Spent Caustic Treatment: The Case For Wet Air Oxidation Over Incineration

In the Middle East, incineration is a popular method for treating spent caustic, the harsh byproduct of ethylene production. However, incineration can be problematic when treating wastewater with a high total dissolved solids content. Wet air oxidation (WAO) offers a solid alternative with potentially lower overall lifecycle costs.

Oil and Gas Online spoke with Mark Clark of Siemens about the downfalls of incineration for treating spent caustic, the business case for using WAO, and the new technology that is making it a viable alternative in water-stressed regions of the world.

How is the largest amount of spent caustic generated and why is its treatment important?
The petrochemical industry, through the production of ethylene, is typically the largest generator of spent caustic. Ethylene is the precursor to many plastics, such as soda bottles, so it is a big part of the packaging industry. The production of ethylene often requires the addition of chemicals to prevent fouling in furnace tubes. Those additives, as well as some of the raw materials, contain contaminants such as hydrogen sulfide and mercaptans that must be removed before the ethylene can be sold to make plastics. Caustic is introduced to the produced ethylene gas to absorb those contaminants and any carbon dioxide that was produced in the cracker. However, that process produces a spent caustic that contains the sulfide and mercaptans that are toxic and highly malodorous. The quantity of spent caustic generated by ethylene production is quite large and represents a significant hazard if not addressed.

In what conditions is incineration popular for treating spent caustic? What are the common problems associated with incineration?
Incineration of spent caustic is fuel-intensive, so it is typically chosen when local fuel is a low-cost or free option. It also tends to be the selected method when wastewater treatment systems are not available to polish spent caustic treated with oxidation or where water is subject to reuse. A downside to incineration is that the process suffers from plugging, which forces operators to shut down the apparatus for cleaning. Additionally, drastic temperature swings that occur with each incinerator shutdown and restart can put significant stress on the refractory. The more cleaning that is necessary, the more often the refractory will need to be replaced.

Why not just add the spent caustic directly to a wastewater stream?
It’s not feasible to send spent caustic directly to a wastewater treatment plant (WWTP) stream. The typical influent at a plant may contain 800 mg/L to 1,600 mg/L of chemical oxygen demand, whereas spent caustic levels range from 10,000 to 30,000 mg/L. This puts raw spent caustic well beyond the capability of traditional wastewater processing.
Additionally, the amount of sulfide and mercaptan in the spent caustic would result in major HSE concerns at the WWTP. However, treating the spent caustic with oxidation can destroy its odorous nature and reduce the toxic characteristics so it can be added to the wastewater stream for treatment.

**How does WAO work?**

WAO occurs in the aqueous phase at relatively low temperature conditions. When wastewater, air, and heat are combined, the unique nature of water results in oxidation reactions that would normally occur at much higher temperatures if oxidized in air. The higher the temperature, the higher the oxidation potential. The oxidation reactions convert sulfides into sulfate, mercaptans into sulfonates, and oxidize high-molecular-weight organic compounds into low-molecular-weight carboxyls, such as formate and acetate, and carbon dioxide.

When oxidation occurs in the aqueous phase, oxygen that is dissolved into the water from the air is consumed and more oxygen dissolves into the water phase, allowing additional oxidation reactions to occur. After a specific amount of time has passed during which the wastewater is held at temperature and oxygen is present, the wastewater will have been oxidized and the liquid effluent and non-condensable gases — mostly nitrogen — are cooled. The non-condensable gases will be separated from the liquid effluent.

**How does WAO overcome the problems associated with incineration?**

WAO works in an entirely different way than incineration, performing oxidation reactions in the aqueous phase and not the gas phase. Since spent caustic is a concentrated salt solution, performing the oxidation in the aqueous phase prevents salt solids from being formed (as they are in incineration). Since the solids are not produced, the process does not suffer from plugging. WAO uses alloys to prevent corrosion, as opposed to refractory, and therefore does not have the issues associated with refractory when the process is cooled and heated. WAO is also very energy efficient and inexpensive to operate.

**Based on the cost of incineration, what’s the rate of payback from switching to a WAO system?**

A single WAO system has a higher capital cost than a single incineration unit but a significantly lower operating cost. It makes financial sense in many situations, but the rate of payback must be calculated on a case-by-case basis, as it is dependent on the cost of fuel and specific problems that a site is experiencing, and also whether more than one incinerator needs to be installed to ensure availability.

**What specifically about Siemens’ Zimpro® WAO system offers better performance than competitor systems?**

Through a rich history of research, testing, development, and operation, Siemens has accumulated decades of experience with spent caustic. As a result, the Zimpro WAO process has been used in treatment for more than 30 years. While Zimpro WAO produces a high-quality effluent, the real benefit is the in-depth understanding that Siemens brings to projects. This experience is applied to prevent issues that would likely plague less-accomplished providers.

**What’s the new development that puts WAO on a level playing field with incineration for spent caustic treatment in water-stressed regions of the world?**

A lot of places in the Middle East, for example, wouldn’t consider WAO before now because it wasn’t a complete solution. After being treated with WAO, low concentrations of biodegradable organics are still present in the treated brine solution. This is problematic in regions where water reuse is common. Approximately three times as much freshwater is required to dilute the WAO stream so biological treatment can be performed in a WWTP. That defeats the purpose of reuse and explains why incineration is so popular in those regions, as the resulting salt stream can simply be released to sea.

What’s changed very recently is the development of a biological treatment system by Siemens that can polish the spent caustic effluent from its WAO units, providing biological treatment without the need for dilution, thereby resulting in a salt stream that can meet the environmental requirements to be discharged to the sea.

Based on the Siemens PACT® MBR system — biological and powdered-activated-carbon treatment with membrane bioreactor — the technology is so new it’s just starting to be proposed as a solution. Siemens has extensively pilot tested the process for more than three years, evaluating both the tenacity of the PACT system and the durability of the MBR in this high salt service.

**While the technology is newer to the market, isn’t it supported by decades of development experience?**

Yes, from an advanced wastewater treatment analytical laboratory and testing facility in Rothschild, Wisconsin, Siemens works to ensure that its customers can meet their goals. Siemens facilities include the most extensive WAO process test system available, which enables the conducting of bench-scale as well as continuous flow pilot-scale studies for solutions to a customer’s specific requirements. WAO system configurations are highly customized based on the specific process approach.

The Rothschild WAO and membrane pilot system facilities are unparalleled. They include various systems with different configurations and materials of construction that reside in a pilot plant that spans 10,000 square feet (930 square meters). The facility is permitted for hazardous waste testing.