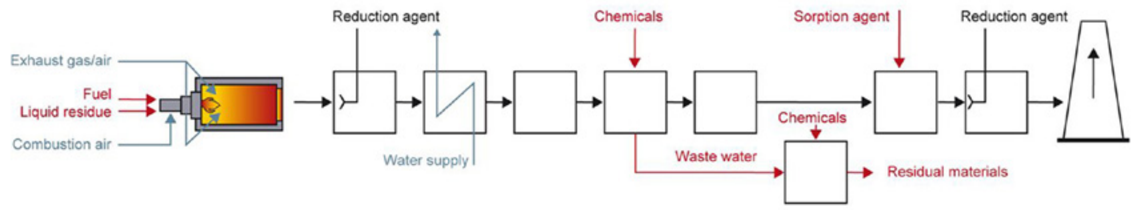
INSTALLING NEW production processes or upgrading and expanding existing lines requires a review of the expected emissions. The right emission control system for Hazardous Air Pollutants (HAPs) and Volatile Organic Compounds (VOCs) can help efficiently and economically dispose of these environmentally 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_x 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.

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:

WASTE LIQUIDS



	Combustion chamber	SCNR-	Heat recovery	Quench	Scrubber	Aerosol-separator	Waster water treatment	Adsorption	SCR	Stack
Organic solvents CHO-bonds	x		x							
Halogenated compounds	x		x	x	x	x	x	x	x	
Nitrogenous compounds	x	x	x				x		x	
Sulphurous compounds	x		x	x	x	x	x	x		
Heavy metals and mercury	x		x	x	x	x	x	x		
Other liquids containing salts	x		x	x	x	x	x	x		
Particles (ash) in liquids	x		x	x	x	x	x	x		

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

- 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 selection 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 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.

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.

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 and hydrobromic acid in the oxidizer flue gas result in a design that limits the heat recovery in the economizer to keep the outlet

FIRE TUBE STYLE BOILER

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

QUENCH AND ACID SCRUBBER

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

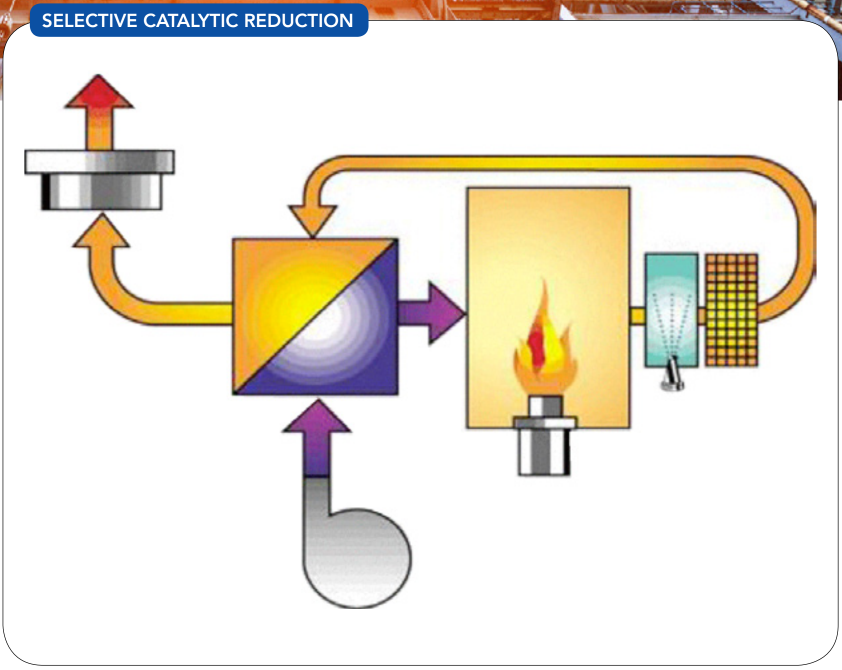


Figure 4. This diagram highlights the process flue gas takes in a selective catalytic reduction (SCR) system for NO$_x$ control.

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_2, HBr, Br_2, HF and SO_2 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 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$_x$ emissions from combustion processes, and oxidizers are no exception. In the case of a boiler or process heater, the majority of NO$_x$ emissions form as "thermal NO$_x$" from N_2 in the flame front of gas and oil-fired burners. In the case under study here, the vast majority of the expected 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 NO$_x$ reduction were evaluated, including

COMPLETE DFTO SYSTEM VIEW

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

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 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 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 NO_x, before the flue gas enters the catalyst beds where greater than 95% of the NO_x is converted to N_2 and H_2O. 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°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 NO_x to confirm proper operation of the system.

The low 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_x 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 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.

Set Up an Effective Greenhouse Gas Monitoring Plan

Several steps play a crucial role for success

By Anna Koperczak, SSOE Group

SEPTEMBER 30, 2011, marked an important date for the new mandatory Greenhouse Gas Reporting Program (GHGRP) of the U.S. Environmental Protection Agency (EPA). It was the first nationwide deadline for companies to report their annual greenhouse gas (GHG) emissions levels. More than 10,000 industrial facilities across the U.S. had to submit data for the year 2010.

With the first report deadline complete, many plant managers are starting to breathe a little easier and feel the challenges and confusion surrounding the process are behind them. However, the deadline to report the inventory for 2011 is March 31, 2012. For those facilities that will be reporting inventory for the first time, it's essential they establish a GHG emissions monitoring plan to obtain and submit accurate data.

GHGRP OVERVIEW

The EPA's Mandatory Reporting of GHGs Rule (40 CFR Part 98) is the basis of the GHGRP, and is the first nationwide regulation requiring companies to report their GHG emissions data and other relevant information annually, starting with 2010 calendar year emissions. The rule applies to certain industry-specific sources and facilities that emit at least 25,000 metric tons of GHGs per year.

This federal GHGRP is separate from any state-mandated GHG reporting programs or air emission reporting required by greenhouse gas permitting programs. The reporting requirements under each program may have similar elements but also can differ significantly.

The goal of the GHGRP is to give federal authorities an accurate depiction of who is emitting GHGs and at what level. The information reported to the EPA under this program will become public knowledge and the data will help shape future carbon-control policy decisions by the EPA.

The first challenge many companies face is understanding all the requirements. The initial focus of the GHGRP is on stationary combustion sources at all industrial facilities, and includes additional emission sources for specific industry sectors (as identified in the GHG Rule subparts). A facility must determine if it is subject to any of the specific industry sector subparts based on type of processes on-site.

THE MONITORING PLAN

An important element of the program is developing and implementing a reliable written monitoring plan that describes how the facility will comply with the requirements. An effective monitoring plan defines the GHG emission source; processes and schedules for collecting emissions data; calculation methodology; and quality assurance for these data. It's the key to simplifying the data collection process and increasing reporting accuracy. A site must keep the monitoring plan current and modify it as necessary to reflect changes in regulatory requirements, production processes, monitoring instrumentation, and quality assurance procedures. The monitoring plan itself is a recordkeeping requirement only if the facility exceeds the 25,000-mt/yr reporting threshold, or if it contains specific source categories that must report emissions. The monitoring plan need not be submitted to the EPA; however, it should be compiled in a format that can be audited by the agency if requested.

Setting up a successful monitoring plan involves a few important steps, including identifying sources of GHGs; determining the proper methods for monitoring; collecting the data; and selecting the procedures and methods for calculating and quality-checking the data from each measurement device or method.

Successfully developing and implementing the monitoring plan requires a team with a wide variety of skills and expertise. The team may include, but is not limited to, purchasing, accounting, operations, maintenance, information systems, environmental services, quality, engineering and outside resources.

Many companies augment their internal team with outside resources. Because understanding current regulations, reporting,

monitoring and permitting require special skills, these firms, rather than adding to staff, use an experienced outside expert who knows how EPA wants the information structured and how to compile it efficiently. Another approach is to use an outside resource to train staff to handle some of the activities such as calibrating measurement devices and analyzing data.

SOURCE IDENTIFICATION

The first step of a successful monitoring plan is to identify and document sources that produce GHGs and describe what's included or excluded in the relevant industry source category. Many facilities at this time only will need to report stationary combustion sources such as boilers, process heaters, small heaters and combustion turbines. Reporting of emissions from pilot lights isn't required. GHG Rule updates, finalized in September 2011, exempt emissions from emergency generators and equipment.

A site also must evaluate the GHG Rule's industry-sector-specific emission sources, if applicable, for inclusion or exclusion from the list of identified sources. For example, the technical clarifications, finalized in September 2011, require a petrochemical production facility to include and report GHG emissions from process vent stacks not associated with stationary combustion units. The site must trace such process vent stacks back to the process being vented that's generating the GHG emissions. Other specific industry sectors, like suppliers of industrial GHG as a final product, needn't report emissions from the destruction of fluorinated GHGs removed during the production process as byproducts or other wastes.

The source determines which covered GHGs must be documented — for example, CO_2, CH_4 and N_2O are required for stationary combustion sources while CO_2 and CH_4 are required for asphalt blowing.

Tools that teams can use to identify GHG emission sources include process flow diagrams, piping and instrumentation drawings, equipment lists, stack location diagrams, as well as total process byproducts or wastes generated throughout the site. The team should conduct a walkdown and visual verification of the facility and sources because diagrams and drawings may not always be accurate or up to date.

MONITORING TECHNOLOGY

The next step is to determine the monitoring methods and measuring device or procedure based on the specific source. Various methods can measure GHGs; it's imperative to use ones that not only are accurate but also suit a facility's operations. Sometimes installing a monitoring device will require shutting down the process. The EPA has provisions in the rule for utilizing best available monitoring methods until the facility has a scheduled shutdown. A plant must identify these interim methods in the plan along with the schedule for implementing permanent ones.

A site may develop measuring strategies based on the source and source categories listed in the rule subparts. The specific calculation methodologies for each source type will help determine what data must be collected. Examples of potential measuring methods and strategies include:

- Grouping or aggregating smaller stationary combustion units combined with larger units if they share common fuel sources. Consider physical proximity of grouped units when sharing a measuring device.
- Material balance.
- Direct measurement of GHGs via continuous emissions monitoring systems (CEMS) already in place to comply with other EPA programs such as the Acid Rain Program that applies to most power plants.
- Indirect measurement using process parameters such as fuel consumption, material throughput, heat and temperature, pressure, or mass or volumetric flow rates that will require specific calculations to determine the GHG emissions. Consider updating only measurement sensors or transmitters for newer, more-accurate devices instead of replacing the system, to reduce the cost of upgrades. Also consider wireless transmitters where capital costs and potential production disruptions to install a hardwired system aren't cost effective.
- Invoices or purchasing records for utilities such as natural gas. Don't use these "as is" for a material utilized both as a fuel and as a raw material in processes that don't generate GHG unless the amounts for each purpose are clearly separated.

- Personnel and instrumentation for collecting data. Location of the measuring device readout and the amount of labor required to gather and utilize the data may favor automatic data collection instead.
- Automatic data collection through the use of process control software. A site only may need some reprogramming to obtain and use data collected for other purposes.

A facility also must build quality assurance (QA) requirements for the data collected into the plan. This must include the following details:

- Frequency of data collection (based on source category) and any change in monitoring required based on production changes.
- Calibration of meters or data collection equipment. Consider opting for instrumentation that can be remotely calibrated when replacement is required.
- Certification and QA testing of CEMS, if utilized.
- Maintenance and repair of meters and instrumentation.
- Preservation of all instrumentation records and certifications.
- Record of missing data events and data computations.

The methodologies required in the monitoring plan also include the specific emission factors and calculation methodology used to determine the GHG emissions by source.

DATA HANDLING

The monitoring plan must outline data collection, calculation and data maintenance procedures. Devote considerable thought to how to handle and store data. Spreadsheets may be appropriate for some facilities but may be too labor intensive and difficult to maintain for sites with many processes. A large plant should consider using environmental management software that allows data analysis on a facility and corporate level. In any case, a facility must maintain the data in an organized, accessible and auditable form. The plan should outline where data from each source is to be stored and maintained. The site must keep these data for at least three years.

A facility must review and analyze the data on a regular basis — at a minimum monthly — throughout the year. This will enable spotting trends in emissions that may warn of potential operational problems.

The time required to set up a monitoring approach greatly depends on the size of a facility and the dedication of the team. It can take approximately three to four months to identify sources, establish the best monitoring approach, calibrate equipment and collect data. It's important to develop a detailed schedule for each step of the process that will assure adequate time to meet EPA deadlines.

REPORT SUBMITTAL

GHG Report submittal for GHG emissions must be via the electronic greenhouse gas reporting tool (e-GGRT) available online at http://goo.gl/5O5Qe4. Users must register online for access through the EPA's CDX server. The electronic certification of the report requires a signatory for the site to register and be verified. A plant must register — a process that takes several weeks — prior to filing a report, and should maintain records of the data reported.

A facility can stop monitoring and reporting GHG emissions to the EPA if its emissions are below 25,000 mt/yr for five consecutive years, or under 15,000 mt/yr for three consecutive years. However, the site must notify the EPA and satisfactorily explain how it reduced emissions.

THE REGULATORY FUTURE

There's little doubt that the EPA intends to eventually mandate that companies reduce their emissions regardless of whether they are seeking permits. It would be wise for a company to examine its current emission levels and evaluate possible ways of reducing them now so it can incorporate suitable investments into future capital budgets.

In addition, as part of the new regulations, a company's emission levels will become public knowledge. So, a firm must consider how the public's knowledge of its emissions will impact aspects of its business, including its relationships with customers, partners and vendors. Reducing GHG emissions now certainly will help a company improve its public image and distinguish it as an environmental sustainability leader.

ANNA KOPERCZAK is a senior environmental specialist at SSOE Group, Toledo, Ohio. Email her at Anna.Koperczak@ssoe.com.