

# Wet Oxidation as a Complementary Variant to Conventional Processes for Wastewater and Sewage Sludge Disposal

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**Abstract:** The basic principle of wet oxidation has been known for over 75 years; the first patent concerning this process dates back to 1912. Until the middle of the last century, wet oxidation was not used in the field of waste disposal, but only in the scope of chemical processes. In the fifties, wet oxidation was used for the first time for cleaning wastewater and sewage sludges. However, for a long time, application possibilities were limited to technically less demanding corrosive wastewaters from domestic, slaughterhouse, paper factory sources etc.

Since the beginning of the eighties, this process has also been successfully implemented on highly corrosive process wastewaters derived from chemical production.

**Keywords:** Green chemistry · Sewage sludge treatment · Wastewater treatment · Wet oxidation

Environmental protection and safety in chemical production have to be considered simultaneously as a challenge and as a stimulation. The important point is to find the optimum balance between what is ecologically necessary and desirable, technically feasible and financially acceptable. In the long run, success will come only to those who implement modern technology and research for products and production processes that respect the environment, that reduce the remaining wastes and apply the safest disposal methods.

Environmental protection and safety are expensive. Billions are spent to develop new, environment-friendly products and environment-compatible processes, to reduce harmful substances, limit risks and to dispose of unavoidable waste in state-of-the-art techniques.

The fact is that, despite all the progress achieved in process develop-

ment, waste will continue to originate from the synthesis of chemical products, some in the form of contaminated wastewater. This is reason enough to search for new and efficient methods to treat wastewater and to apply existing procedures in the best possible way.

In this context, wet oxidation stands as a complementary and economical method of disposal between biological treatment and disposal *via* incineration.

## Definition of the Wet Oxidation Process

Wet oxidation is a process during which the organic and oxidisable inorganic contents of aqueous substances or aqueous suspensions are oxidised by atmospheric oxygen or pure oxygen at temperatures between 200 and 300 °C and pressures of up to 150 bar. Table 1 gives an outline of the major pollutants contained in chemical process waters and the resulting post-wet oxidation decomposition products.

The decomposition products carbon dioxide, nitrogen and traces of carbon monoxide are evacuated during the process in form of gases, whereas all the other products, including NH<sub>3</sub>, remain in the

acidic wastewaters. The decomposition products can then either be eliminated as ecologically safe or subjected to further treatment. The waste gas issued by the process is, contrary to the exhaust gas from combustion, free of dust, nitrous fumes and sulphur dioxide.

The treatment capacity, expressed as TOC (Total Organic Carbon) decomposition rate, depends on the temperature, pressure and the residence time of the reaction parameters as well as the specific properties of the harmful substance. The decomposition process can, in many cases, be accelerated by adding the appropriate catalysts. If sufficiently drastic reaction conditions are applied, a TOC elimination rate of 99% can be achieved for most of the substances contained in the wastewaters.

## Wet Oxidation Process Technology

Technically the wet oxidation process is usually carried out as a continuous process. The wet oxidation facility has only a few components (Fig. 1). Wastewaters are collected in a tank, if necessary mixed, and then delivered by means of a high pressure pump to the reactor over a

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Table 1. Decomposition products of the pollutants

Reactant	Product
Hydrocarbons	Carbon dioxide and water
Organic nitrogen compounds	Nitrogen and/or ammonia
Organic sulphur compounds	Sulphuric acid
Organic chlorine compounds	Hydrochloric acid
Organic phosphorous compounds	Phosphoric acid

heat exchanger unit. Ambient air is taken in as oxidation air, compressed to reaction pressure and mixed to the wastewater stream. Pure oxygen can be used as an alternative.

The exothermal oxidation reaction of the pollutants is carried out in a bubble column reactor whose back-mixing capacities are determined by baffles. The requisite residence time depends on the operating parameters, pressure and temperature, the decomposition kinetics of the organics to be eliminated and the degree of treatment required. Practice has shown that the operation can take between one and a number of hours.

The mixture of wastewaters/gas heated during the oxidation reaction leaves the top of the reactor and gives off its heat content through the heat exchanger unit to the crude wastewater stream, giving rise to an autothermic process. Generally, excess energy can be used to produce steam. In the last part of the installation, the gas and liquid phases are separated and the pressure let down. If necessary, the gas and liquid phases then undergo further treatment.

### Pre and Post Treatment of a Wet Oxidation Unit

Different pre-treatment steps may be necessary, depending on the wastewater composition, the operating data and design of the wet oxidation unit as well as the choice of material for the high pressure apparatus.

The important and typical pre-treatment operations are:

- Setting the pH value according to the application limits of the materials
- Concentration or dilution of the crude wastewaters to fit operating specifications of the respective installations. The criterion is the COD value (Chemical Oxygen Demand) of the wastewater
- Elimination of the extremely high salt concentrations that can lead to precipitation and plugging during reaction.

Post-treatment steps for the process gases and the clean oxidised wastewaters are

usually dictated by the emission and discharge value limits. The only component that remains to be eliminated in the process gas are the approx. 1000 ppm of carbon monoxide. The only post-treatment as regards gases is a

- catalytic CO oxidation.
- Post treatment of wastewaters are necessary depending on the composition of the wastewaters in the crude wastewaters (see Table 1) and the authorised emission concentrations:
- Phosphate and/or sulphate precipitation step
  - Ammonia stripping unit
  - Separation of a possible catalyst (introduced for the process of oxidation)
  - pH

### Scope and Limits of the Process

The upper limits of the wet oxidation process are determined according to the maximum concentration of the pollutants (measured as the COD value) and the evaporation rate of the water during the reaction. The requisite oxidation air, whose quantity rises linearly with the COD value of the wastewaters, is saturat-

ed according to the pressure and temperature with water vapour. Fig. 2 shows the relation between pressure, temperature and the saturation of the gas phase. The upper COD operating limits are exceeded when the total amount of water needed to saturate the gas phase has evaporated, *i.e.* the reactor has dried up.

The lower limit for operating the wet oxidation plant is determined by economic and technical aspects. This lower limit is reached when no further autothermal operation is possible. Decisive is the degree of heat recovery in the heat exchanger unit as well as the lack of insulation of the installation. Further limitations to wet oxidation operations for process waters are set by the corrosion limits of the installation.

Titanium and titanium alloys show, with high concentrations of halogen, a good resistance to corrosion, so long as certain side specifications are respected regarding wastewater substances and operating parameters.

Furthermore, cations that can lead to scaling of the heat exchanger must also be kept under control. These scale builders are mainly calcium, iron and aluminium. The most important parameters which limit the application of wet oxidation are shown in Table 2.

### Comparison of Wet Oxidation with other Wastewater Treatment Processes

In Fig. 3, application of wet oxidation is compared with the main established

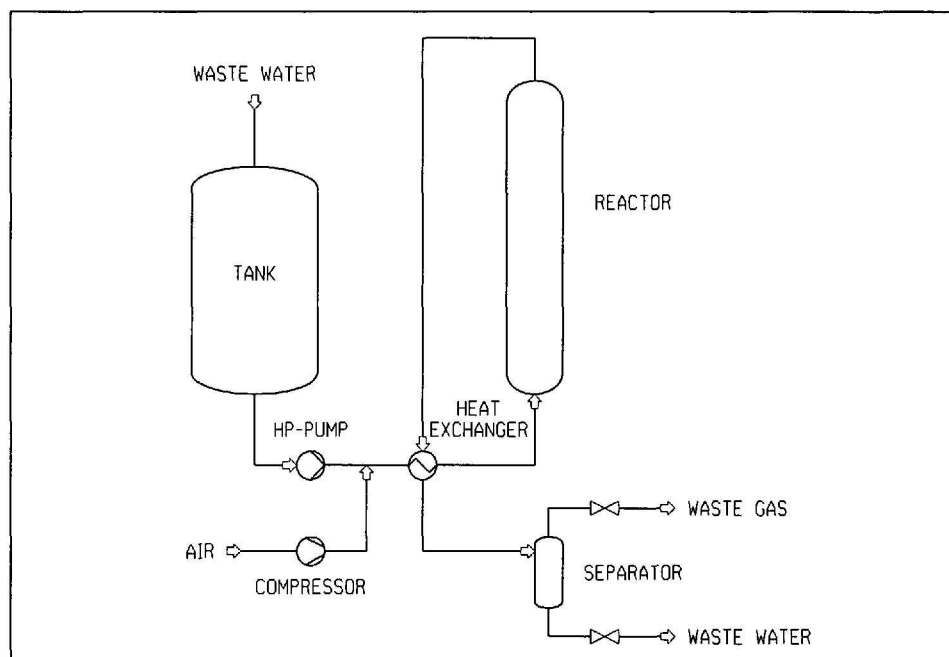


Fig. 1. Basic flow scheme of the wet oxidation plant

cleaning processes: biological wastewater treatment and wastewater incineration.

Biological purification – assuming the biological degradability of the substances contained in the wastewater – is traditionally used in conditions where pollutants are in low concentrations and with nearly unlimited flow. Combustion, on the other hand, if used in economical conditions, needs a very high concentration of pollutants, but the quantity of water to be incinerated is limited by the incinerator capacity.

Wet oxidation is best used when dealing with average pollutant concentrations, and also in cases of non-biodegradable substances.

A cost comparison for the elimination of 1 kg COD in wastewater, considering its own specific field of operation, shows that wet oxidation is superior to other processes. The disposal costs for one 'unit' of pollutant amount to approx. CHF 0.50–3.–/kg COD. The costs for the treatment of sewage sludges, depending on the capacity of the plant, are between CHF 500.– and 1000.–/t of dried substance.

**Process Safety**

Wet oxidation is considered to be a safe process. Permission to transfer the wastewater and sludges into the wet oxidation process is only granted after checking the safety relevant concentration parameters.

Pressure and temperature are monitored and limited. In normal operation, pressure sources are secured from non-admissible pressure increases. In case of disorders, the reactor is isolated from the periphery. This leads to a rapid separation of the phases so that the residual oxygen in the gas phase can only react very slowly with the remaining organics. The residual oxygen dissolved in the liquid phase will react and give CO<sub>2</sub>. Should the pressure increase despite a limited content of oxygen, it will be let down by means of a relief system.

There is no danger from an increase in temperature. For this to happen and in the current operating conditions, a vaporisation energy, not present in the system, would be necessary. There is also no danger of explosion as the O<sub>2</sub> concentration is controlled and limited and, furthermore, the water vapour acts as a stabiliser.

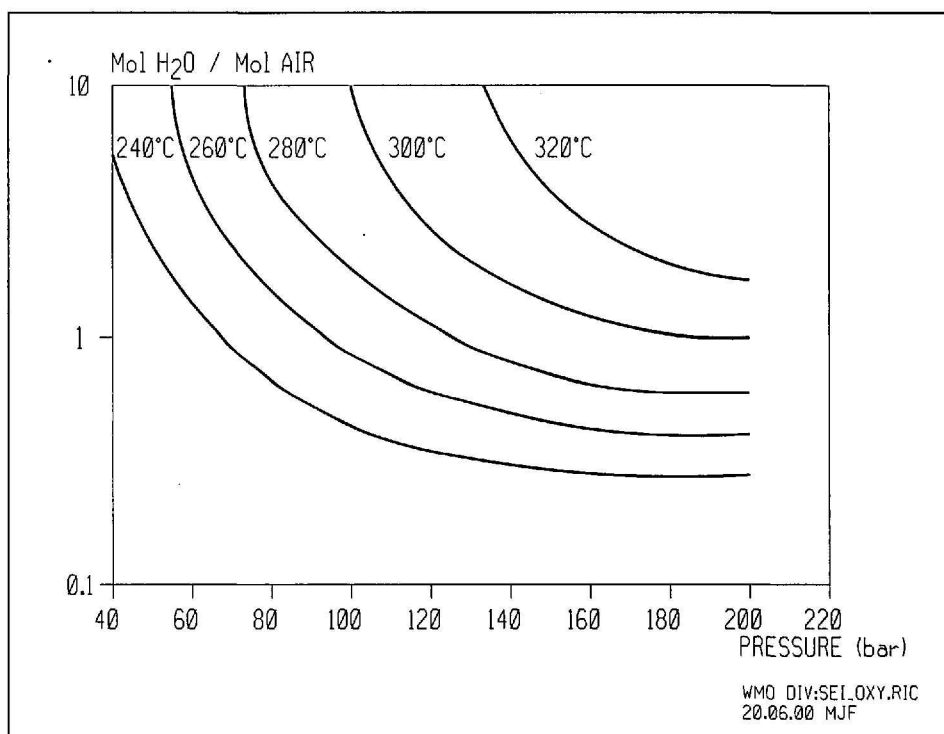


Fig. 2. Saturation of the gas phase

Table 2. Wastewater requirements. Construction material: Titanium

Total salt content	< Solubility under reaction conditions	
Anions :	Chlorine Bromide Fluoride	} a few percent a few ppm
Cations :	Iron Calcium Aluminium	lowest possible (danger of scaling in the heat exchanger)
pH		1–7

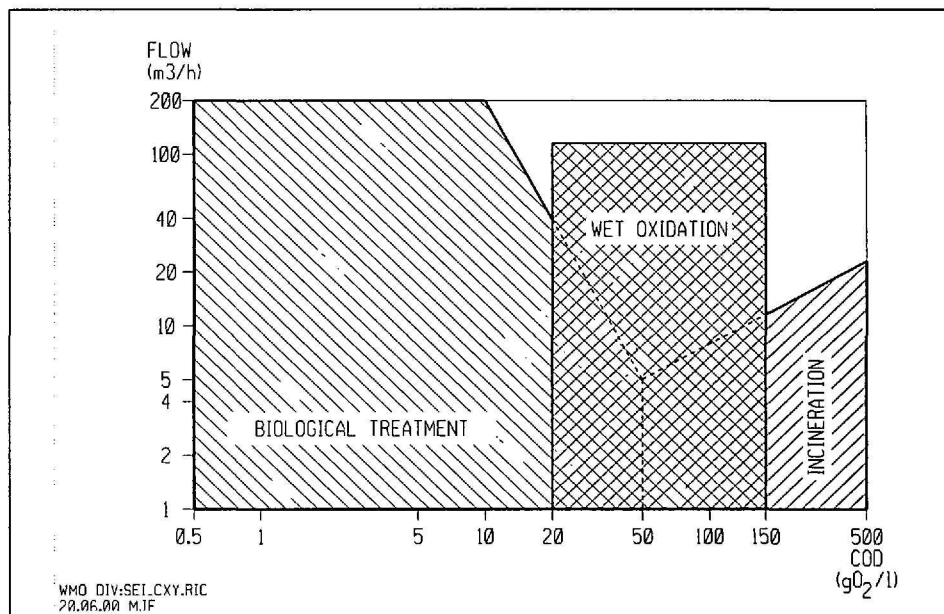


Fig. 3. Applications of the different wastewater treatment processes

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