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Absorption Tower Provides Important Benefits

Sulfuric acid plant achieves enhanced efficiency and reliable pollution control

By Gabriele Pazzagli, Nuova Solmine, and Giovanni Marchesi, DuPont Clean Technologies Southern Europe

Nuova Solmine is a leader in the production of sulfuric acid in Italy and the Mediterranean basin. It operates a double absorption sulfuric acid plant with a capacity of approximately 1,700 mt/d in Casone di Scarlino. The plant originally was built in the 1960s to treat SO_2 gas from a pyrite roaster. This was upgraded with sulfur burning in 1994 and the pyrite roaster was shut down. At that time, all the facility's towers were constructed with brick lining. By early 2017, the brick lining was beginning to deteriorate and require frequent maintenance. Because Nuova Solmine plants work in a continuous production cycle 365 days per year, any increase in maintenance time potentially impacts production. So, the company decided to replace the final absorption tower (FAT) with a new, highly efficient one that would guarantee constant reliable emissions control and require less maintenance.

In July 2017, Nuova Solmine awarded a turnkey contract for the design, execution, supply and erection of the new FAT to DuPont Clean Technologies. The decision was taken to use DuPont's proprietary MECS ZeCor alloy because of its light weight and corrosion resistance. One important factor in the choice of technology was the speed of replacement as Nuova Solmine was keen to limit lost production time when switching from the old to the new FAT. DuPont was able to provide a definite delivery and installation schedule. Other key criteria for the selected equipment and design strategy were optimal performance efficiency, low lifecycle costs and minimal maintenance.

To limit time spent on site, the new FAT tower was prefabricated in a DuPont Clean Technologies workshop.

DuPont Clean Technologies is a recognized specialist in sulfuric acid plant and tower design, as well as sulfuric acid emissions-reduction technology and was able to give Nuova Solmine both a performance and mechanical guarantee for the new FAT tower. Nuova Solmine had specified that the new FAT should keep outlet acid mist below 30 mg/Nm^3 — a more stringent limit than that imposed by the local authorities (35 mg/Nm^3).

KEY TECHNOLOGIES

DuPont Clean Technologies therefore set about designing and engineering a FAT with tower internals that would enable Nuova Solmine to stay well below its target emissions threshold. The new FAT included advanced equipment such as:

- a MECS UniFlo acid distributor to deliver continuous and precise distribution of acid for optimum absorption efficiency, minimal mist production and maximum service life for downstream equipment;
- a MECS ZeCor alloy packing support that features a greater-than-80% flow area to allow for very good gas distribution and enable the lowest possible gas pressure drop combined with high efficiency; and
- MECS Brink CSII Plus mist eliminators to collect the most-difficult-to-capture aerosol mists down to submicron size.

Key to achieving the fast turnaround Nuova Solmine wanted, while also providing the desired performance and longevity for the new FAT, was the use of MECS ZeCor, which not only is extremely resistant to corrosion from acid and other substances but also is very light in weight.

To limit time spent on site, the new FAT tower was prefabricated in a DuPont Clean Technologies workshop, shipped to the Italian port of Piombino in four separate sections and transported 40 km by road to Scarlino, where final assembly and installation took place.

IMPRESSIVE RESULTS

From start to finish, the entire project took 11 months. The replacement of the brick-lined tower with the new MECS ZeCor FAT was carried out to schedule during a planned plant turnaround in August 2018. Installation only required about two weeks and the pre-assembled new tower was lifted into position in exactly the same location as the old one (Figure 1).

DuPont Clean Technologies handed over operation of the FAT to Nuova Solmine just after startup in August. Final testing took place between September and December 2018 to assess mg/Nm^3 levels of acid mist. The results came in well below the contractual performance guarantee (30 mg/Nm^3).

To date, the new MECS ZeCor FAT is performing very well, achieving a pressure drop that is under the contractual target, as well as SO_3 acid mist emissions well below the environmental limit.

The design of the MECS ZeCor alloy FAT tower at Nuova Solmine is the result of several years of research, during which DuPont Clean Technologies developed alloy towers with improved absorption efficiency and acid distribution. Added benefits have been a reduced pressure drop, a decrease in packing height and lower operating cost. These qualities have provided Nuova Solmine with a very effective and timely way to meet its emissions, maintenance and installation goals.

TOWER INSTALLATION
Figure 1. New FAT was lifted into place during a plant turnaround in August 2018.

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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_2), 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.

Regardless of the oxidizer size or type, all require supplemental fuel to support emission combustion.

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_2 and water vapor (H_2O). 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_2 and nitrogen oxides (NO_X). Knowing the detrimental effects of increasing GHGs into our atmosphere, reducing CO_2 and NO_X 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 terepthalic acid (PTA) production, formaldehyde production, organic chemical manufacturing, pthalic 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 CO_2 and H_2O. 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

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

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.

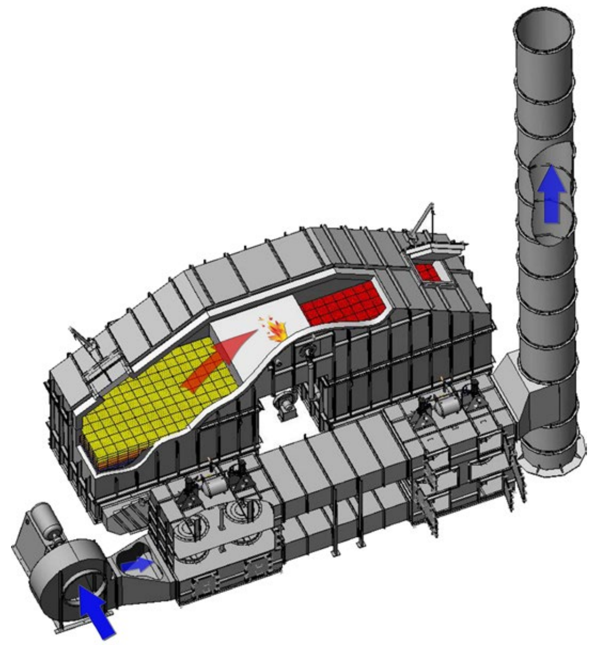
Reduced lifetime causes. The specific causes of reduced lifetime are poisoning, masking and sintering. The precious metal catalysts can be deactivated when exposed to certain chemicals, called poisons in this context. With platinum as a substrate, heavy metals such as mercury, lead and cadmium can bond 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.

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_2 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.



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

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

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 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 exchangers. 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.

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

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.

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Reduce NO_x via Wet Scrubbing

Gas ratio determines the best approach

By Phil Reynolds, P.E. and John Leung, CR Clean Air

Requests for nitrogen oxide reduction often start something like this: "Hello, I'm looking to remove NO_x." Often, the process engineer or plant manager doesn't have much more information available during the initial discussion.

This is unfortunate, as nitrogen oxide (NO_x) scrubbers have many configurations depending on the exact gas composition and scrubbing liquids to be used.

Proper questions are required to ensure that the end result will be a system that will meet the reduction needs in a cost-efficient manner. NO_x can be treated chemically in many ways, and each has its advantages and drawbacks.

COMPONENTS OF NO_x

NO_x refers to both the nitrous oxide (NO) and nitrogen dioxide (NO_2) contained in exhaust gases — the byproducts of a combustion process such as vent gas from a boiler.

NO is a colorless gas and is only sparingly soluble in water. It is inherently difficult to scrub and generally can be removed only by use of a strong oxidizing agent.

NO_2 is orange, ranging from a reddish-orange to almost brown depending on the amount of NO_2 present and the gas temperature. It is moderately soluble in water and can be converted to nitrogen (N_2) by use of an appropriate reducing agent.

SYSTEM DESIGN

When designing an NO_X mitigation system, the ratio of NO to NO_2 has an impact on the optimal design approach.

For NO-heavy systems, a two-stage solution is used (Figure 1). In the first stage, NO is oxidized to NO_2. Strong oxidizers are preferable, and treatment options include ozone (O_3) injection or sodium chlorite, $NaClO_2$. $NaClO_2$ is more cost-effective as ozone generation systems historically are cost-prohibitive.

For $NaClO_2$-based systems, the NO is oxidized in the presence of an acid to NO_2 as follows:

$$10\ NO + 2\ H_2SO_4 + 5\ NaClO_2 \rightarrow$$
$$10\ NO_2 + 2\ Na_2SO_4 + NaCl + 4\ HCL$$

CONDITIONS FOR ALTERNATIVE APPROACHES

Of course, some clients are hesitant to use such a strong chemicals to treat their NO. Thankfully, other chemistries can be utilized under certain conditions. Two alternatives are hydrogen peroxide (H_2O_2) and sodium hydroxide (NaOH).

For either of these alternatives to be practical, some NO_2 must be present in addition to the NO. Ideally the NO_2: NO molar ratio should be 1:1 or greater because the NO and NO_2 react in equal proportion, as follows:

TWO-STAGE NO_X SCRUBBER
Figure 1. For nitrous oxide heavy systems, a two-stage solution is employed.

$$NO + NO_2 + 2\ H_2O_2 \rightarrow 2\ HNO_3 + H_2O$$
for hydrogen peroxide

$$NO + N_2 + 2\ NaOH \rightarrow 2\ NaNO_2 + H_2O$$
for caustic

It should be noted that, of these two options, with regard to dispositioning the wastewater, many facilities find it easier to deal with the nitric acid (HNO_3) than the sodium nitrates ($NaNO_3$).

Additionally, H_2O_2 systems require smaller towers than caustic systems. This is due to the lower L/G ratio needed and lower resonance time required to ensure full scrubbing.

JET VENTURI SYSTEM
Figure 2. This scrubber system with separator tank, packed tower and fiber bed mist eliminator requires periodic maintenance for optimal performance.

SPRAY NOZZLE
Figure 3. Spray nozzles must be replaced periodically, with the frequency depending on the nature of the fluid.

KEEP YOUR SYSTEM UP AND RUNNING

Although many scrubbing systems need very little maintenance to keep them in optimal running condition, they are not maintenance-free. Just as a vehicle needs its oil changed and tires rotated periodically, scrubbers need parts replaced from time to time.

All scrubbers, be they jet venturi (Figure 2), high energy venturi or packed tower, will need their spray nozzles (Figure 3) replaced periodically. How frequently replacement is needed depends on the nature of the fluid. Some systems last decades between replacements, while others need to be changed out more regularly.

The best way to tell whether a nozzle needs replacement is to compare the observed flow rate to what the system was designed for. Too little flow indicates possible plugging of a fouling, and system capacity will drop as a result. Too high of a flow indicates excessive wear and leads to an unnecessary increase in pumping power and utility use.

It is wise to have a set on hand, rather than wait until right before a scheduled shutdown. A spare set of gaskets is also advisable to ensure that the equipment seals correctly when it is reassembled.

MESH MIST ELIMINATOR
Figure 4. Mesh pad designs need periodic replacement to ensure optimal liquid removal.

TOWER PACKING
Figure 5. Packing usually needs replaced once fouling occurs.

For high-energy systems and packed towers, as well as jet/separator tank systems, the mist eliminator element also will need periodic replacement. For situations in which excessive fouling can be anticipated, wash-down nozzles can be integrated into the design.

Mist eliminators, particularly the mesh pad designs (Figure 4), need periodic replacement to ensure optimal liquid removal.

Often the first sign of an excessively fouled mist eliminator is an increase in pressure drop through the scrubber.

Finally, for the packed towers, the packing (Figure 5) will need to be replaced periodically. As with mist eliminators, excessive fouling usually is the best indicator that replacement is advisable. Given that each tower is designed with a specific packing size and type to suit the application, it is best to contact your packing vendor for replacement packing as this will ensure that the performance characteristics, including pollutant removal rate and pressure drop, are consistent with the original system design.

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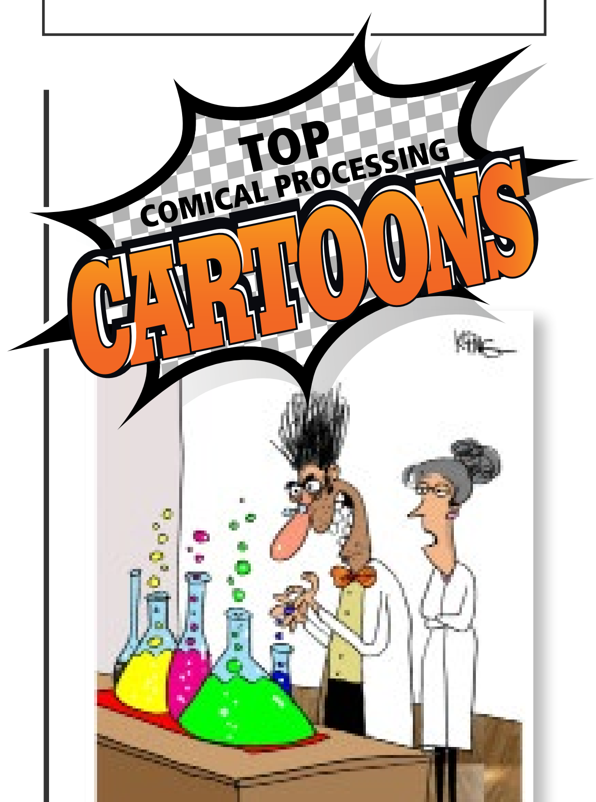

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