Wet air oxidation for the treatment of industrial wastes. Chemical aspects, reactor design and industrial applications in Europe

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Abstract

Aqueous wastes containing organic pollutants can be efficiently treated by wet air oxidation (WAO), i.e. oxidation (or combustion) by molecular oxygen in the liquid phase, at high temperature (200–325°C) and pressure (up to 175 bar). This method is suited to the elimination of special aqueous wastes from the chemical industry as well as to the treatment of domestic sludge. It is an enclosed process, with a limited interaction with the environment, as opposed to incineration. Usually, the operating cost is lower than 95 Euro m⁻³ and the preferred COD load ranges from 10 to 80 kg m⁻³. Only a handful of industrial reactors are in operation world-wide, mainly because of the high capital investment they require. This paper reviews the major results obtained with the WAO process and assesses its field of possible application to industrial wastes. In addition, as only a very few studies have been devoted to the scientific design of such reactors (bubble columns), what needs to be known for this scientific design is discussed. At present, a computer program aimed at determining the performance of a wet air oxidation reactor depending on the various operating parameters has been implemented at the laboratory. Some typical results are presented, pointing out the most important parameters and the specific behavior of these units. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Wet air oxidation; Wastewater treatment; Industrial organic waste; Reactor design; High temperature; High pressure; Liquid phase; Oxidation; Oxygen

1. Introduction

We should consider our environment as being borrowed from future generations and refrain from leaving a legacy of problems we are not able to solve. There is growing concern about the problems of waste elimination. Among the various types of processes which can be used for treating aqueous wastes polluted with organic matter, wet air oxidation (WAO) is very attractive. Unlike incineration, which is handicapped by its bad ecological image of a process which can disseminate products of incomplete combustion and dust in the atmosphere, this process is enclosed and has a very limited interaction with the environment.

The basic idea of the process [1] is to enhance contact between molecular oxygen and the organic matter to be oxidized. High temperature conditions convert the organic matter to carbon dioxide and water. The liquid phase is maintained by a high pressure which also increases the concentration of dissolved oxygen [2] and thus the oxidation rate. Typical conditions are 200–325°C for temperature, 50–175 bar for pressure and 1 h for the residence time; the preferred COD load ranges from 10 to 80 kg m⁻³. The process can treat any kind of organic aqueous waste, even toxic, produced by various branches of industrial activity, or it can be coupled with a biological treatment facility to eliminate the sludge. WAO is one of the few processes that does not turn pollution from one form to another, but really make it disappear. This process has been used under mild conditions that alter molecular structures and improve biodegradability in spite of a limited COD reduction, but, usually, it is run under conditions that give almost...
entire oxidation of the organic matter and that can allow mechanical power generation [3] because the reaction releases energy. It has been established [4,5] that the energy self-sufficiency is obtained provided that the COD load exceeds 12–15 kgm$^{-3}$.

There are only some tens of industrial plants in operation around the world [4]. In western Europe, the main plants can be divided into two classes. In the first, extremely specific tubular reactors have been adapted from the mining industry (Stignaes, Denmark) or from the oil extraction branch (Apeldoorn, The Netherlands). The very high capital cost and the operating problems (scaling up, lack of turbulence and homogenization leading to sedimentation problems, maintenance) are very serious disadvantages in this technology. In the second class, much more conventional bubble column reactors are found (Newcastle, England; Monthey, Switzerland and Grenzach, Germany, etc.). But, despite this industrial experience, very few documents [6,7] are available for the scientific design of such bubble column reactors. This article reviews the major results available for the process and describes a method for designing such bubble column reactors.

### 2. History of wet air oxidation

More than 40 years ago, Zimmermann [8] was looking for an alternative method to treat special black liquors from papermills. Because of their very high silica content, the usual evaporation and combustion method (Kraft process) was unsuitable. Zimmermann found he could burn pulpmill liquors and described a method using air at high pressure leading to the combustion of organic compounds dissolved or suspended in liquid water, at relatively low temperatures, as long as oxygen was present. Wet air oxidation was beginning to take off. Zimmermann added that this new method was quite

<table>
<thead>
<tr>
<th>Nomenclature</th>
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<tbody>
<tr>
<td>C: Actual concentration of an organic compound</td>
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<tr>
<td>COD: Concentration of organics, expressed as the chemical oxygen demand</td>
</tr>
<tr>
<td>D: Axial dispersion coefficient for the liquid (or the gas) in the reactor</td>
</tr>
<tr>
<td>E: Activation energy for the chemical reaction</td>
</tr>
<tr>
<td>EOS: Equation of state</td>
</tr>
<tr>
<td>f: Backflow ratio parameter</td>
</tr>
<tr>
<td>FP: Poynting factor</td>
</tr>
<tr>
<td>Gi,j: Partial flow rate for a specific component in the gas phase of the reactor at cell 'j'</td>
</tr>
<tr>
<td>H: Enthalpy of the liquid (or the gas)</td>
</tr>
<tr>
<td>Hcell: Height of an elemental cell in a WAO bubble column reactor</td>
</tr>
<tr>
<td>Hi/w: Henry’s law constant for the solubility of a gas in water</td>
</tr>
<tr>
<td>k0: Pre-exponential factor for a reaction rate</td>
</tr>
<tr>
<td>ki,a: Overall mass transfer coefficient</td>
</tr>
<tr>
<td>Ki: Apparent constant for a chemical rate of oxidation</td>
</tr>
<tr>
<td>Li,j: Partial flow rate for a specific component in the liquid phase of the reactor at cell ‘j’</td>
</tr>
<tr>
<td>n: Number of cells</td>
</tr>
<tr>
<td>(O2): Actual concentration of oxygen dissolved</td>
</tr>
<tr>
<td>P: Total pressure</td>
</tr>
<tr>
<td>Pe: Peclet (Bodenstein number) for axial dispersion</td>
</tr>
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<td>R: Constant for ideal gases</td>
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<tr>
<td>β: Partial order of the reaction with respect to the oxidant</td>
</tr>
<tr>
<td>ΔH: Heat of reaction (1.04 $10^5$ cal.(mol O$_2$)$^{-1}$)</td>
</tr>
<tr>
<td>εg: Gas hold up</td>
</tr>
<tr>
<td>Φi: Fugacity coefficient for component ‘i’, obtained from the Peng and Robinson EOS</td>
</tr>
<tr>
<td>yi: Activity coefficient for component ‘i’ in the solution</td>
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<tr>
<td>λ: Backflow ratio for the liquid phase in the reactor</td>
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<tr>
<td>ξ: Backflow ratio for the gas phase in the reactor</td>
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<table>
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<tr>
<th>Subscripts</th>
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<tr>
<td>i: Subscript for a specific compound</td>
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<tr>
<td>j: Subscript for a specific cell</td>
</tr>
<tr>
<td>g: Gas phase</td>
</tr>
<tr>
<td>l: Liquid phase</td>
</tr>
<tr>
<td>0: Inlet or initial condition</td>
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</table>
similar to incineration as the organic residues where mainly burned up to carbon dioxide, to nitrogen (ammonia or molecular) and to ashes, together with a limited amount of volatile fatty acids (acetic) and traces of carbon monoxide. When the temperature was about 300°C, the organic matter removal efficiency exceeded 95% and enabled the mineral fraction of the oxidized liquor to be recycled. Because of the vapor pressure of water (86 bar at 300°C) and because of nitrogen from the air, the total pressure figure came to 175 bar or so and the energy aspect (gas compression and energy recovery) of WAO was obviously an important feature to consider.

By the early 1970s, wet air oxidation was regenerating spent powdered activated carbon from wastewater treatment processes and from chemical industries. The process had been used on sewage sludge since 1960, with different results achieved through changes in the operating temperatures and pressures. But the process was rediscovered during the 1980s, it enjoyed renewed popularity as a means of detoxifying liquids prohibited from land disposal by restrictions related to new regulations decreed worldwide for environmental protection.

3. Chemical aspects of wet air oxidation

3.1. General aspects and results

Various authors have determined the dependency on the operating parameters and the mechanism of oxidation [9–11]). At about 250°C, nearly all the compounds can be completely transformed except for acetic and propionic acids. Furthermore, under such conditions, the final product is not only carbon dioxide, but also various carboxylic acids, mainly acetic, according to Pujol et al. [12]) and Imamura et al. [13]). The oxidation proceeds according to a chain reaction mechanism, presented in Fig. 1, which highlights the particular role of acetic acid. In a previous paper, [10] we have compared the ability of WAO to oxidize various organic substances; acetic acid indeed appears to be refractory and needs the most extreme conditions to oxidize to carbon dioxide. Nevertheless, by increasing the temperature to 310°C, it can be oxidized to over 90% within 1 h.

Several kinds of wastes were studied in batch reactors for the dependency of the reaction rate on temperature, oxygen pressure and organic compound concentration, including: biological sludge and papermill black liquors, which are of industrial concern; various wastes from the pharmaceutical and the phytosanitary industries; and oxalic, acetic and formic acids, which are significant intermediates for oxidation of industrial wastes and model molecules. As organic carbon is oxidized to carbon dioxide, organic nitrogen is usually turned to ammonia, but elemental nitrogen has been reported with nitrous compounds. Sulfur compounds give sulfurous acid or sulfates, phosphorus compounds give phosphates and chlorine compounds give hydrochloric acid. Thus, the general material balance for the WAO process can be described with reaction 1 where the heat value is close to 435 kJ (mole O2 reacted)^-1.

\[
\begin{align*}
C_mH_nO_xCl_wN_yS_zP_r + (m + 0.25(n - 3x)) & \rightarrow mCO_2 + 0.5(n - 3x) \\
H_2O + xNH_3 + wCl^- + ySO_4^{2-} + zPO_4^{3-} + \text{heat} & \end{align*}
\]

Reaction 1

3.2. Mechanism of the reactions and catalysis

The series of reactions 2–6 indicates that the reaction is propagated by an organic radical \( R^* \) during a coupling with molecular oxygen [reaction (2)]. According to Lixiong et al., [14] this radical is normally obtained by reaction between oxygen and the weakest C–H bonds [reaction (3)] and during an attack by the radical \( HO_2 \) obtained [reaction (4)]. Because of the temperature, the hydrogen peroxide obtained decomposes rapidly [reaction (5)] to hydroxyl radicals. Reaction (6) is a propagation step leading to hydroperoxides and, more generally, to oxidized species. For most of the molecules, the initiation step [reaction (3)] is the limiting one and is extremely dependent on temperature, with an activation energy which can exceed 100 or 200 kJ mol^-1. This result explains why air oxidation, impossible at room temperature, becomes fairly rapid at temperatures greater than 250 or 300°C. On the other hand, the propagation step [reaction (2)] is usually rapid and the rate constants are about 10^7 to 10^9 l mol^-1 s^-1 according to Jouffret [15].

\[
O - O + R^* \rightarrow ROO^* \]  

Reaction 2

![Fig. 1. Simplified diagram for wet air oxidation.](image-url)
The importance of the free radicals in this mechanism has encouraged the search for catalysts and promoters which could overcome the thermal limitation of reaction (3). In a review paper, Luck [16] lists a large number of heterogeneous catalysts which have been studied in the last decades. Most of them are based on unsupported composite metal oxides, like Co/Bi [17], or on supported metal oxides, like Cu/Zn [18]. In some cases [19] precious metals like Pt, Rh and Ru are supported on TiO2 or on activated carbon. A Mn/Ce composite metal oxide, first described by Imamura et al. [20] is efficient for carbon elimination, but also for the transformation of ammonia to molecular nitrogen. For homogeneous catalysis, ions like Fe2+, Fe3+, Cu2+, Ni2+, Ag+ and Cr3+, associated with hydrogen or organic peroxides are very attractive [21]. The temperature can be lowered to 200°C and the dependency of the rate on the oxygen partial pressure is less marked. In every case, the mechanism is close to that for noncatalyzed oxidation as acetic acid is also identified as a final product, besides carbon dioxide.

Nippon Shokubai and Osaka gas have developed rather similar catalytic WAO processes using heterogeneous catalysts based on precious metals (Pt, Pd) deposited on TiO2 and ZrO2 honeycomb carriers. At a plant in Monthey (Switzerland), Ciba Geigy (1990) has developed a copper catalyst which is recovered and recycled by a precipitation/filtration technique. The Loprox process from Bertrams AG is catalyzed by a combination of Fe2+ and quinone-generating substances, to compensate for a mild reaction temperature. Djafer et al. [22] have patented a process using a Cu2+ catalyst which settles with the solid residue after treatment and is then recycled and reused.

### 3.3. Kinetic aspects of the chemical reactions

The practical aim of understanding reaction mechanisms is to improve the development of kinetic models required for the design of industrial reactors. Fundamental studies have determined the dependency of the oxidation rate on the various operating parameters [9,11]. The partial order with respect to the organic compound is almost always 1. It is close to 0.4 with respect to dissolved oxygen [5,23]. WAO reactions have been extensively studied in laboratory batch reactors for kinetic purposes, over a wide range of temperatures and pressures. The global rate of an elementary chemical reaction is usually calculated assuming a general power law form and Eq. (1) is often used.

Nevertheless, this model cannot properly describe the rate observed with a complex mixture of compounds, as found in real wastes. In such cases, as WAO proceeds according to Fig. 1 and to reaction (6), some of the organic compounds are destroyed to the final oxidation products, while others are transformed to intermediates (typically short chain alcohols and fatty acids) having a lower reactivity. The global rate of oxidation depends on the final products’ formation rates as well as on the rates of formation and destruction of the intermediates. Thus, Lixiong et al. [14] have proposed a generalized model according to Fig. 2 where group “A” includes all initial and relatively unstable intermediates and group “B” contains the more refractory intermediates represented chiefly by acetic acid. Both groups can lead to oxidation endproducts, like carbon dioxide and Eq. (1) is still used for any of the elemental reactions. In a batch reactor where the concentration of dissolved oxygen remains unchanged over the reaction period, Eq. (2) gives the evolution of the concentration of organic compounds over the time. Parameter [A + B] is a global indication of the actual value of the organic load, usually expressed as COD or TOC values. K1, K2 and K3 are apparent constants for the chemical rates, they depend on the temperature value and on the dissolved oxygen concentration according to Eq. (3). A high value of K2 will indicate accumulation of low reactivity intermediates, like acetic acid, and a low value will indicate a high global reactivity.

\[
r_c = k_0 \exp\left(-\frac{E}{RT}\right) \ast C \ast (O_2)^{d}
\]

\[
\frac{[A + B]}{[A + B]} = \frac{K_2}{K_1 + K_2 - K_3} \ast \exp(-K_3 \ast t) + \frac{[K_1 - K_3]}{K_1 + K_2 - K_3} \ast \exp(-[K_1 + K_2] \ast t)
\]

\[
K_i = k_{0,i} \ast \exp\left(-\frac{E_i}{RT}\right) \ast (O_2)^{d_i}
\]
was conducted in a batch autoclave reactor, the temperature and concentration of dissolved oxygen being maintained constant throughout each of the runs. The experimental results and the model line, obtained after proper adjustment of the $K_i$ values by a least square method, are plotted in Fig. 3 for two runs. As Fig. 3 and Eq. (2) show, the experimental result can be conveniently represented with the model depicted in Fig. 2. This model is valid for temperatures ranging from 250 to 325°C and for oxygen concentrations from 0.5 to 1.5 g/l.

4. Transfer and solubility of gases during WAO

4.1. Transfer between gas and liquid

The overall wet air oxidation mechanism includes two steps. One is the chemical reaction between the organic matter and oxygen dissolved in the liquid phase, producing carbon dioxide. The other one, a physical step, is the transfer of oxygen from the gas phase to the liquid one and the transfer of carbon dioxide to the gas from the liquid. When designing a wet air oxidation reactor, one usually considers that gases diffuse rapidly within the gas phase. The only significant transfer resistance is located at the gas/liquid interface (film model) and the actual conditions within an industrial reactor will depend on its hydrodynamics. For high mixing efficiencies, the oxygen concentration within the bulk liquid is close to the interface (or equilibrium) concentration and the overall rate is close to the chemical rate.

The rate of transfer of a component between the two phases is expressed by Eq. (4) as the mass transfer coefficients [24] are available from the literature for various types of reactors. The fugacity coefficients can be determined using the Peng and Robinson EOS with the usual mixing rules [25,26].

$$r_{i,j} = k_{fi,j} \times \left\{ Y_i \times \Phi_i \times \frac{P}{Y_i} \times H_{i/w} \times FP_i - X_i \right\}$$

4.2. Solubility of oxygen and carbon dioxide

The Henry’s law constant for the solubility of gases in water is also available from the literature [2,10,27,28,38]. Because of the dependency of the Henry’s law constants on temperature, it is clear that, above 250°C, the solubility is greater than at room temperature. This must be pointed out as it is usually believed that solubility just decreases as temperature increases. In WAO reactors, dissolved oxygen concentrations as high as 1.5 g/l are easily obtained as the oxygen partial pressure can be as high as 25 bar.

To determine the total amount of carbon dioxide dissolved, it is necessary to take into account the effect of the pH on the dissociation as in reaction (7) and Eq. (5) where the first ionization constant varies from 4.32 10^{-7} (20°C) to 1.6 10^{-8} (250°C). The second dissociation can be ignored at the usual pH values.

$$\text{H}_2\text{O} + \text{CO}_2, \text{aq} \rightarrow \text{H}^+ + \text{HCO}_3^- \quad \text{Reaction 7}$$

$$H_{\text{CO}_2/\text{w,cor}} = \frac{H_{\text{CO}_2/\text{w}}}{\left(1 + K_{\text{at}}/10^{-\text{pH}}\right)}$$

5. Industrial aspects of wet air oxidation

5.1. Flow diagram

An industrial wet air oxidation unit is typically run continuously. The basic flow diagram of the more usual WAO systems is given in Fig. 4. The raw waste is pumped to the lower part of a bubble column reactor through a series of preheaters. A liquid residence time from 35 min to 3 h is used. Air or oxygen is
compressed and is allowed to bubble at the lower part of the reactor. Usually, the oxygen flow rate does not exceed 110% of the inlet COD flow rate. In some cases, cryogenic oxygen is used and pumped before vaporization to save shaft work during compression. After starting up, the reactor is normally adiabatic and, in most cases, the temperature value is controlled by adjusting the total pressure. The heat absorbed when water vaporizes in the gas stream compensates for the heat released when the organic pollutants oxidize in the liquid phase. The energy content of the liquid and gas outlet streams is sufficient to ensure the preheating of the feed. If the inlet COD exceeds 12–15 g/l, the process gives net energy generation [3,5]. Phase separators and final energy recovery system are not depicted in Fig. 4 but medium pressure steam is usually generated and, according to the industrial site conditions, dedicated to process use throughout the plant or to a specific turbine.

The typical COD removal efficiency seldom exceeds 95% and the treated stream cannot be discharged into the environment. Most of the WAO units are run in connection with biological facilities where a posttreatment is conducted before final release, like in Grenzach — Germany and Stignaes — Denmark. The gas stream coming out of a WAO treatment facility contains a limited amount of volatile organic compounds and carbon monoxide (0.5–25%) together with carbon dioxide, oxygen in excess and water. A simple postcombustion reactor ensures the final oxidation of these gases before they are vented to the atmosphere. The quantity of waste gas is only about one tenth of the quantity which would be emitted by an incineration plant treating the same waste.

5.2. Typical industrial facilities in Europe

Several companies have industrial references concerning this process, including US Filter/Zimpro (by far the leader throughout the world), Ciba Geigy, Bayer and its licensee Bertrams, Vertech Treatment System and its licensee KTI/Manesmann, etc.

5.2.1. Eastman Fine Chemicals (Newcastle, UK)

This facility started up in 1992 to treat the wastewater from a facility producing the pain reliever Paracetamol. This waste contains various organic compounds, including aminophenols, with a COD close to 70 or 80 kg m⁻³, and large amounts of sulfite. US Filter/Zimpro has designed a bubble column reactor according to Fig. 4 with an inner titanium lining. The rated temperature is 265°C, the rated pressure 110 bar (atmospheric air is used) and the nominal flow rate is 0.7m⁻³h⁻¹, corresponding to an actual residence time of about 2.5 h. A 97% removal efficiency is claimed for COD and the effluent is trucked to a nearby public wastewater treatment plant. US Filter/Zimpro has extensive knowledge of this process and has designed and constructed several similar facilities during the last 15 years, including, among others, Casmalia Resources (California, USA) for the treatment of cyanides, phenols and pesticides; Bofor Nobel (Michigan, USA) for treating wastes from the chemical industry and regenerating activated carbon and Dominion Foundries (Ontario, Canada) to detoxify a liquor after scrubbing the gases of a coking plant.

5.2.2. Hoffmann La Roche (Germany)

The Loprox process patented by Bayer AG and licensed to Bertrams AG is used. The process aims primarily at improving the biodegradability of wastewaters and sludge with minimum energy consumption, but leaves the bulk of the decomposition process to a downstream biological treatment unit with its lower operating cost. Thanks to the use of a catalyst (iron plus anthraquinone), preferably under acidic conditions, the process works even at pressures lower than 35 bar and at temperatures lower than 230°C, resulting in reduced investment and operating costs. Under the Loprox conditions, a large proportion of the degradation process ends with the formation of small molecules such as acetic acid and similar substances that are easily biodegraded and the COD reduction seldom exceeds 70%. Companies or subsidiaries of the Hoffmann La Roche group operate plants designed according to Fig. 4 in Germany, Spain and Switzerland.

5.2.3. Ciba Geigy (Monthey Switzerland and Grenzach Germany)

Ciba Geigy [39] has developed its own system for the treatment of various wastes from the chemical industry, with 2 bubble column reactors in series. Each column is lined with titanium, has a diameter of about 1 m and is 25 m high. The nominal conditions are COD: 110 g/l⁻¹, temperature: 295°C, pressure: 160 bar, flow rate: 10 m⁻³ h⁻¹, i.e. 20 tons COD per day and a residence time greater than 3 h. An unsupported copper catalyst is used (separated by filtration and recycled), ammonia is stripped from the liquor and the flue gas is oxidized in a postcombustion reactor for carbon monoxide removal. A 37.5 million Euro capital cost, including the facility itself and the related building, was quoted when Monthey (Switzerland) was implemented in 1989.

5.2.4. Kruger AS (Stignaes, Denmark)

A plug flow reactor (horizontal) was started up in 1993 to treat 25 m⁻³ h⁻¹ of various aqueous wastes from the chemical industry and sludge from a nearby sewage facility. The COD design figure is 35 kg m⁻³. The reactor is merely a stainless steel pipe 3850 m long, with a diameter of 110 mm and allows a residence time close to 1 h. The nominal temperature is 260–290°C and the rated pressure is 120 bar. A specific building houses six
layers of 10 tubes. The tubes are 60 m long and spaced out 1.5 m apart.

5.3. Sludge treatment facilities

US Filter/Zimpro has constructed a number of sludge treatment and dewatering systems [40,41]. The sludge is thickened and then pumped to the Zimpro units. There, sludge is mixed with air, pressurized and brought to the system temperature of about 200°C. Under these mild conditions, only a very limited COD reduction is observed. But the process not only reduces sludge volume, it also produces a conditioned sludge that thickens and dewater to a high solids cake.

The first commercial VrTech WAO plant began operation in 1994 in Apeldoorn (The Nederlands), to treat 400 000 tons per annum of domestic sludge, i.e. 10% of the domestic sludge produced in The Nederlands. This plug flow reactor consists of three steel pipes located in a shaft with a depth of 1200 m. The raw suspension flows downward through the inner part with oxygen. At temperatures between 180 and 200°C, the oxidation of the organic ingredients starts. The oxidized liquor rises back to the surface through the outer part. A part of the heat of reaction is transferred to cooling water, which flows in the third pipe to limit the operation temperature to 280°C. The pressure is about 85 bar at the bottom of the reactor, but it simply results from the hydrostatic pressure and does not require the use of high pressure pumps. The global treatment cost is reported to be only 425 Euro per ton dry solids, i.e. 18.5 Euro m⁻³. Unfortunately, serious problems of scaling and sedimentation of solids during operation have been reported.

In 1998, the OTV Company (Vivendi group) has started a demonstration facility named ATHOS in Toulouse (France) to treat the sludge from 50 000 inhabitants. This facility uses a 2.5 m⁻³ bubble column reactor with a circulation pump in order to prevent sedimentation of the solids. The rated operating conditions are 235°C and 50 bar, with pure oxygen. The system was specially design to use a catalyst in order to remove nitrogen [29].

5.4. Derived facilities

Spent caustic liquors from ethylene manufacturing and petroleum refining are some of the nastiest wastewater’s industry must deal with. These liquors contain sodium carbonate, sodium sulfides, mercaptans, phenols and emulsified hydrocarbons. They are classified as hazardous wastes, they are odorous, they are highly colored and they do not respond to biological treatment. Wet air oxidation is one of the most effective technologies for treating these liquors and about ten plants are in operation or under construction world-wide. Inorganic sulfides are oxidized to sulfates at temperatures ranging from 165 to 200°C and pressures from 7 to 28 bar. The organically bound sulfur is converted to sulfate and the organic portion of mercaptans is converted to the corresponding carboxylic anion. The overall destruction of COD (typically 97%) is tied to the oxidation of sulfides, mercaptans and organics.

6. Wet air oxidation reactors design

World-wide, there are tens of bubble column WAO units but fewer than 5 WAO plug flow reactors. Despite the industrial experience with such bubble column reactors, very few documents [7] are available for their scientific design. In addition, many distinguished scientists are under a misapprehension concerning the running conditions of this kind of industrial plants despite being highly experienced in wet air oxidation reactions in the laboratory. On the other hand, research departments are calling for computer-aided tools intended to reduce pilot plant investigation before the final design of an industrial unit. So, an investigation program was started at the laboratory on the design of such specific bubble columns.

Data for wet air oxidation reactions are available for numerous carbon compounds [14] and the global performance of a bubble column reactor depends obviously on the kinetics of the chemical reaction. But, in addition, several other parameters (hydrodynamics, transfer, thermodynamics) must be considered. The description of the fluid dynamic flow conditions [30] is related to the liquid and gas circulation and axial dispersion properties. Literature on mass transfer coefficients in such systems is abundant [24,31,32]. The thermodynamic behavior of the gas phase can be conveniently described using the Peng and Robinson equation of state (EOS), and Henry’s law for gas solubility allows the equilibrium constants to be determined. But, wet air oxidation can be used to treat very special process wastewater and brine solutions and it appears that information is needed on the solubility of carbon dioxide in water/salt solutions, in particular the activity coefficient [33,34].

6.1. The stagewise backmixing model for reactor design

A basic diagram for a wet air oxidation unit is presented in Fig. 4. Typically, the column is 10 or 15 m high, with a diameter of about 1 m. The residence time for the liquid is about 1 h and just a very few minutes for the gas. But assuming perfect mixing for the liquid and plug flow for the gas is not satisfactory for an accurate design; the axial dispersion must be taken into account for both phases. The most efficient method, on a computational basis, is the stagewise backmixing model.
For a one-phase reactor, Mecklenburg and Hartland [30] have developed a model where the reactor is divided into ‘n’ (usually about 10–25) identical cells. Each cell is a perfectly mixed reactor connected to the previous one and to the following one, using a backflow ratio parameter ‘f’ linked with the Peclet (Bodenstein) number for axial dispersion by Eq. (6) and having a unique value all along the reactor. But, wet air oxidation reactors are two-phase reactors and the flow rate of each phase can change significantly throughout the reactor, because of the thermal effect of the reaction that vaporizes water. So the model is adapted by defining backflow ratio parameters for each phase (‘f’ for the liquid, ‘f’ for the gas) and for each cell ‘j’. These parameters are called local parameters, they depend on the local flowrates and hydrodynamics conditions, according to Eq. (7) for the liquid phase and Eq. (8) for the gas.

\[
\frac{(f+1/2)}{n} = \frac{1}{Pe} = \frac{Axial \, dispersion \, coefficient}{Velocity \times Length} \quad (6)
\]

\[
\dot{i}_j = \left( \frac{D_{l,j} \times (1 - \varepsilon_{g,j})}{H_{cell} \times U_{l,j}} \right) - 0.5 \quad \dot{i}_0 = \dot{i}_n = 0 \quad (7)
\]

\[
\xi_j = \left( \frac{D_{g,j} \times \varepsilon_{g,j}}{H_{cell} \times U_{g,j}} \right) - 0.5 \quad \xi_0 = \xi_n = 0 \quad (8)
\]

For an adiabatic cocurrent gas/liquid flow pattern, this model is presented in Fig. 5. For each cell and each phase, the material balances are established as shown in Eq. (9), for water, oxygen, carbon dioxide and any other component. The balances are also established for the chemical oxygen demand (COD) of the waste and for the total organic carbon (TOC). The chemical reactions take place only in the liquid phase and the organic compounds are assumed to be nonvolatile. In addition, a thermal balance [Eq. (10)] assuming that the two phases have the same temperature takes into account the heat of vaporization of water and the heat of the oxidation reaction, i.e. 435 kJ (mol O₂)⁻¹ [35]. A hydraulic balance, taking into account the specific weight of the phases, allows the pressure in each cell to be determined.

\[
\begin{align*}
\left(1 + \dot{i}(j-1)\right) \times L_{l(j-1)} + \dot{i}_j & \times L_{l(j+1)} \\
- \left(1 + \dot{i}_0 + \dot{i}(j-1)\right) \times U_{l(j-1)} + r_{c,j} + r_{r,j} &= 0 \quad (9)
\end{align*}
\]

\[
\begin{align*}
\left(1 + \dot{i}(j-1)\right) \times H_{l(j-1)} + \dot{i}_j & \times H_{l(j+1)} \\
- \left(1 + \dot{i}_0 + \dot{i}(j-1)\right) \times H_{l(j-1)} - AH \\
+ \left(1 + \xi(j-1)\right) \times H_{g(j-1)} + \xi_j & \times H_{g(j+1)} \\
- \left(1 + \xi_0 + \xi(j-1)\right) \times H_{g(j-1)} &= 0 \quad (10)
\end{align*}
\]

6.2. Equations, variables and problem resolution

For any cell, once the partial flows of each compound in the liquid and in the gas phase, the COD and TOC flows in the liquid, the temperature and the pressure are known, everything can be determined. The local gas composition, fugacity coefficients, enthalpy, volumetric properties, flow and superficial velocity can be determined by using the Peng and Robinson EOS with the usual mixing rules and interaction parameters [25,26]. For the liquid phase, the similar parameters are taken from specific data for pure water, assuming that small amounts of dissolved gases and organic compounds have no significant effect on the volume and thermal properties.

The local chemical reaction rates can be determined from the slope of Eq. (2) (or Fig. 3) considering the temperature, the dissolved oxygen concentration and the ‘COD/COD₀’ (or TOC/TOC₀) ratio, i.e. the local COD (or TOC) flux compared to the inlet one. The local gas hold-up, which depend mainly on the superficial velocity of the gas can be determined using a specific correlation adapted from Oyevaar and Westterterp [32]. The local mass transfer coefficients can be determined from the correlation proposed by Akita and Yoshida [24]. The local transfer rates can be determined from Eq. (4). The local axial dispersion parameters in the liquid and in the gas are taken from correlations [31,32]. The local mass transfer coefficients can be determined from the correlation proposed by Akita and Yoshida [24]. The local transfer rates can be determined from Eq. (4). The local axial dispersion parameters in the liquid and in the gas are taken from correlations [31,32]. The local mass transfer coefficients can be determined from the correlation proposed by Akita and Yoshida [24]. The local transfer rates can be determined from Eq. (4). The local axial dispersion parameters in the liquid and in the gas are taken from correlations [31,32]. The local mass transfer coefficients can be determined from the correlation proposed by Akita and Yoshida [24]. The local transfer rates can be determined from Eq. (4). The local axial dispersion parameters in the liquid and in the gas are taken from correlations [31,32]. The local mass transfer coefficients can be determined from the correlation proposed by Akita and Yoshida [24]. The local transfer rates can be determined from Eq. (4). The local axial dispersion parameters in the liquid and in the gas are taken from correlations [31,32].
equation for the partial flows, the temperatures and the pressures in all the cells. A specific subroutine was developed for each parameter (chemical, thermo-dynamical, hydrodynamical, etc.) to be determined; any subroutine can be modified independently, making it possible to change any model (EOS, mass transfer, etc.) according to the data available. A step by step procedure, first solving a simplified problem, was used to determine consistent values to be used as initial values at the resolution step.

### 6.3. Computed reactor profiles

Various profiles of the operating parameters along the column can be determined, as exemplified in Figs. 6 and 7. The main column parameters are listed in Table 1, the pH and activity coefficient γ for carbon dioxide are given values, not computed ones. The liquid flow rate corresponds to a liquid residence time of about 45 min. The kinetic laws used for the COD variation and for TOC were determined at the laboratory from batch tests (see Fig. 3) and correspond to a compound with intermediate reactivity. Temperature is the most important parameter. In an adiabatic reactor, it will increase because of the thermal effect of the chemical reaction and, on the contrary, it will decrease when water is vaporized with the gas stream. It can be seen that an activity coefficient different from 1 for carbon dioxide will have a significant effect on the profiles. But the most marked effect is related to the pH [see reaction (7) and Eq. (5)] which modifies the solubility of carbon dioxide. At high pH values, the gas flow rate is lower, thus limiting the vaporization of water. This results in a higher adiabatic temperature and, consequently, in a better COD removal efficiency.

In Fig. 8, outlet efficiencies obtained with pure oxygen and air are compared. It is obvious that nitrogen increases the global gas flow rate and then the rate of vaporization of water. This results in a lower adiabatic temperature in the reactor and thus in a much lower efficiency. This result is important as the advantages and disadvantages of pure oxygen versus air are debated among specialists. In addition, this diagram (Fig. 8) shows that for pure oxygen, the optimal oxidant ratio is the stoichiometric one; this stoichiometric ratio is actually used in most of the industrial plants.

As shown in Table 2, the operating pressure is also a very important parameter. The fugacity (partial pressure) of water vapor depends only on temperature, but the fugacity (partial pressure) of the other gases increases with the total pressure. So, for a fixed value of the

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**Table 1**

| Main characteristics used during the bubble column reactor simulation |
|--------------------------|----------|-----------------|-----------------|-----------------|-----------------|
| Waste characteristics | Oxidant | Bubble column reactor |
| COD 40 gl⁻¹ | TOC 17.1 gl⁻¹ | Flow rate 3.5 m³ h⁻¹ | O₂ content 100% | Ratio 1.25*COD | Height 10 m | Diameter 0.65 m | Cells 20 |

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**Fig. 6.** Wet air oxidation. Temperature profiles versus height of reactor. Feed: T = 260°C; Pressure = 90 bar.

**Fig. 7.** Wet air oxidation. COD reduction profiles versus height of reactor. Feed: T = 260°C; Pressure = 90 bar.

**Fig. 8.** Wet air oxidation. Dependency of the COD removal efficiency on the oxidant flowrate Feed: T = 280°C; Pressure = 110 bar.
partial flow of dry gases, the partial flow of water vapor decreases when the pressure increases, resulting in a higher adiabatic temperature and in a better removal efficiency.

In practice, the removal efficiency is governed by residence time and temperature. Thus, the operating pressure is adjusted so as the overall thermal balance of the reactor is closed: the heat losses of the system and the heat content of the liquid and gas exit streams compensate for the heat content of the feed and the heat released when the organic pollutants oxidize. In all cases, the liquid exit stream is used for partly preheating the feed (see Fig. 4). For diluted wastes (<10 g/l), as the flow rate of gas and vapor exiting is low, no energy recovery is possible and an auxiliary heating device is needed. On the contrary, for concentrated wastes (>20 g/l), net energy production is observed. Only one part of the flow rate of gas and vapor exiting is used as preheating makeup and the remaining part is available for powering turbines or as a heating source.

7. Conclusions

The WAO process presented in this paper is very efficient, as the COD reduction can easily reach from 90 to 95% for most wastes. Numerous industrial facilities, in particular several branches of the organic synthesis industry (pesticides, pharmacy, etc.) have not yet implemented methods to prevent any harm to the environment from their waste products and have serious difficulties in handling the wastes they produce, which are prohibited from land or river disposal because of their environmental impact. So, there is a need to develop solutions to detoxify these liquids. A number of plants in operation have been reviewed; they show that WAO can be a solution for a wide variety of problems occurring with wastes.

The design of a wet air oxidation reactor (bubble column) is a complex process as the global performance depends on many parameters: fluid dynamic flow conditions, liquid and gas circulation and axial dispersion properties, mass transfer coefficients, thermodynamic properties of the phases, equilibrium constants and kinetic parameters. Although we have a reasonable knowledge of most of these points, complementary studies are made necessary by the specificity of the WAO conditions (temperature, pressure, brine solutions, etc.), and by the variety of wastes that can be treated. As an example, it has been shown that temperature, pressure, inert gas flow rate and pH evolution during oxidation are important parameters to take into account during reactor design and prediction of the performance of a wet air oxidation unit. The importance of the nature of the gas (air or pure oxygen) which is continuously debated among specialists has also been clearly pointed out from a rational point of view.

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