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Wet air oxidation: past, present and future

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Abstract

Wet air oxidation (WAO) is a liquid-phase reaction between organic material in water and oxygen. The WAO process is used around the world to treat industrial wastewaters and sludges, at moderate temperatures (180–315°C), and at pressures from 2 to 15 MPa. Under these conditions, complex organic compounds are mostly oxidized into carbon dioxide and water along with simpler forms which are biodegradable. Unlike other thermal processes, WAO produces no NO_x, SO_2, HCl, dioxins, furans and fly ash.

The efficiency of aqueous phase oxidation can be largely improved by the use of catalysts, either heterogeneous or homogeneous. However, key points to be solved are stability of heterogeneous catalysts and recycling of homogeneous catalysts. This paper presents an update on the development of commercial catalytic WAO (CWAO) processes, which started as early as the mid-fifties in the United States. Several Japanese companies developed CWAO technologies relying on heterogeneous catalysts based on precious metals deposited on titania or titania–zirconia. Conversely, the focus in Europe was more on homogeneous CWAO, where three processes are already commercial and one under development.

Compared to conventional WAO, CWAO offers lower energy requirements and much higher oxidation efficiencies. Further developments of this technology should include high durability/low cost catalysts. Catalytic wet air oxidation would, thus, provide an environmentally attractive option to manage the growing organic sludge and toxic wastewater treatment problems.

1. Introduction

Wet air oxidation (WAO) is an attractive treatment for waste streams which are too dilute to incinerate and too concentrated for biological treatment. It can be defined as the oxidation of organic and inorganic substances in an aqueous solution or suspension by means of oxygen or air at elevated temperatures and pressures. Typical conditions for wet oxidation range from 180°C and 2 MPa to 315°C and 15 MPa. Residence times may range from 15 to 120 min, and the chemical oxygen demand (COD) removal may typically be about 75–90%. Insoluble organic matter is converted to simpler soluble organic compounds which are in turn oxidized and eventually converted to carbon dioxide and water, without emissions of NO_x, SO_2, HCl, dioxins, furans, fly ash, etc. In contrast to supercritical water oxygen (SCWO), a complete mineralization of the waste stream is impossible by WAO, since some low molecular weight oxygenated compounds (especially acetic and propionic acids, methanol, ethanol, and acetaldehyde) are resistant to oxidation. For instance, removal of acetic acid is usually negligible at temperatures lower than 300°C. Organic nitrogen compounds are easily transformed into ammonia, which is also very stable in WAO conditions. Therefore, WAO is a pre-treatment of liquid wastes which requires additional treatment of the process liquid and gas streams.

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After a first patent claiming the oxidation of a sulfite liquor from pulp production by compressed air at 180°C [1], most of the original WAO development work took place in the US some 50 years ago. Zimmerman did extensive testing of wet air oxidation technology and its application to treating spent pulp mill liquor [2]. The Zimpro company built in the early 1960s several large WAO plants for the treatment of municipal wastewater sludge, either to improve sludge dewatering by thermal conditioning, or to achieve complete oxidation of the sludge [3].

Fig. 1 shows a basic flow diagram of a WAO plant, which consists mainly of a high-pressure pump, an air or oxygen compressor, a heat-exchanger as well as a reactor with a relief valve and a downstream separator. The waste is retained in the reactor for a sufficient period of time to achieve the desired chemical oxidation (30–120 min). The simplest reactor design is usually a cocurrent vertical bubble column with a height-to-diameter ratio in the range of 5–20. Some design aspects of WAO reactors have already been reported [4–6].

About 90 plants are in operation today, mostly to treat waste streams from petrochemical, chemical and pharmaceutical industries as well as residual sludges from wastewater treatment. These plants aim either at a complete oxidative decomposition of pollutants or at a partial oxidation into low-molecular weight compounds which can then be treated further by conventional biological processes.

2. WAO reactions

Several studies have been devoted specifically to the elucidation of the mechanism of WAO, most of them using either carboxylic acids [7] or phenol [8] as model compounds. The free radical chain mechanism involving the formation of hydroperoxides and oxyradicals allows to describe correctly the gaseous and liquid oxidation products. As first step hydrogen abstraction from the α, β and γ-CH_2 groups of carboxylic acids by O_2 results in the formation of free radicals which react immediately with O_2 to form peroxy radicals. The peroxy radicals can lead to decarboxylation and formation of CO_2 by H abstraction from the –COOH group of another molecule of carboxylic acid. The predominance of acetic acid as major by-product is explained by the relative stability of the ethoxyl radical [7].

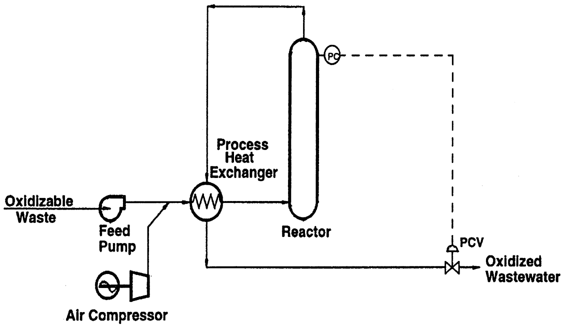


Fig. 1. Flow diagram of a wet oxidation process.

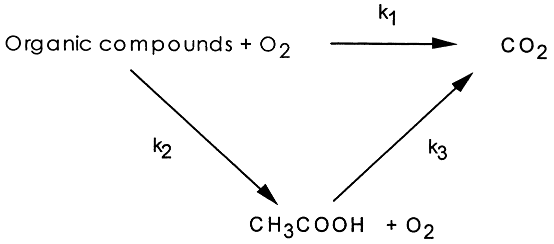
The oxidation rate of ammonia becomes significant only at temperatures above 540°C [9]. This is confirmed by the results obtained in the first commercial SCWO unit, which treats wastes containing long-chain alcohols and amines. Only with the addition of nitrite which is a selective agent for ammonia oxidation can very stringent discharge limits for residual nitrogen be achieved [10].

A generalized kinetic model based on a simplified reaction scheme with acetic acid as the rate-limiting intermediate (Fig. 2) has been proposed by Li et al. [11] and is usually used to represent the kinetic data of WAO reactions with reasonably good fits [12–13].

3. Main technical features of some commercial non-catalytic WAO processes

3.1. The Zimpro process

More than 130 Zimpro units, the first commercial WAO process, were installed in the US and in Europe for the oxidation of sewage sludge, most of them for ‘low-pressure’ conditioning by partially oxidizing the organic fraction – breaking up the structure of the sludge floc so that it would more easily release its bound water for improved dewatering. Some of these units were used for wet air carbon regeneration. After use in the PACT® process, the mixture of spent powdered activated carbon (PAC) and biomass from the aeration basin was oxidized to destroy excess biolog-



$$\frac{[\mathrm{O.C.} + \mathrm{CH_3COOH}]}{[\mathrm{O.C.} + \mathrm{CH_3COOH}]_0} = \frac{k_2}{k_1 + k_2 - k_3}\, e^{-k_3 t} + \frac{k_1 - k_3}{k_1 + k_2 - k_3}\, e^{-(k_1 + k_2)t}$$

Fig. 2. Simplified kinetic model for wet air oxidation [11].

ical solids, oxidize carbon adsorbed organics and reactivate the PAC for reuse in the biological/adsorption system.

Details of installation and operation of Zimpro plants in wastewater treatment plants were already reported [14–15]. Sludge destruction is carried out with air as oxidant, at 250–270°C and under pressures of 8.5–12 MPa, in reactors presenting a ratio height–diameter ranging between 5–20, while thermal conditioning is performed at 210–240°C.

The largest Zimpro unit currently in service for sludge conditioning is located in New Jersey (Passaic Valley Sewerage Commissioners). It treats sludge thickened to 4% dry solids (100 000 t DS per year), which is disinfected and easily dewatered to 55% DS on a filter press. The process is used there for thermal conditioning, since the treated sludge is intended after lime treatment to reuse in land application and restoration of landfills [16].

Other Zimpro WAO units are in operation in chemical, petrochemical and pharmaceutical plants worldwide [17]. Some of these units use optionally a homogeneous copper catalyst to help achieving higher COD removal. In the 1990s, 25 Zimpro units have been sold for oxidation of ethylene plant spent caustic [18]. The gas from the hydrocarbon cracking furnace is scrubbed in a caustic wash tower leading to a purge which is laden with sulfides and organics such as condensed oils and benzene. WAO achieves oxidation of reactive sulfide to soluble thiosulfate, sulfite and sulfate. This treated stream is then suitable for biotreatment in the plant's wastewater treatment system.

3.2. The VerTech process

The VerTech aqueous phase oxidation process (APO) treats sludge using pure oxygen in a sealed below-ground oxidation vessel consisting of two concentric tubes (downcomer and upcomer) and a heat exchange system [19] (Fig. 3). The underground portion of the APO system extends to a depth of approximately 1200 m with a diameter of 0.95 m, and uses drilling and casing technology developed in the natural gas and oil industries. The depth of the vessel results in high bottom pressures due to the hydraulic head without the need for aboveground, high pressure pumps. This original system facilitates heat exchange and minimizes the cost of pumping, but implies a weekly stop for descaling of the tubes with nitric acid, in order to preserve an effective heat exchange.

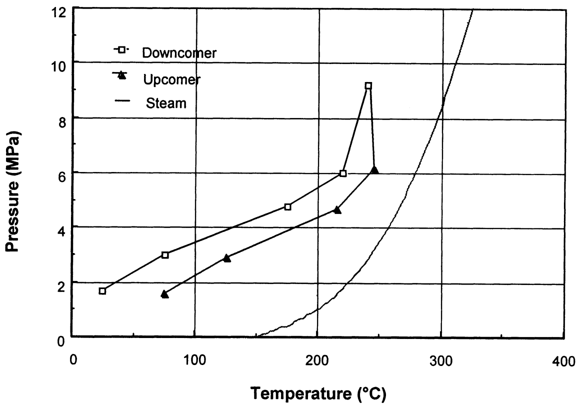


Fig. 3. Typical temperature/pressure profiles in the APO reactor during the start-up period [19].

In the VerTech unit brought into service in 1994 at Apeldoorn (The Netherlands), the temperature reaches approximately 275°C at the bottom of the reactor, under a pressure of 100 bar. This unit requires 55 t/day of oxygen to eliminate 70% of the COD from the 80 dry tons of sludge it processes daily. The residual solids are landfilled after dewatering to 55% DS, while most of the nitrogen load of the sludge is treated by biological nitrification-denitrification on the site of the VerTech unit. The off-gas is treated by thermal incineration with a catalytic reactor as backup.

4. Heterogeneous CWAO processes

The challenging operating conditions of WAO provided a strong driving force to investigate catalysts which would allow substantial gains on temperature, pressure and residence time. Another major benefit of using catalysts in WAO is the oxidation of the refractory compounds, namely acetic acid and ammonia, at much lower temperatures than in the absence of catalysts.

Several crucial issues have to be solved related to chemical and physical stability of the heterogeneous oxidation catalysts during WAO: leaching and sintering of the active phase and loss of surface area of the support. Leaching can be controlled to a large extent by a proper choice of the catalytic metal or metal oxide according to the available solubility data, and by pH control during CWAO. The same parameters are also of importance to control the hydrothermal stability of the catalyst carrier. Oxides of Al, Hf, Zr, and Ti have been shown to be stable in SCWO conditions and should be selected as catalyst supports [20]. However, high surface area metastable oxides such as γ–Al_2O_3 could undergo phase transitions detrimental to the durability of the supported catalytic metals and oxides. In addition to these deactivation factors associated with the physical properties of the liquid phase (temperature, pressure, and pH), poisoning of the active sites by deposition of organic or inorganic compounds may also compromise the durability of the catalyst.

The first patent was filed by DuPont in 1950 to claim a catalytic composition based on Mn–Zn–Cr oxides to perform CWAO at temperatures in the range of 120–200°C, for the destructive catalytic oxidation of industrial wastes of an organic nature, to permit their economical disposal, to abate stream pollution, to inhibit stream contamination and to otherwise eliminate industrial and health problems associated therewith [21]. Several types of heterogeneous catalysts were studied in the last decades, based first on supported or unsupported base metal oxides and more recently on supported precious metals [22–41] (Table 1). Supported precious metal catalysts are generally less prone to deactivation by leaching of the active phase, and present higher overall activities for the oxidation of various pollutants, especially acetic acid and ammonia. Additional information about academic studies of CWAO can be found in three recent reviews [42–44].

This research paved the way for the development of several commercial catalytic WO systems especially in Japan, where three CWAO technologies have been developed since the mid-eighties based on heterogeneous catalysts containing precious metals deposited on titania or titania–zirconia carriers. Compared to standard WAO, these processes are able to oxidize two refractory compounds, namely acetic acid and ammonia, thus allowing the treated water to be discharged directly or reused as process water.

4.1. The NS-LC process

The NS–LC process involves a Pt–Pd/TiO_2–ZrO_2 honeycomb catalyst. Two-phase flow in vertical monoliths gives in a broad range of G–L velocities a very beneficial flow pattern, the slug flow (segmented gas–liquid flow). Since each liquid plug is sandwiched between two gas plugs, a recirculation pattern is developed within each liquid plug, which improves mass transfer significantly [45] and prevents solids deposition. In addition, a thin liquid film is formed between the gas and the channel wall which allows high mass-transfer rates while keeping the catalyst continuously wetted.

Typical operating conditions of the NS–LC process are temperature 220°C, pressure 4 MPa and SV 2/h. In these conditions the oxidation of compounds such as phenol, formaldehyde, acetic acid, glucose, etc. reaches or exceeds 99% [46]. In the absence of catalyst the removal efficiencies would be limited to 5–50% [41].

Table 1
Summary of reported heterogeneous catalytic WAO research

Catalyst		Application	Reference
Active phase	Carrier		
Cu	alumina	phenol	[22]
	alumina	phenol	[23]
	alumina	p-cresol	[24]
Cu	alumina, silica	chlorophenols	[25]
Cu–Zn	alumina, silica	phenol compounds	[26]
Cu–Mg–La	Zn aluminate	acetic acid	[27,28]
Mn	alumina	phenol	[22]
Mn	SR 115	chlorophenols	[25]
Mn–Ce	none	poly(ethyleneglycol)	[29]
Mn–Zn–Cr	none	industrial wastes	[30]
Cu–Co–Ti–Al	cement	phenol	[31]
Co	none	alcohols, amines, etc.	[32]
Co–Bi	none	acetic acid	[33]
Co–Ce	none	ammonia	[34]
Fe	silica	chlorophenols	[25]
Ru	cerium oxide	alcohols, phenol, etc.	[35]
Ru	cerium oxide	acetic acid	[36]
Ru	titania-zirconia	industrial wastes	[37]
Ru–Rh	alumina	wet oxidized sludge	[38]
Pt	titania	phenol	[39]
Pt–Pd	titania-zirconia	industrial wastes	[40]
Pt–Pd–Ce	alumina	black liquor	[41]

4.2. The Osaka Gas process

The Osaka Gas CWO process is based on a mixture of precious and base metals on titania or titania–zirconia carriers (honeycomb or spheres). It has been demonstrated to work on several industrial and urban wastes:

1. a coal gasifier effluent in a pilot plant at British Gas's London Research Station [47];
2. wastewater from coke ovens [48];
3. concentrated cyanide wastewater of the Tufftride process (a soft nitriding process for steel) [49];
4. sewage sludge and residential wastes [48].

Table 2 shows some operational data on the treatment of wastewater from coke ovens in a test plant built in 1979 with several reactors (0.30 m inner diameter, 6,50 m height, total capacity 6 m^3/day). Highly concentrated COD and ammonia are decomposed to a level of 10 mg/l or less after 24 min contact time (SV = 2.5/h). Phenol and cyanide, the major pollutants present together with ammonia, are decomposed to levels below the detection limit. Furthermore, there is no detectable emission of NO_x or SO_x, and a catalyst lifetime larger than 8 years is claimed [48].

Without catalyst, there is no removal of ammonia and the COD decomposition rate is very low. With a two- to six-fold increase of contact time, a residual COD value of ca. 1000 mg/l is left in the effluent (acetic acid).

4.3. The Kurita process

Ammonia can also be selectively oxidized into N_2 and N_2O by the $NO_2{}^-$ ion at lower temperatures than in presence of oxygen. The Kurita company developed recently a process tailored to abate ammonia with nitrite at 170°C in the presence of a supported platinum catalyst [50]. With a catalyst close to those of the above-mentioned processes, the use of nitrite instead of oxygen allows operating temperatures 50–100°C lower.

Table 2
Typical coke oven wastewater WO results (Osaka gas process [48])[a]

Treatment conditions				Raw Waste water	Treated water	Exhaust gas composition	
Temperature (°C)	250	pH	(–)	10.5	6.4	O_2 (%)	9.9
Pressure (Mpa)	6.86	T–N	(mg/l)	3.750	160	N_2 (%)	83.1
Liquor volume (1/h)	200	NH_3–N	(mg/l)	3.080	3	CO_2 (%)	7.0
Air volume (Nm^3/h)	14.4	COD_{Mn}	(mg/l)	5.870	<10	NO_x (mg/Nm^3)	ND (<0.5)
Reaction time (min)	24	TOD	(mg/l)	17.500	ND	SO_x (mg/Nm^3)	ND (<2.0)
Catalyst	Type A	T–CN	(mg/l)	15	ND	NH_3(mg/Nm^3)	ND

[a] ND: not detected.

5. Homogeneous catalytic wet oxidation processes

An alternative to insoluble precious metals catalysts is the use of homogeneous transition metal catalysts which need, however, to be separated and recycled to the reactor or discarded. Several processes based on different variations of this concept have been developed in the last decade.

5.1. The Ciba–Geigy process

The Ciba process involves a copper salt which is separated as copper sulfide and recycled into the reactor which is lined with titanium to withstand corrosion. Compressed air was selected as oxidant in the three units installed in the 1990s within German and Swiss plants of the pharmaceutical company. They achieve high oxidation efficiencies (95–99%) on chemical and pharmaceutical wastes at elevated temperature (300°C). Such temperatures coupled with copper catalysis are essential for the oxidation of the rate-limiting acetic acid, but ammonia is still present in the treated waste. The unit located in Grenzach, Germany (near Basle) is currently highly reliable with 97% availability [51]. The off-gas from this unit is purified by catalytic oxidation.

Recently, this process has been marketed for the treatment of industrial wastewaters and sewage sludge, in catalyzed as well as uncatalyzed versions, by the Swiss company Granit [52].

5.2. The LOPROX process

The LOPROX process (low pressure wet oxidation) was developed by Bayer AG for the separate treatment of organic substances which degrade too slowly in normal biological plants or adversely affect the degradation of other substances. Oxidation takes place with oxygen in the acidic range in a multistage bubble column oxidation reactor, under relatively mild operating conditions (temperature below 200°C and pressures in the range 0.5–2.0 MPa) and is catalyzed by a combination of Fe^{2+} ions and quinone-generating substances. To compensate the mild reaction temperature, a residence time of ca. 2 h in the reactor is needed (range 1–3 h). At a reaction temperature of 150°C, a concentration of about 10 g COD/l effluent is sufficient in order to allow the process to take place autothermally [53]. Fig. 4 shows modification of chemical oxygen demand and biological oxygen demand i.e., BOD/COD ratio with temperature with the LOPROX process. Values of the BOD/COD ratio higher than 0.50 correspond to readily biodegradable effluents [54].

Several LOPROX plants are in operation at Bayer AG. The process serves also as an alternative in the handling of sludge from wastewater treatment plants

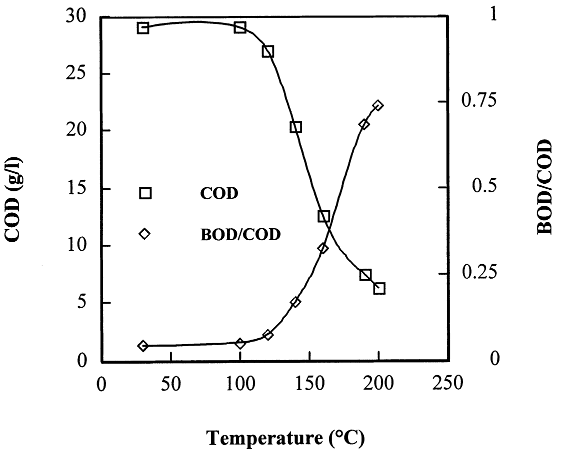


Fig. 4. Evolution of COD and BOD/COD as a function of temperature in the LOPROX process.

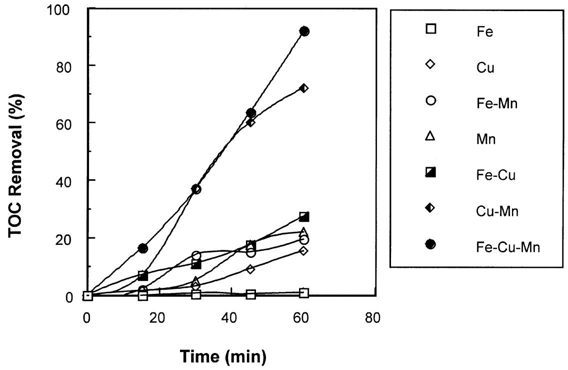


Fig. 5. Determination of synergetic effects of metals (Fe, Cu, Mn) for oxidation of a mixture of oxalic, malonic, succinic and acetic acid (total organic carbon = 5 g/l) with H_2O_2 at 98°C, pH 3.5 and $[MSO_4] = 5.4$ mM [58].

[55]. About 85–90% of the organic matter will be eliminated in the overall process, with 60–65% oxidized to CO_2 directly in the oxidation reactor at approximately 190°C and 25% dissolved in the treated liquid phase as well biodegradable COD to be recycled in the waste water treatment plant. The catalysts Fe^{2+} and quinones are provided by the sludge. The operating costs for sludge treatment by the LOPROX process are estimated by Bayer in the range 125–175 €/t of dry matter. A pilot unit with a capacity of 600 l/h is under operation in Switzerland, in the wastewater treatment plant Birs II, in order to optimize the process for the treatment of sludge.

5.3. The WPO process

The WPO process derived from the classical Fenton's reagent by IDE (France) and INSA-Toulouse allows high oxidation efficiencies (up to 98%) in mild conditions (90–130°C, 0.1–0.5 MPa), using as oxidant hydrogen peroxide catalyzed by Fe^{2+} in solution at pH 3. This process was successfully operated in Spain in 1992 on two different sites (aquifers) with a 5 m^3/h demonstration unit.

On both sites the process was able to achieve a COD removal efficiency of at least 95% [56]. Recently, a homogeneous Fe–Cu–Mn catalyst was developed to treat refractory oxidation by-products such as acetic acid and bicarboxylic acids (oxalic, succinic, etc.) (Fig. 5). The catalyst is recovered after reaction by precipitation at pH 9 and filtration [57,58].

6. Recent developments

6.1. The ORCAN process

A modified WPO process has been recently developed in Switzerland based on R and D performed at ETH Zürich [59]. The oxidation reactor for carbon and nitrogen compounds (ORCAN) process pretreats refractory wastes at 120°C and 0.3 MPa, with air as stoechiometric oxidant. The oxidation is catalyzed by Fe^{2+} ions as well as minor amounts of hydrogen peroxide (H_2O_2/COD = 0.20). The decomposition of H_2O_2 is likely to initiate the free radical chain mechanism at the relatively low temperature, since with oxygen only and Fe^{2+} ions the oxidation reactions are initiated at ca. 150°C. A first commercial unit came into operation in 1996 in a textile factory (feed 4 m^3/h, COD 7–10 g/l).

6.2. The ATHOS process

Sludge is by far the most important by-product of wastewater treatment, whose final destination must be managed from the standpoint of a global and sustainable protection of the environment. The current production of sludge within the EU is around 6.5 million tons of dry solids per year, but the staged implementation of the Urban Wastewater Treatment Directive (91/171/EEC) will substantially increase the EU sewage sludge volume, while some current disposal and re-use practices will be prohibited or questioned. In France, Generale des Eaux/Anjou Recherche is developing a CWAO process based on a cupric ion catalyst, to open a novel acceptable disposal option for sludges. The main design objectives were lowering the temperature, elimination of ammonia, and process integration within the wastewater treatment plant.

The initial studies of sludge oxidation were performed in a 1 l agitated batch autoclave, with typical operating conditions 7 MPa for the pressure, 235°C for the temperature and 1 h of residence time. Depending on the temperature in the range 215–285°C, between 56 and 83% of the COD was removed (Fig. 6). Acetic acid, very refractory to oxidation, was the rate-limiting intermediate for COD removal. However, acetic acid can be used within the treatment works as a carbon source to perform nutrient removal (denitrification)

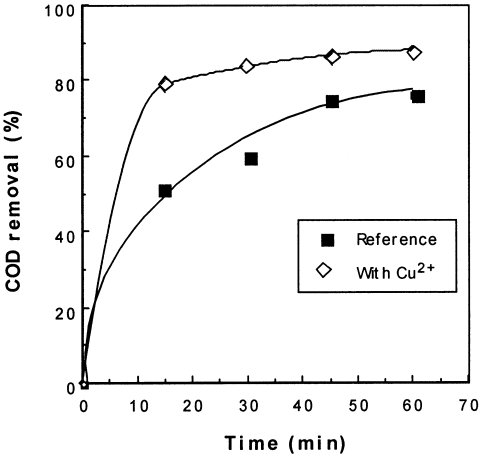


Fig. 6. Influence of Cu^{2+} (Cu^{2+}/COD = 0.01 g/g) and reaction time on the removal of COD at 235°C.

by returning the WAO liquor to the plant inlet. Other by-products such as low molecular weight carboxylic acids, methanol, ethanol, acetaldehyde and acetone could also be identified [60]. Biodegradability tests showed that the return liquor is easily biodegraded.

In order to reach substantial gains on temperature, pressure and residence time, both heterogeneous and homogeneous catalysts were investigated [61,62]. Cu^{2+} in solution or supported copper oxide were found the most effective catalysts (Fig. 6). In the presence of copper, the results obtained at 235°C were equivalent to those obtained at 285°C without catalyst.

Even at 285°C in the presence of a copper catalyst, acetic acid remained refractory to oxidation. The effect of copper was mainly to accelerate the chain reactions transforming organic compounds into acetic acid. This limited COD removal to 85% at temperatures lower than ca. 300°C. After reaction the copper catalyst is lost as copper oxide/carbonate precipitated within the matrix of the residual solids.

The oxidation process converted the organic nitrogen in the sludge into ammonium whose further oxidation was quite difficult (Table 3). In order to enhance ammonia oxidation, some process parameters were modified and catalysts were added to promote oxidation into nitrogen gas while limiting nitrate formation [63]. The extensive nitrogen elimination in the process reduces the amount of nitrogen sent back to the head end of the plant to loads close to those generated by sludge dewatering.

Table 3
Modification of the nitrogen content of the sludge by wet oxidation[a]

Nitrogen content (g/l)	Initial sludge	Oxidized sludge	Catalytically oxidized sludge
NH_3-N	0.62	1.41	0.56
TKN-N	1.90	1.49	0.58
NO_3-N	0	0.03	0.08

[a] Operating conditions: temperature 235°C, contact time 1 h (TKN: total Kjeldahl nitrogen).

The wet oxidation of sludge was further studied in a continuous flow tubular reactor with high effluent recycle. This equipment allowed to confirm at the scale of 25 l/h all the results obtained during batch autoclave tests. This installation, equipped with a catalytic treatment of the off-gas, demonstrated also that the oxidation of sludge led to negligible gas emissions in terms of CO, NO_x and VOCs (a few ppm to a maximum of a few 10 of ppm vol).

The ATHOS® wet oxidation process was then developed one step further with a demonstration unit combining in a modular 12 m × 6 m × 10 m facility three main steps: preparation of the sludge, oxidation, and dewatering of the residual solids (Fig. 7). This unit was transported to the Toulouse, France wastewater treatment plant in February 1998 to treat 3 m^3/h of thickened sludge (4% DS).

In the unit sodium hydroxide is added to the sludge to maintain the pH of the oxidized sludge between 7.5 and 8.0, and the copper oxidation catalyst added. A high pressure pump is then used to pump the thickened sludge into a regenerating heat exchanger to bring it to a temperature of 110°C. It then enters a second series of exchangers which bring it to the set temperature. Once the process reaches a steady state, it is autothermal without any energy input. Oxygen is stored on-site in liquid form. Oxidation is carried out at a temperature of 235°C and a pressure of about 4 MPa, in order to keep the sludge liquid.

Separation of the liquid and solid phases is carried out in a settler from which the supernatant is cooled at ambient temperature and sent back to the head end of the plant. The solid phase is extracted from the settling tank and dewatered in a filter press to 50% DS. Catalytic oxidation, which is an integral part of the process, enables to discharge a gaseous effluent in which carbon monoxide, volatile organic compounds, and ammonia have been extensively removed.

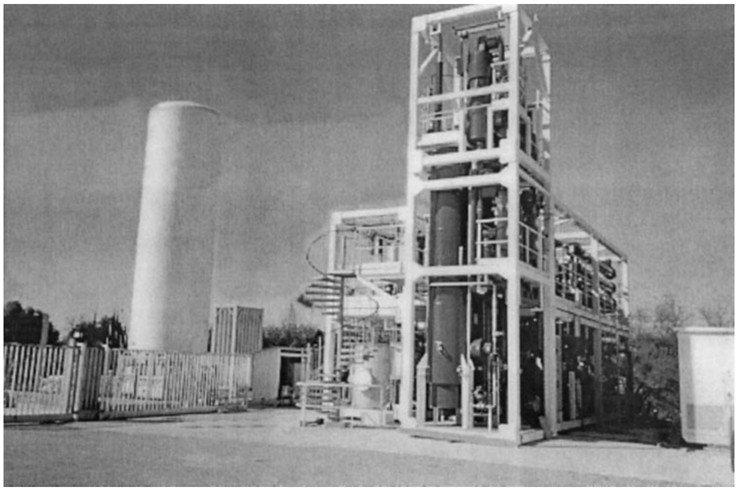


Fig. 7. A view of the ATHOS® demonstration unit in operation at the Toulouse wastewater treatment plant.

The ATHOS unit was commissioned stepwise during the 2nd quarter of 1998, in order to achieve the following treatment goals: removal of 75% COD and 70% ammonia. During a continuous run test of 30 h in October 1998, these goals were achieved even at 220°C: 75% COD removal (residual COD 9 g/l) and 63% TKN abatement (inlet TKN 1320 mg/l, outlet 490 mg/l). At 235°C, 85–90% COD removal was routinely obtained. The demonstration unit has since been kept in operation to gain sufficient experience on different types of sludges as well as operation and maintenance issues.

6.3. Other developments

In France, several projects investigated recently heterogeneous precious metal catalysis for the oxidation of refractory compounds, acetic acid and ammonia, at temperatures below 200°C and pressures below 4.0 MPa [64–66]. These projects supported by chemical and waste treatment companies led to a series of patents claiming catalysts based on supported Ru [67–69].

Heterogeneous as well as homogeneous catalysis was also studied at the Imperial College of London, for different WAO cases. An interesting integrated process consisting of a CWAO reactor, a closed catalyst recirculation loop and a reverse osmosis (RO) membrane was investigated. The high pressure of the CWAO reactor was used as driving force for the RO separation, which offered high rates of rejection for organics and catalyst metal ions [70].

7. Conclusions

Compared to conventional wet air oxidation, catalytic wet air oxidation offers lower energy requirements and much higher oxidation efficiencies. Commercial catalytic wet oxidation processes rely either on supported precious metal and/or base metal oxide catalysts or on homogeneous catalysts such as Fe or Cu. In some cases, the overall performance of CWAO can be close to that of supercritical water oxidation operating typically at pressures around 25 MPa and temperatures around 550°C.

The practical applications of heterogeneous catalysts are likely to be restricted to processes which treat industrial wastewaters presenting well-defined compositions, to minimize the challenge linked to the variability of wastewater characteristics in terms of pH and presence of poisons. The risk of hydrothermal sintering of the catalytic phase or support should also be considered carefully.

Homogeneous catalysts based on iron or copper are now being applied in several commercial wet air oxidation which are operating successfully to treat industrial effluents and sludges. The fate of the catalyst has to be studied early in the process design stage according to the existing discharge regulations either in the liquid or solid phases.

Thanks to catalysis, wet air oxidation is today a cost-effective solution for the treatment of organic sludge and refractory industrial wastewater.

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