

Age Old Solution for Today's SO_2 and NO_x

Wet air oxidation (WAO) was originally called the Zimmermann Process, after its developer, F.J. Zimmermann.¹ Today, the hydrothermal treatment process is still widely known as the Zimpro® process, of which more than 200 full-scale systems, treating a variety of municipal and industrial applications, exist worldwide.

WAO technology has evolved considerably during its 90-year history. Initially developed to destroy spent pulping liquor, it has also been used to manufacture artificial vanilla flavoring (vanillin), condition wastewater sludge and treat industrial wastewaters. In the last two decades, WAO

has been used primarily to treat both refinery spent caustic and ethylene spent

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Typical WAO flow diagram

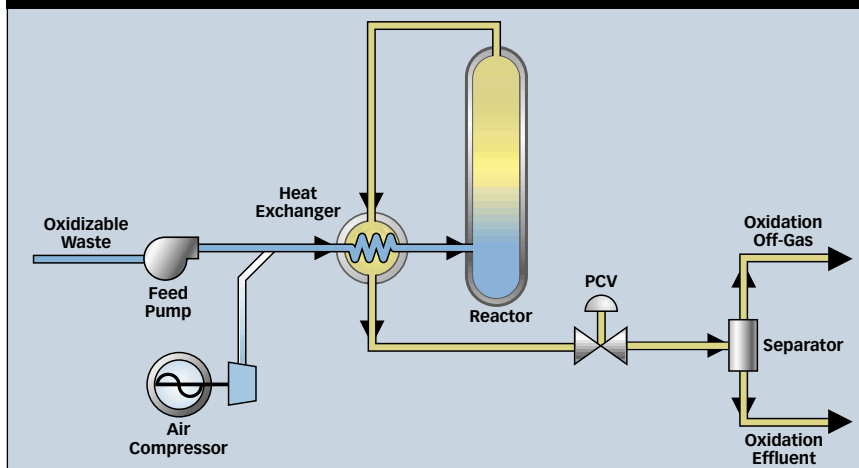


Figure 1

caustic. The technology destroys certain hard-to-treat petrochemical processing waste products while releasing minimal SO_2 and NO_x .

Nine decades of use

Patented in Sweden in 1911 for destroying spent pulping liquor, WAO technology was used in the 1930s and '40s primarily for manufacturing vanillin. The technology was later applied to other paper mill waste treatment applications.

The 1960s and '70s witnessed many municipalities using WAO to condition wastewater sludge to enhance de-watering and reduce landfill volume. Under the Clean Water Act, the application gained popularity as more wastewater treatment plants were built and subsequently more sludge was produced.

In the 1970s, water management professionals began using WAO to treat industrial wastewaters, particularly sulfide-laden spent caustics. In such instances, the technology was sometimes paired with a powdered activated carbon treatment (PACT®) system, an advanced wastewater technology that combines biological oxidation and assimilation with adsorption on powdered activated carbon. WAO would regenerate the spent activated carbon for

reuse in the PACT system through an application known as wet air regeneration.

The WAO process

WAO dissolves oxygen at elevated temperatures to oxidize soluble or suspended materials in water. Because it applies a direct chemical oxidation process, the process is not susceptible to toxic upsets that can occur in biological treatment. See the flow diagram in **figure 1** for a demonstration of a typical WAO system.

Oxidation takes place in an aqueous environment, where water provides a medium for the dissolved oxygen to react with the organics and other oxidizable components. Water is an integral part of the process and acts as both a catalyst and a hydrolysis reactant. Oxygen- and water-derived radicals attack organic compounds, forming organic radicals. Such free radicals are a suspected key ingredient in WAO chemistry. Catalysts, such as homogeneous copper and iron, their heterogeneous counterparts or precious metals, can be used to enhance the WAO reaction.

WAO chemistry is characterized by the formation of carboxylic acids as well as the primary end-products CO_2 and water. The yield of carboxylic acids varies greatly depending on the design of the WAO

system. A small portion of the total organic carbon (TOC) from a feed stream remains as carboxylic acid by-products. These mainly acetic, formic and oxalic acids are biologically degradable and can generally be removed using a cost-effective conventional biological post-treatment.

The off-gas from WAO contains negligible NO_x , SO_x and particulates. Depending on the feed stream composition, volatile organic compounds such as aldehydes, ketones and alcohols may be in the off-gas but can be removed by thermal oxidation. In a general WAO process, the waste is delivered through a high-pressure pump – usually a standard reciprocating diaphragm pump for liquids and a more specialized high-pressure pump for slurries. Ambient air or pure oxygen supplies the required oxygen. The mixed air and liquid pass through a feed/effluent heat exchanger, where the fluid is heated to near reaction temperatures. The two-phase fluid then flows to a bubble reactor, where an exothermic reaction takes place. The oxidized effluent and off-gas pass through the hot side of the feed/effluent heat exchanger for cooling while simultaneously heating the influent. Auxiliary heaters and coolers are also used.

After cooling, the effluent passes through the WAO system's pressure control valve. A separator downstream allows the depressurized and cooled vapor to separate from the liquid, which is then discharged, typically for conventional biological treatment. The gas is usually vented to some form of thermal oxidation such as a boiler or a flare header.

Application spectrum

To maintain water in the liquid phase, wet oxidation reactions usually take place between 212 and 700°F at elevated pressures. This range is subdivided into low, medium and high temperatures. Systems can be designed to operate at still higher temperatures (608 to 700°F), but high capital costs make such systems rare. Commercial applications of low-

temperature oxidation (212 to 392°F) include thermal conditioning of sludge and treatment of low-strength sulfidic spent caustics. Other industrial materials treated by low-temperature oxidation include cyanide and phosphorus wastes as well as non-chlorinated pesticides. Medium temperature (392 to 500°F) oxidation is used for typical ethylene spent caustics, as well as for auto-thermal sludge conditioning and treatment of other industrial wastes. High-temperature (500 to 608°F) processes are used for refinery spent caustics, sludge destruction, most industrial wastewaters and wastes like pesticides, solvents, pharmaceutical wastes and military wastes.

Spent caustics treatment from ethylene production

Today, WAO is primarily used for treating spent caustics from ethylene production and petroleum refining. In ethylene production, ethane, propane or naphtha gas is cracked in a furnace, forming CO₂ and H₂S by-products. A caustic scrubbing tower removes these by-products, which are absorbed out of the gas phase and into the caustic solution. Over time, the caustic material becomes spent. Disposing of this solution is difficult because spent aqueous caustic material is considered a hazardous waste that contains high pH and odorous sulfides. WAO destroys these sulfides and neutralizes the acids. Virtually all new ethylene facilities use this low-temperature (248 to 428°F) treatment method, introduced in the 1980s, to treat spent caustic materials.

Spent caustics treatment from petroleum refining

Refineries generate three types of spent caustic materials – sulfidic, naphthenic and cresylic. The three are often mixed together before disposal.

Sulfidic spent caustic comes from caustic washing liquid propane gas for

sulfur removal and can be treated much like ethylene spent caustic.

Naphthenic spent caustic results from the Merox² treatment of diesel and jet fuels for sulfur and naphthenic acid removal. It contains a much higher COD and TOC than ethylene spent caustic due to the presence of organic naphthenic acids. As these acids foam under low-temperature WAO conditions, higher temperatures are necessary to destroy them and control foaming.

Cresylic spent caustic comes from the Merox treatment of gasoline for sulfur and cresylic acid removal. It is very similar to naphthenic spent caustic in COD and TOC behavior and treatment requirements.

WAO at work

WAO has been applied successfully worldwide. Refinaria de Petroleos de Manguinhos, S.A., a producer of liquid fuels in Rio de Janeiro, Brazil, has treated refinery spent caustic with WAO since 1995. The system operates at 2 gpm and 500°F with a one-hour residence time. It removes sulfides, mercaptans and thiosulfates and significantly reduces phenols and overall COD. The oxidized spent caustic is sent to the refinery's biological treatment system. Residents nearby reported that they greatly appreciated reduced odors from the plant.

After evaluating a number of alternatives, The Chinese Petroleum Corporation (CPC) in Kaohsiung, Taiwan selected WAO for treating ethylene spent caustic at a 500,000-metric ton-per-year ethylene plant. CPC now has three systems, each with a capacity of 32 gpm.

ATOFINA Italia in Rho, Italy, uses WAO to handle byproducts from methyl methacrylate production. Crystallizers recover the byproduct, ammonium sulfate (AMS), in a high-quality form suitable for farm fertilizer. To ensure that the AMS quality remains acceptable, a purge stream is generated from the crystallizers. This stream passes through the WAO system, where

organic components are destroyed. The treated AMS returns to the crystallization system. The exothermic process releases energy that is returned as steam to the crystallizers, and AMS in the effluent is returned to the crystallizer for recovery. The company no longer has to truck large volumes of crystallizer blow-down liquor off site for third-party disposal. The reactor operates at 536°F, using a homogenous copper catalyst that is recycled within the system.

Conclusion

In almost a century, Zimmermann's process has evolved to effectively handle a variety of waste treatment projects, from sludge conditioning to the destruction of waste liquors with extremely toxic components such as cyanides and pesticides. With its high thermal efficiency and low air emissions, WAO offers an economical and environmentally sound alternative to liquid waste incineration. **PE**

References:

1. Frederick J. Zimmermann, a London-born graduate chemical engineer, formed Salvo Chemical Co. in 1935, producing artificial vanillin from spent pulping liquor. In 1942, as part of Sterling Drug Inc., he developed wet air oxidation as a method of obtaining vanillin directly from pulping liquor. He received a patent for the process in 1950. Zimmermann died in 1976.
2. Merox™ is a trademark of UOP LLC.

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