Can you treat the most difficult wastewater with only air?

Zimpro® Wet Air Oxidation Systems:

The cleanest way to treat the dirtiest water

Answers for industry.
The wet air oxidation process can be traced back to the 1930s in Rothschild, Wisconsin, USA. F.J. Zimmermann developed the wet air oxidation process and became founder and namesake of the company Zimpro (now Siemens Water Technologies).

Zimmermann and his staff used spent pulping liquor from a local paper mill to produce artificial vanilla flavoring (vanillin) by partial wet air oxidation of ligno-sulphonic acids. Zimmermann and his colleagues perfected the wet air oxidation process (or the “Zimmermann Process” as it was known), and expanded it to other applications, including wastewater treatment. Since then, applications for the wet air oxidation process have become as varied as its history is long.
The Process
The wet air oxidation process is the oxidation of soluble or suspended components in an aqueous environment using oxygen as the oxidizing agent. When air is used as the source of oxygen the process is referred to as the wet air oxidation (WAO) process. The oxidation reactions occur at temperatures of 150 °C to 320 °C (275 °F to 608 °F), and at pressures from 10 to 220 Bar (150 to 3200 psi). The required operating temperature is determined by the treatment objectives. Higher temperatures require higher pressure to maintain a liquid phase in the system.

The typical wet air oxidation system uses rotating equipment to raise the feed stream and air (or oxygen) to the required operating pressure. Heat exchangers are routinely employed to recover energy from the reactor effluent and use it to preheat the feed/air mixture entering the reactor. Auxiliary energy, usually steam, is necessary for startup and can provide trim heat if required. The reactor vessel provides residence time at a temperature which enables the oxidation reactions to proceed towards completion. Since the oxidation reactions are exothermic, sufficient energy may be released in the reactor to allow the wet air oxidation system to operate without any additional heat input.

Wet Air Oxidation or Hydrolysis?
Hydrolysis is a process similar to the wet air oxidation process for the treatment of wastewaters when oxygen is not a necessary reactant. In hydrolysis, certain constituents of wastewaters and sludges can react directly with water at elevated temperatures and pressures to yield a treated effluent that is detoxified or meets the desired treatment objective.

What is the Zimpro® WAO System?
Is there a specific Zimpro® wet air oxidation system design? No.

A broad range of both industrial and municipal application experience allows us to custom design a wet air oxidation system based on the specific application and objectives. Our experience runs from extensive R&D projects to the design and construction of more than 150 systems worldwide.

Applications have involved:
- A wide range of temperatures and pressures
- The use of air, oxygen, or simply hydrolysis in the absence of oxygen
- A multitude of reactor designs and flow configurations, including the use of catalyst

This diverse capability has led to our most recent projects involving the co-development of applications and designs for major industrial clients. Some of the new industrial applications being developed go beyond wastewater treatment, where wet air oxidation or hydrolysis is applied for inprocess recycle or end product recovery.

Typical WAO Process Reactions
The process can convert organic contaminants to carbon dioxide, water and biodegradable short chain organic acids. Inorganic constituents such as sulfides and cyanides can also be oxidized. The wet air oxidation process can involve any or all of the following reactions:

- **Organics**: $\text{Organics} + O_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{RCOOH}^*$
- **Sulfur Species**: $\text{Organic Cl} + O_2 \rightarrow \text{Cl}_2^- + \text{CO}_2 + \text{RCOOH}^*$
- **Organic N**: $\text{Organic N} + O_2 \rightarrow \text{NH}_3 + \text{CO}_2 + \text{RCOOH}^*$
- **Phosphorus**: $\text{Phosphorus} + O_2 \rightarrow \text{PO}_4^{3-}$

$^*$Short chain organic acids such as acetic acid make up the major fraction of residual organic compounds.
Industrial Applications

A Zimpro® wet air oxidation system treats industrial waste at Atofina Italia’s methyl methacrylate production facility in Rhoo, Italy.

Zimpro® wet air oxidation system uses oxygen to treat high strength styrene monomer and polyol wastewater at Repsol YPF, Tarragona, Spain.

Zimpro® wet air oxidation system treats the spent caustic effluent generated by the world’s largest naphtha steam cracker at the BASF ethylene facility, Port Arthur, Texas.

Wastewater and In-process Treatment

Typical industrial applications for the wet air oxidation process have a feed flow rate of 1 to 50 m³/h (4 to 220 gpm) per train, with a Chemical Oxygen Demand (COD) from 10,000 to 150,000 mg/l (higher CODs with dilution). Objectives for industrial applications can include pretreatment of difficult wastewater streams to make them suitable for conventional treatment such as biological polishing, or as treatment for product recovery. The process can be applied to treat difficult process or wastewater streams to satisfy a variety of objectives, such as:

- Destruction of specific compounds
- Elimination of toxicity or reactivity
- Pretreatment to produce readily biodegradable residual organics
- Process liquor treatment for recycle/recovery
- Gross reduction in COD

Spent Caustic Treatment

A common industrial application for the wet air oxidation process is treatment of spent caustic wastewater streams generated by ethylene plants and refineries. The process is used for complete oxidation of reduced sulfur species such as sulfides and mercaptides. By increasing temperature and pressure, complex organic contaminants such as phenols can also be broken down to either carbon dioxide and water, or biodegradable short chain organics.

By applying the wet air oxidation process, odor associated with sulfides and mercaptides will be eliminated and the treated spent caustic is suitable for discharge to a conventional biological treatment process.
Sludge Applications

The wet air oxidation process is used to destroy biological solids and regenerate carbon at a Tosco refinery. In this application, the wet air oxidation process is referred to as the wet air regeneration process.

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The Passaic Valley, New Jersey, municipal treatment plant uses twelve Zimpro® wet air oxidation systems for municipal sludge treatment, each with a capacity of over 60 m³ per hour.

Sludge Treatment and Destruction
Another widespread application of the wet air oxidation process has been for treatment of municipal sludge. The majority of these systems are low temperature and low pressure designs, commonly referred to as low pressure oxidation (LPO). An LPO system uses temperatures and pressures of less than 220 °C (425 °F) and 35 Bar (500 psig), respectively. Under these conditions, sludge is broken down to enhance dewaterability. When higher temperatures and pressures are applied, destruction of volatile solids occurs and wet air oxidation can be used for sludge destruction, a possible alternative to incineration.

Zimpro® Wet Air Regeneration System
Biological treatment can be enhanced by incorporating powdered activated carbon, known as the PACT® system. A specialized wet air oxidation design referred to as the Zimpro® wet air regeneration system is applied to sludge generated by the PACT biological treatment system. The wet air regeneration process will simultaneously destroy organic solids and regenerate powdered carbon for reuse in the PACT system. The wet air regeneration process has been used for municipal and large industrial PACT systems.
Full Spectrum of Testing Capabilities

Bench-scale Testing
We have the most extensive wet air oxidation process test facilities in the world, capable of conducting bench-scale as well as continuous flow pilot-scale studies. Bench-scale autoclave testing is used to establish preliminary design criteria for a full-scale design, allowing for evaluation of process economics.

Materials-of-construction testing is also conducted to identify suitable alloys for the application. Studies can involve the wet air oxidation process and other treatment processes, like biological treatment, that can be coupled with the wet air oxidation process for effluent polishing. Our Enviroscan Analytical™ nationally accredited analytical laboratory is used to support in-house test work.

World-class Pilot Plant Facilities
Our wet air oxidation pilot system facilities are unparalleled. The facilities include various pilot systems housed in a 930 m² (10,000 ft²) pilot plant that is RCRA Part B permitted by the U.S. Environmental Protection Agency and the Wisconsin Department of Natural Resources.

Continuous flow pilot studies can be performed under a wide range of operating conditions. Pilot plant studies are performed to optimize the design conditions for custom applications. Pilot testing produces representative treated product for evaluation and testing, giving the customer a better understanding of the operating characteristics of the wet air oxidation process. Pilot systems are constructed of many alloys, including titanium, high-nickel and stainless alloys. The wet air oxidation or hydrothermal system configurations are highly customized based on the specific process approach.
Engineering, Design, Construction and Manufacturing

**Full Scale Systems**
Our in-house engineering staff provides complete engineering and design for full scale wet air oxidation systems. Certified welders and electricians work in our 2300 m² (25,000 ft²), ASME-certified manufacturing facility, which specializes in high alloy welding. This includes certifications for a variety of alloys, including nickel and titanium. We can supply wet air oxidation or hydrolysis systems as modular skid- and tower-mounted equipment packages. Custom engineered system modules are piped and wired to the greatest practical extent, incorporating customer specifications and vendor preferences.

Our manufacturing group holds the ASME PP (Power Piping) and U (Unfired Pressure Vessel) stamps, NBIC R (Repair) stamp, and are UL Listed. We are also Manufacturer’s License (ML) certified in the People’s Republic of China. And in 2008, we achieved ISO 9001:2008 registration.

In addition, we realize that safety and quality go hand in hand. Our Rothschild, Wisconsin, facility has an exemplary safety record, reaching 16 years without a lost time accident in 2010. We were awarded the Wisconsin Corporate Safety Award in 2000, 2004 and 2008.