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Wet air oxidation: a review of process technologies and aspects in reactor design

S.T. Kolaczkowski[a,*], P. Plucinski[a], F.J. Beltran[b], F.J. Rivas[a], D.B. McLurgh[a]

[a]*Department of Chemical Engineering, University of Bath, Bath, Avon BA2 7AY, UK*

[b]*Departamento de Ingenieria Quimica y Energetica, Universidad de Extremadura, 06071 Badajoz, Spain*

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Abstract

Wet air oxidation is one of the available technologies for the treatment of aqueous wastewaters. In wet air oxidation aqueous waste is oxidized in the liquid phase at high temperatures (400–573 K) and pressures (0.5–20 MPa) in the presence of an oxygen-containing gas (usually air). The advantages of the process include low operating costs and minimal air pollution discharges, while the main limitations are the high capital costs and safety implications associated with a system operating at such severe operating conditions. As a consequence, significant development in wet air oxidation technology has concentrated on methods of reducing the prohibitive capital costs. In the design of the process a balance must therefore be made between the enhancement of overall reaction rates with temperature and pressure against their effect on capital cost and operational difficulties such as corrosion and scaling of equipment. In this paper the wet air oxidation process is introduced and a number of commercial and emerging technologies presented. These technologies employ a variety of methods to ameliorate the limitations of the technology whilst maintaining acceptable overall reaction rates. These include methods to improve mass transfer as well as the use of both homogeneous and heterogeneous catalysts to enhance reaction rate. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Wet air oxidation; Process technology; Kinetics; Mass transfer; Catalysts

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1. Introduction

The generation of wastewater from both industrial and domestic use results in a wide variety of effluents requiring treatment. To treat these wastes a number of disposal techniques are available, such as chemical treatment, physical treatment, biological treatment, incineration, etc., which can be used in either isolation or combination. In selecting the most suitable disposal route for a specific effluent, both the feasibility of treatment and process economics needs to be considered. Each available technology will consequently have its own application range depending on the quantity of wastewater produced and the composition and concentration of pollutants it contains. One available option is wet air oxidation which is suitable for processing oxidizable organic or inorganic waste which is either soluble or suspended in an aqueous waste stream [1,2]. Wet air oxidation is a destructive wastewater technology based on the oxidation of pollutants at high temperature and high pressure in the liquid phase. In the system molecular oxygen dissolved in the wastewater reacts with the organic and inorganic pollutants. The oxidizing power of the system is based on the high solubility of oxygen at these severe conditions and the high temperature that increases the reaction rates and production of free radicals. In this system, aqueous waste is oxidized in the liquid phase at high temperatures (398–573 K) and pressures (0.5–20 MPa) in the presence of an oxygen-containing gas (usually air). The organic material is not normally completely destroyed, but converted via a free radical mechanism to intermediate end products with a significant reduction in toxicity and chemical oxygen demand [3]. In addition, wet air oxidation usually results in the formation of an off-gas and a liquid effluent requiring further treatment.

In recent reviews covering wet air oxidation the main focus has been to summarize published kinetic data and discuss the suitability of the process for treating specific effluent streams. The purpose of this paper is to identify the principle issues in the design of wet air oxidation process and explore their impact on system design. The paper also includes a description of process technology, though this section is not exhaustive and does not represent all enter-

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*Corresponding author.

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prises working in this field. The wet air oxidation reactor contains a heterogeneous system, which necessitates consideration to be given to mass transfer and the kinetics and mechanism of the chemical reaction. An understanding of how these steps are influenced by reactor configuration and selected operating conditions is therefore the key to the optimization of the process. This review highlights the importance of such factors and illustrates their influence on not only overall reaction rates, but also on reaction selectivity and reaction mechanism. It follows that a better understanding of system performance would be attained if the mechanisms behind the processes occurring in the reactor could be elucidated and the complex nature of their interdependence identified.

Although the principles behind wet air oxidation are well established, with the first commercial units for the treatment of sulphite liquors dating back to the late 1950s [1,4], its widespread use has been restricted by the high capital cost of the process. This high initial capital investment coupled with safety concerns of combined high pressure and high temperature operation can be a barrier to the proliferation of the technology. To rectify these limitations wet air oxidation research has primarily concentrated on ways of reducing the prohibitive capital costs of the process, whilst still maintaining acceptable mass transfer and reaction kinetics. To achieve this goal techniques for enhancing reaction kinetics and oxygen mass transfer have been investigated. In the area of reactor design this has led to investigations into design factors such as degree of reactant mixing (i.e. mixed or plug flow), reactant contacting, hydrodynamic flow regime and catalyst incorporation. In the design of the process as a whole, further consideration has been given to heat recovery, scaling problems, effective utilization of space and safe operation when dealing with the pressures, temperatures and hazardous waste associated with the system. This paper begins with an overview of wet air oxidation which highlights its advantages, limitations and general application range. This is followed by specific sections on non-catalytic systems and both homogeneous and heterogeneous catalytic systems. In these sections the influence of mass transfer and reaction kinetics on the overall reaction rate are discussed. A review of process technology is also provided, which illustrates how the reactor engineering issues have been addressed in order to ameliorate the limitations of the process.

2. Background

Wet air oxidation is applicable to the treatment of the majority of organic compounds found in wastewaters [2]. In the process, the organic waste is oxidized to carbon dioxide, water and intermediate oxidation products which are predominantly low molecular weight organic compounds including carboxylic acids, acetaldehydes and alcohols. Although the degree of oxidation depends upon the process conditions, retention time and feed composition, in most operations low molecular weight compounds will accumulate as they tend to be refractory to further oxidation [2]. An advantage of wet air oxidation is that the majority of contaminants remain in the aqueous phase. Elemental sulphur is converted to sulphate, halogens to halides and phosphorous to phosphate, they all, therefore, remain in the aqueous phase forming inorganic salts and acids. The production of acids results in a decrease in the pH of the aqueous phase [2]. The wet air oxidation of nitrogen-containing compounds can produce various species including ammonia, nitrate, nitrogen gas and nitrous oxide depending on the pollutant and reaction conditions. For most cyanide and amine-containing compounds, ammonia is produced as essentially a stable end-product. Ammonia can be removed in the process by the use of a suitable catalyst [1,5].

The final aqueous liquid effluent will contain a considerable quantity of low molecular weight organics, ammonia, inorganic acids and inorganic salts. This effluent is usually biologically treated during which the majority of organics and ammonia are removed. If the liquid contains significant quantities of suspended solids, due to a build-up of metal oxides and insoluble sulphate and phosphate salts, these must be dewatered and landfilled. The off-gas contains principally nitrogen, carbon dioxide, steam and oxygen. It may also contain ammonia, carbon monoxide and a proportion of low molecular weight compounds which due to their volatility are found in both waste streams. The off-gas can be treated by adsorption, scrubbing or incineration techniques [3].

The majority of installed wet air oxidation units are used for the treatment of sewage sludge. Sewage sludge treatment at mild conditions (<473 K) leads to modest reductions in the chemical oxygen demand (COD) of between 5% and 15%, but significant improvement in the sterility, filterability and dewatering properties of the sludge. Treatment at more intensive operating conditions is used to economically reduce the volume of solids remaining for landfill disposal [6,7]. Wet air oxidation has successfully been used to treat a range of industrial wastewaters including pulp and paper mill black liquor wastes, spent caustic scrubbing liquids and cyanide/nitrile bearing wastes such as acrylonitrile plant wastewater [1,3,8]. In addition, wet air oxidation has been used to regenerate spent activated carbon with simultaneous destruction of the adsorbed pollutants and small carbon loss (1–5%) [1]. For a full review of the suitability of wet air oxidation to treat specific compounds and industrial wastes see the review of Mishra et al. [1].

The economics of wet air oxidation make it a practical disposal option for wastes that are both too dilute to incinerate and too concentrated for biological treatment [9]. The chemical oxygen demand of a waste suitable for wet air oxidation is typically between 20 and 200 g l^{-1}, though direct economic comparisons with alternative treatment processes will depend on the throughput and type of waste to be treated [3,6]. In addition, the process is applicable to the detoxification of hazardous wastes, detoxification of wastes toxic to micro-organisms in biological processes and as a means of converting non-biodegradable components into ones readily biodegradable.

In general, when compared with incineration the capital costs for wet air oxidation are higher, but the operating costs are lower [10]. The capital costs for a wet air oxidation system depend on the flowrate, wastewater composition, extent of oxidation and the required operating conditions [6].

The capital costs for wet air oxidation depend on the materials of construction selected for the main process items, which must be suitable for the severe operating conditions (high temperature and high pressure) and the corrosion problems resulting from the waste. Although industrial experience in the treatment of domestic sewage sludge has shown austenitic stainless steel (American designation AISI 316) to be resistant to chloride ion concentrations of up to 300 mg l^{-1} at temperatures of 450 K to 560 K, with wastes containing higher chloride ion concentrations, stress corrosion cracking and pitting have been experienced [11]. This leads to the use of alternative materials such as titanium, inconel and hastelloy, all of which are more expensive, but have the advantage of an increased resistance to chloride ions [11–13]. For very high chloride ion concentrations (>1000 mg l^{-1}) titanium has the best corrosion resistance [11,12]. However, as titanium is capable of spontaneous combustion in the presence of oxygen and water at elevated pressures, it is unsuitable for operation in pure oxygen or oxygen enriched systems [14,15]. The high capital cost of the main process items may render wet air oxidation technology uneconomic. A reduction in the severity of the operating conditions would allow savings in the capital cost to be made, due to thinner equipment wall thicknesses, diminished corrosion problems and smaller design duties for the compressor, feed pump and heat exchangers.

There are a number of process advantages, including reduced capital costs, in using oxygen instead of air as the source of oxidant. Prasad and Materi [16] compared air and oxygen based non-catalytic wet air oxidation systems for two levels of organic waste concentration (COD of 4000 and 70 000 mg l^{-1} respectively). They found that oxygen-based systems showed lower capital costs and greater profitability than air based systems. However, the use of pure oxygen raises significant safety implications for system design.

The lower operating costs of wet air oxidation compared with incineration results from the lower energy requirements of the process. In normal operation the only heat input to the system is the difference in enthalpy between the influent and effluent streams, with for most wastes the recovered exothermic heat of oxidation being sufficient to sustain autothermal operation. In addition, for high COD wastes there is the possibility of energy recovery in the form of heat, mechanical or electrical energy [17,18]. By comparison incineration needs to provide enough energy to vaporize the water and heat the reactants to the higher temperatures required for combustion, this can lead to substantial energy demands for dilute waste streams [3,8]. The principal operating costs for wet air oxidation are labour costs and electrical power for air compression and high pressure liquid pumping [2,10].

Depending on the composition of the waste feed, the build-up of scale on the walls of equipment and piping can be a problem as it leads to a decrease in the efficiency of the heat exchangers and an increase in system pressure drop. The scale is predominantly hard anhydrite scale, comprised of calcium sulphate Al-phosphates, which tend to deposit heavily in the hottest sections of the system. This is due to the decrease in solubility with increasing temperature of calcium sulphate and other scale materials at wet air oxidation conditions [19,20]. If scaling of equipment surfaces is a serious problem then it has to be removed periodically by acid washing. Alternatively, in an attempt to prevent scale formation, reagents such as Na_2HPO_4 can be added to the waste stream to bind the Ca^{2+}, Al^{3+} and Mg^{2+} ions [1]. In addition to inorganic scale, fouling problems can be experienced due to the formation of polymeric reaction intermediates which can adhere to equipment surfaces. Operational experience in treating steam cracker spent caustic in a low pressure wet air oxidation unit at Grangemouth, Scotland, has shown problems due to fouling of the sparger by insoluble inorganic carbonates and polymerized organic material. This problem was overcome by using a 100-mesh screen in a simplified sparger arrangement and by supplying a small quantity of pre-heat steam via the air supply to ensure that the nozzle remained hot enough to prevent solidification of organic polymer [21].

3. Non-catalytic operation

3.1. Kinetics and mass transfer

The required reaction time for waste treatment, and therefore reactor volume, depends upon the reactor type, overall reaction rate and specified degree of oxidation. An increase in the overall reaction rate is therefore advantageous as it reduces the required reaction time allowing a decrease in reactor volume. In non-catalytic wet air oxidation the overall reaction rate is governed by two steps, firstly the mass transfer of oxygen from the gas to liquid phase and secondly the reaction occurring in the liquid phase. In selecting the required operating conditions, a balance is made between the enhancement of mass transfer and reaction rate with increased operating temperature and pressure, against the consequent rise in capital costs and safety implications. The mass transfer of oxygen across the gas–liquid phase boundary can be considered in terms of the combination of resistances in the gas and liquid phases, where diffusional resistance is assumed to be concentrated in a thin film either side of the interface. For slightly soluble gases such as oxygen in water, the transport of oxygen in the gas phase is much more rapid than that in the liquid. The gas phase resistance can therefore be ignored with the liquid film resistance controlling mass transfer [22–24]. For gas–liquid reactions the location of the kinetic regime depends on the relative rates of reaction and mass transfer, typically residing in the liquid film for rapid reactions and in the bulk of the liquid for slow reactions [23]. For wet air oxidation systems the slow oxidation reaction takes place essentially in the bulk of the liquid [22,24]. For such reactions a reactor is required that provides a large liquid hold-up with sufficient interfacial area to avoid mass transfer limitations. Wet air oxidation has been completed in bubble columns, mechanically agitated reactors, jet reactors, loop reactors, monolith and trickle bed reactors [25].

Detailed kinetic studies for the treatment of real wastewaters are not generally available, thus reactor design is based on empirical methods. For non-catalytic wet air oxidation the reaction kinetics are usually simplified to a global rate expression based on the removal of either a specific compound or a general parameter (e.g. COD, TOC, BOD), with the chemistry of the mechanism being described by simple reaction schemes. The oxidation reaction is exothermic and follows Arrhenius dependence, therefore, the reaction rate increases with increasing temperature. For a non-catalytic reaction the reaction rate can be described as follows:

$$r_\mathrm{r} = A \times \mathrm{e}^{-\left(\frac{E}{RT}\right)} \times (C_\mathrm{P})^m \times (C_{\mathrm{O}_2,\mathrm{L}})^n \tag{1}$$

where r_r is the reaction rate, A is the pre-exponential factor, E is the activation energy, R is the gas constant, T is the reaction temperature, C_P is the pollutant concentration in the bulk liquid, $C_{\mathrm{O}_2,\mathrm{L}}$ is the oxygen concentration in the bulk liquid and m, n are the orders of the reaction. Reported values in the research literature show the kinetics to be usually first order with respect to the pollutant concentration and between zero and one for oxygen [1].

An increase in temperature also increases the equilibrium water vapour pressure which rises rapidly in the region typical for wet air oxidation operation as highlighted in Fig. 1. It follows that an increase in operating temperature necessitates an increase in total operating pressure in order to maintain the oxygen partial pressure. As the reaction is exothermic it releases energy which raises the temperature of the liquid and gas streams leading to further water evaporation. In this way water serves as a heat sink, preventing the reaction from running away. Water is also an excellent heat transfer medium. As the oxidation reaction occurs in the aqueous phase, however, it is essential that an adequate proportion of water is maintained in the liquid state. For a fixed gas flowrate the quantity of water vaporized at a given reactor temperature, and consequently the aggregate latent heat of vaporization, decreases with increasing operating pressure. It follows that the operating pressure can be used to control the proportion of water in the liquid state [7].

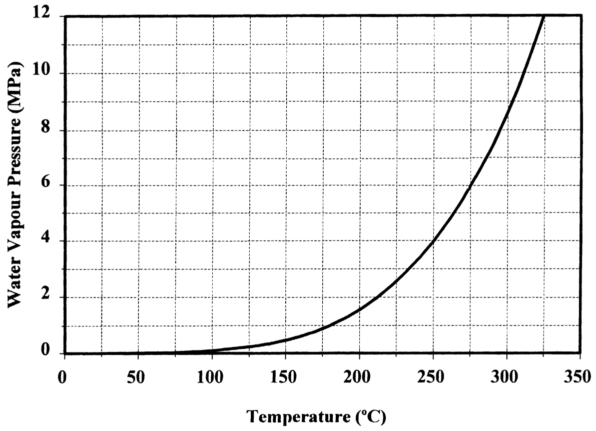

Fig. 1. Variation of water vapour pressure with temperature (based on data in Rogers and Mayhew [105]).

The important mechanisms for wet air oxidation are not well understood. However, it has been proposed that wet air oxidation involves a chain reaction mechanism in which oxygen and hydroxyl, hydroperoxyl and organic hydroperoxy free radicals actively participate [3]. A pattern of pollutant removal typical of free radical reactions has been observed in batch systems, with the presence of an initial induction period where the oxidation rate is slow, followed by a steady state rapid reaction step. The length of the induction step represents the time taken to establish a minimum free radical concentration and decreases with both increased temperature and oxygen partial pressure. As the reaction progresses it becomes increasingly complex as the oxygen and radicals formed in the process also react with oxidation intermediates. These parallel reactions with the oxidation intermediates lead to the consumption and generation of additional radicals, including new organic radicals of differing activity. It follows that due to the free radical nature of the process, global reaction rates can change depending on the mechanism of pollutant destruction. As the disappearance of a compound can be attributed to interaction with a number of different species, depending on reaction conditions, the relative contribution of each of these elemental reactions can change, which will affect overall kinetics.

Given the involvement of radicals in the process, a number of aspects affecting the initiation, propagation or termination of free radicals in the reactor, should be taken into account at the design stage. These aspects can have a considerable influence on the selectivity, applicability and rate of the overall reaction. For example, the addition of a free radical promoter such as hydrogen peroxide has been reported to significantly increase the efficiency of the process [26], while the use of an appropriate catalyst can lead to a significant enhancement in radical initiation steps [27]. In addition, the geometry and nature of the reactor can be an important factor in heterogeneous free radical termination and initiation [28], with the kinetic constants involving the wall of the reactor (e.g. radical termination, hydrogen peroxide decomposition) being specific to each reactor. They should only coincide for reactors made of the same material and with the same ratio of surface to volume. This was illustrated at the laboratory scale where the observed rate of phenol removal was faster in a glass lined vessel compared with that in a stainless steel vessel [29]. This confirms the results mentioned by Emanuel et al. [28] for the liquid phase oxidation of butane, in which it was established that termination of oxidation promoting organic radicals is increased to a considerable extent by metallic surfaces. In a large full scale system, which will have a smaller surface area to volume ratio, the influence of these wall effects will be much less pronounced. However, this illustrates the difficulties in both the scale-up of wet air oxidation systems from laboratory to full size and in the comparison of results from different reactor set-ups. Finally, the free radical nature of the process can lead to synergistic effects when treating a mixture of compounds (the case for most wastewaters), where the reaction rate for refractory compounds is enhanced by the presence of a more easily oxidizable compound. This is illustrated by experimental results for mixtures of diethanolamine (DEA) and morpholine, which were found to oxidize faster than that expected from individual oxidation rates. It was speculated that in the mixed solution, the free radicals generated by the oxidation of DEA (individually DEA reacts faster than morpholine) attack morpholine increasing its rate of oxidation [30].

The significance of operating conditions on the selectivity of reactions can be further illustrated by considering the role of non-oxidation reactions in the wet air oxidation system, such as thermal hydrolysis, isomerization, etc. For example, in a wet air oxidation environment maleic acid degradation can occur via a parallel pathway involving its isomerization to fumaric acid. This reaction occurs both in the presence and absence of oxygen, with its contribution to maleic acid removal being dependent on the operating conditions [31]. In addition, investigations into the oxidation of phenol have illustrated its involvement in parallel reactions which result in the formation of tars. The appearance of tars is apparently dependent on the ratio of phenol to oxygen in the aqueous phase. Pruden and Le [22] found that black viscous tars were produced in experiments in a continuous system with high phenol concentrations (3.4% phenol) and long residence times. They concluded that these were probably partially oxidized polymers. Vortsman and Tels [32] also found an increase in the amount of suspended matter in the exit stream if phenol concentration was high, while at high phenol concentrations, the formation of polymeric material was observed by Baillod and Faith [9].

Assuming that the gas side mass transfer resistance is negligible, the mass transfer of oxygen from the gas to the liquid phase is enhanced by an increase in either the overall volumetric gas–liquid mass transfer coefficient ($k_L a$) or the oxygen solubility in the liquid phase, in accordance with

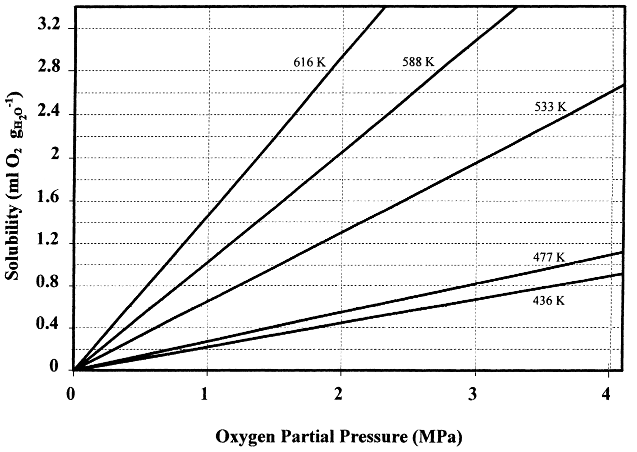

Fig. 2. Solubility of oxygen in water (adapted from Pray et al. [106]).

$$r_m = k_L \times a \times (C^*_{O_2} - C_{O_2,L}) \tag{2}$$

where r_m is the oxygen mass transfer rate, k_L is the liquid side mass transfer coefficient, a is the gas–liquid interfacial area and $C^*_{O_2}$ is the saturated oxygen concentration.

The saturated oxygen concentration, $C^*_{O_2}$, rises significantly with both increased temperature and oxygen partial pressure in the operating range typical for wet air oxidation (see Fig. 2). The increased oxygen solubility in water at these conditions provides a strong driving force for mass transfer. The overall mass transfer coefficient ($k_L a$) is influenced by operating parameters such as reactor geometry, gas flowrate, temperature, pressure and liquid properties, and their effect on the system characteristics such as gas hold-up, flow regime, bubble diameter, interfacial area and the mass transfer coefficient [33,34]. The specific gas–liquid interfacial area a, is defined for bubble systems as

$$a = \frac{6\varepsilon}{d_{vs}} \tag{3}$$

where ε is the gas hold-up and d_{vs} is the mean bubble diameter [33]. Gas hold-up is the ratio of gas volume to total fluid volume and determines the quantity of gas in the reactor and therefore the extent of interfacial area for mass transfer [34].

$$\varepsilon = \frac{V_G}{V_G + V_L} \tag{4}$$

where V_G is the volume of gas in the column and V_L is the quantity of liquid in the column. It follows that to optimize the mass transfer of oxygen to the liquid phase the effect of operating parameters on bubble diameter, gas hold-up and liquid mass transfer coefficient need to be investigated. Over the past 15 years laboratory studies have been completed to ascertain the influence of high pressure on bubble hydrodynamics.

The smaller the size of bubbles in the reactor the larger will be the area available for mass transfer. The bubble size achieved in the reactor depends on sparger type, flow regime, media properties and operating conditions. Although the size of bubbles leaving the sparger are smaller for porous spargers than for orifices and perforated discs, the size at the sparger may not be maintained throughout the reactor due to a combination of bubble coalescence or break-up [35,36]. The advantage of a porous sparger can, therefore, be diminished as the bubbles pass through the reactor due to bubble coalescence. This is especially the case in large columns [37]. Investigations into bubble behaviour in bubble columns have found that, for a constant superficial gas velocity, an increase in column pressure leads to a decrease in bubble diameter and a narrowing in the bubble size distribution [38–41]. At laboratory scale, studies for an air–water system in a bubble column found that at atmospheric pressure the average bubble size depended on distributor type, with porous distributors delivering the smallest bubbles. However, this effect gradually diminished as the pressure was raised from 0.1 to 15 MPa. The increase in pressure resulted in a decrease in the average bubble diameter for perforated plate distributors, while that for porous distributors did not alter appreciably [38]. For a perforated plate with 1 mm holes the influence of pressure on the average bubble diameter has been described by the correlation proposed by Idogawa et al. [42]

$$d_{\mathrm{vs}} = 3.91\times10^{-3}\times\rho_{\mathrm{G}}^{-0.07}\times\left(\frac{\sigma_{\mathrm{L}}}{72}\right)^{0.22\times\exp(-P)} \qquad (5)$$

where ρ_{G} is the gas density and σ_{L} is the surface tension.

The experimental ranges for the parameters given in Eq. (5) are as follows, where ν_{G} is the superficial gas velocity and P is the system pressure

$$0.5\times10^{-2}\leq\nu_{\mathrm{G}}\leq5\times10^{-2}\,\mathrm{m\,s^{-1}}$$

$$0.084\leq\rho_{\mathrm{G}}\leq120.8\,\mathrm{kg\,m^{-3}}$$

$$22.6\leq\sigma_{\mathrm{L}}\leq72.1\,\mathrm{mN\,m^{-1}}$$

$$0.1\leq P\leq5\mathrm{MPa}$$

Gas hold-up increases with increasing superficial gas velocity. An increase in gas flowrate therefore enhances mass transfer. However, capital and operating costs will also increase due to the increased capacity of the gas compressor. The dependence of gas hold-up on superficial velocity has also been described by a correlation proposed by Idogawa et al. [42]:

$$\frac{\varepsilon}{1-\varepsilon} = 1.48\times10^{-3}\times\nu_{\mathrm{G}}^{0.8}\times\rho_{\mathrm{G}}^{0.17}\times\left(\frac{\sigma_{\mathrm{L}}}{72}\right)^{-0.22\times\exp(-P)} \qquad (6)$$

with the units and operational range as for Eq. (5).

From Eqs. (5) and (6) it can be seen that for an air–water system, at a constant superficial gas velocity of 0.01 m s^{-1}, the gas hold-up increases by a factor of 2.7 and the average bubble diameter decreases by a factor of 0.6, when the pressure is increased from 0.1 to 5 MPa. This results in an increase in the interfacial area by a factor of 4.5 [43]. An increase in system pressure has also been found to shift the transition point from the bubble to the turbulent regime to higher gas velocities and thus to larger gas hold-ups [37,44].

The gas hold-up is also dependent on the rise velocity of the bubble which depends on bubble diameter and liquid properties. Bubble diameter is the most significant parameter with rise velocity decreasing with decreasing diameter [35]. Investigations at high pressure have shown that gas hold-up increases with increasing pressure [38–41]. Idogawa et al. [38] found that at atmospheric pressure average gas hold-up varied considerably depending on gas distributor type, being highest for a porous plate. These differences decreased with increasing pressure, becoming indistinguishable for most distributors above 10 MPa (see effect of pressure on bubble diameter).

The liquid side mass transfer coefficient k_{L} is dependent on bubble size and liquid properties. For small bubbles of diameter less than 0.002 m, k_{L} decreases significantly with decreasing bubble size [34]. Oyevaar et al. [45] found that the liquid phase mass transfer coefficient was not affected by an increase of gas pressure ($0.1\leq P\leq6$ MPa). Their experimental values of mass transfer coefficients agreed well with the relationship of Calderbank and Moo-Young [33]

$d_{\mathrm{b}} > 2.5$ mm:

$$k_{\mathrm{L}} = 0.0042\left(\frac{(\rho_{\mathrm{L}}-\rho_{\mathrm{G}})\mu_{\mathrm{L}}g}{\rho_{\mathrm{L}}^2}\right)^{1/3}\left(\frac{\mu_{\mathrm{L}}}{\rho_{\mathrm{L}}D}\right)^{-1/2},$$
$$1000\leq\rho_{\mathrm{L}}\leq1178\,\mathrm{kg\,m^{-3}},\ 0.0006\leq\mu_{\mathrm{L}}\leq0.0897\,\mathrm{Pa\,s},$$
$$1000\leq\rho_{\mathrm{L}}-\rho_{\mathrm{G}}\leq1178\,\mathrm{kg\,m^{-3}} \qquad (7)$$

$d_{\mathrm{b}} < 2.5$ mm:

$$k_{\mathrm{L}} = 0.0031\left(\frac{(\rho_{\mathrm{L}}-\rho_{\mathrm{G}})\mu_{\mathrm{L}}g}{\rho_{\mathrm{L}}^2}\right)^{1/3}\left(\frac{\mu_{\mathrm{L}}}{\rho_{\mathrm{L}}D}\right)^{-1/3},$$
$$698\leq\rho_{\mathrm{L}}\leq1160\,\mathrm{kg\,m^{-3}},\ 8.4\times10^{-4}\leq\mu_{\mathrm{L}}\leq0.001\,\mathrm{Pa\,s},$$
$$174\leq\rho_{\mathrm{L}}-\rho_{\mathrm{G}}\leq1160\,\mathrm{kg\,m^{-3}} \qquad (8)$$

The overall mass transfer coefficient ($k_{\mathrm{L}}a$) is therefore dependent on liquid properties, gas flowrate and bubble diameter. Bubble diameter has conflicting effects, with a decrease in diameter increasing gas hold-up and interfacial area, but decreasing k_{L} for small bubbles. In general small bubbles are desirable with the benefits in interfacial area more than offsetting the decrease in liquid side mass transfer coefficient [33]. It should be noted that the composition and properties of the liquid also have a significant influence on water and mass transfer properties such as saturated vapour pressure and the mass transfer coefficient. For example, Gurol and Nekouinaini [46] found that the presence of 0.4 mM of acetic acid and phenol in water increased the overall mass transfer coefficient by over 300% and 200% respectively for experiments completed at atmospheric temperature and pressure.

In bubble columns the degree of liquid backmixing can be extensive. Although this provides temperature uniformity, it also leads to non-uniform residence times in the reactor which can influence reactor selectivity and yield [47]. The degree of backmixing increases with both increasing gas flowrate and reactor diameter. However, for the bubble flow regime the extent of axial mixing is suppressed (more uniform bubble size), with mixing increasing significantly as transition is made to the turbulent regime.

Furthermore, the formation of carbon dioxide and consumption of oxygen can influence the oxygen partial pressure with both time and position in some reactors, resulting in a decrease in the driving force for mass transfer. For instance, although total pressure may remain unchanged as the reactants pass through a continuous reactor, the proportion of oxygen in the gas phase will steadily decrease due to oxygen consumption and dilution by either the formation of gases (e.g. carbon dioxide) or an increase in water vapour as a result of the exothermic nature of the process. This can have a significant effect on reaction rate. For example, in a deep shaft wet air oxidation process (discussed further in the section on non-catalytic technology) the use of three reactors in series gave a greater reduction in chemical oxygen demand (COD) than a single reactor having the same retention time. This was apparently due to the removal of carbon dioxide in-between reactors [48].

It should be remembered that if wet air oxidation processes are to operate at significantly lower temperatures and pressures, realizing the associated advantages in process safety and economics, there will consequently be a significant decrease in saturated oxygen concentration (see Fig. 2). This will result in a decrease in both the maximum concentration of oxygen in the liquid phase and the driving force for mass transfer. In this case design factors affecting the overall mass transfer coefficient will need to be considered if the oxygen concentration in the bulk liquid is to be maximized. Further, in the selection of oxygen partial pressure and temperature, consideration will need to be given to the concentration of pollutants in the liquid and the consequent oxygen concentration required in the liquid phase. When treating concentrated wastes the attainment of an acceptable ratio of pollutant to oxygen in the liquid phase may require the selection of a recirculating reactor (containing some form of liquid recycle) or alternatively feed dilution.

To summarize, an increase in temperature increases not only the reaction rate and oxygen solubility but also the water vapour pressure. The reaction is exothermic with the released energy raising reactor temperature and vapourizing water. Increasing pressure increases oxygen solubility and reduces the equilibrium quantity of water vaporized, which reduces the total latent heat of vaporization. Pressure can, therefore, be used to control the proportion of water in the liquid state and maintain fluid temperature. In the design of wet air oxidation reactors the overall oxidation rate is dependent on both mass transfer and reaction kinetics. The rate controlling step depends on a number of different factors including reactor type, operating conditions and pollutant. In addition, the rate controlling step may change with time and position within the reactor.

Giving consideration to some of the issues discussed above, the next section reviews various non-catalytic wet air oxidation technologies and the methods that have been employed to improve the process.

4. Non-catalytic technology

4.1. Zimpro process

The Zimpro process is by far the most widely commercialized wet air oxidation system on the market. Originally developed in the 1930s by Mr. F.J. Zimmermann, it was not until the 1940s that its application for more complete destruction was discovered with process development at laboratory and pilot plant scale culminating in the installation of the first commercial units in the late 1950s [4]. By 1996 approximately 200 commercial units had been installed, over half for sludge treatment, around 20 for activated carbon regeneration and some 50 systems to treat industrial wastewater [49,50].

The Zimpro process reactor is a co-current bubble column, with or without internal baffling depending on the desired mixing conditions [3]. The use of a bubble column reactor can lead to axial or longitudinal mixing of the waste and consequently a non-uniform residence time distribution. This limitation means that the required waste destruction efficiency may be difficult to obtain, with further downstream processing being required [51]. However, Zimpro do not view wet air oxidation as an economical complete destruction technology, but as a detoxification step prior to final polishing [2]. In addition, mixing will transport radicals towards the front end of the reactor which will prevent the occurrence of an induction period [32].

The reactor operates at temperatures of between 420 K and 598 K and pressures of 2.0 to 12.0 MPa depending on the degree of oxidation required and the waste being processed [52]. The temperature range of 420 K to 473 K is used for sludge dewatering, 473 K to 523 K for spent activated carbon regeneration and conversion of refractory wastes to biodegradable substances, while higher temperatures are used to attain more complete destruction [3]. Typically the reactor is designed for a retention time of 60 min [3] though this can range from 20 min to 4 h depending on the application [51].

A typical schematic of the Zimpro process is detailed in Fig. 3. In the system air is injected into the waste upstream of the feed exchanger in order to improve heat transfer [51]. This mixture is then heated to the required feed temperature by heat exchange with the hot effluent. The recovery of heat in this way leads to autothermal operation for most wastes. The waste is oxidized as it progresses up

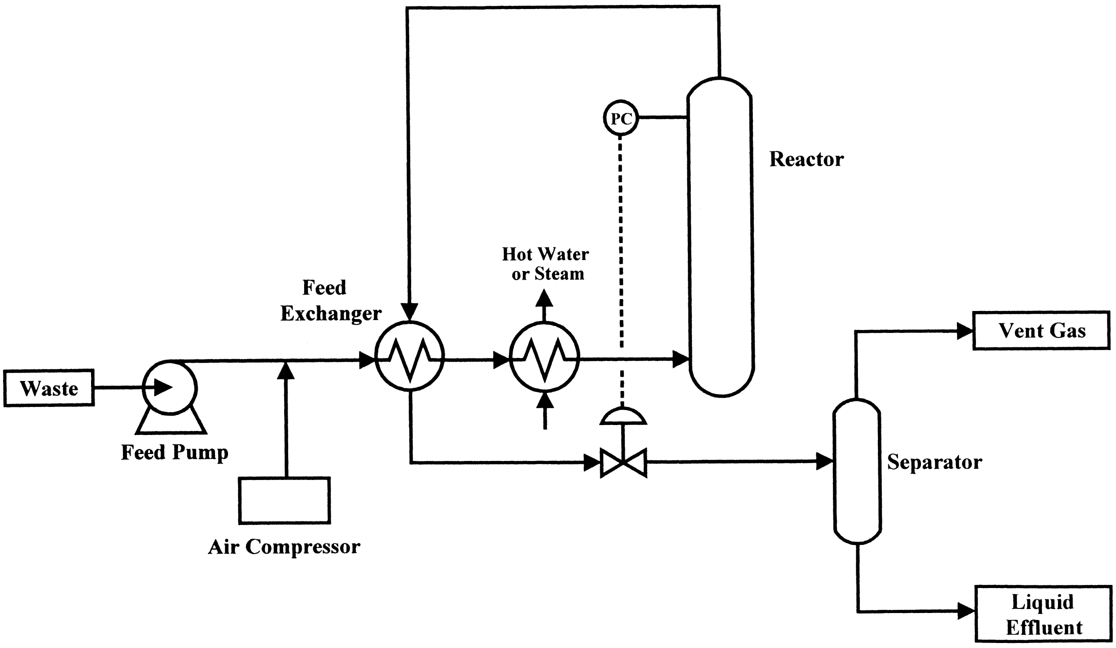

Fig. 3. Zimpro process schematic (adapted from Copa and Gitchel [3]).

the reactor with the released heat of oxidation further increasing the temperature of the mixture. The hot effluent is cooled in the feed exchanger before pressure let-down across the control valve. The effluent stream is then separated into vapour and liquid phases before further downstream processing [53].

4.2. Wetox process

The main feature of this process is the 'Wetox' reactor which is a horizontal autoclave, comprising four to six compartments that essentially act as a series of continuous stirred tank reactors [3]. This reactor arrangement moves closer to plug flow behaviour as the number of reactors in series is increased [23]. Developed in the 1970s by Fassell and Bridges [54,55] the key to its design is the agitation and addition of oxygen in each compartment, which is claimed to improve the transfer of oxygen to the waste [56]. The design achieves this improvement by

(a) Increasing the effective area for mass transfer by decreasing the air/oxygen bubble size.
(b) Increasing the contact time for mass transfer by creating eddy currents which suppress the escape of air.
(c) Reducing resistance to mass transfer by creating turbulent shear which reduces the thickness of the stagnant film around the bubble [57].

The Wetox reactor typically operates at temperatures between 480 K and 520 K, with the temperature successively increasing in each compartment due to the heat of oxidation of the waste [57]. The operating pressure is about 4.0 MPa [56] with typical liquid retention times of 30 to 60 minutes [51]. The reactor can be operated to achieve complete destruction or as a polishing step prior to biological treatment [56].

A typical schematic of the Wetox process is detailed in Fig. 4. The compartmental arrangement with the vapour and liquid phases being removed separately from the reactor is claimed to increase effective liquid retention time, reduce liquid effluent volume and improve heat exchanger efficiency [57]. The liquid effluent is used to heat the in-coming waste, with for concentrated wastes autothermal operation being obtained by heat recovery from the liquid phase alone. The vapour phase is cooled with heat recovered in the form of low pressure steam or hot water [56].

A disadvantage of the use of mechanical agitators in the Wetox reactor is their energy consumption, maintenance requirements and need for high pressure seals at the shaft entrance port. In addition, as the reactor is horizontal a larger area of land is required than that for a vertical reactor [51].

4.3. Vertech process

The VerTech process uses a vertical sub-surface reactor, comprising two concentric tubes (downcomer and upcomer), which descend in a shaft to a depth of 1200 to 1500 m. Developed in the 1970s, early pilot work was followed by a demonstration plant at Longmont, Colorado which became operational in 1983 processing sludge from the adjacent sewage treatment plant. In September 1983, Bow Valley Resource Services exercised its option to purchase the patent and rights to the technology and formed a wholly owned subsidiary, VerTech Treatment Systems, to develop and commercialize the process [58].

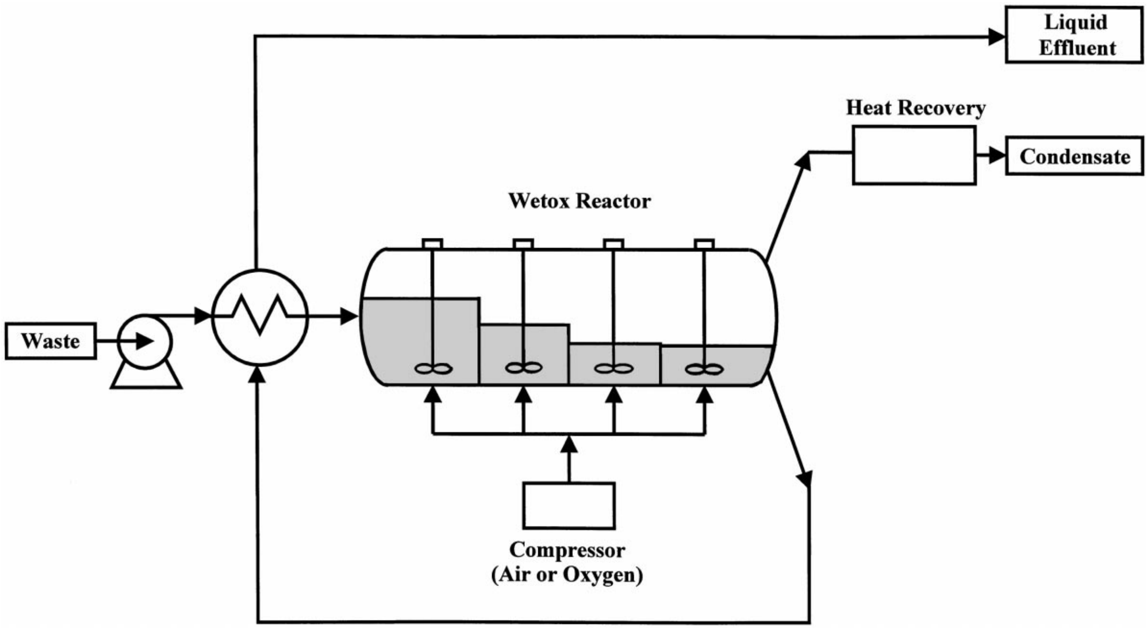

Fig. 4. Wetox process schematic (adapted from Cadotte and Laughlin [56]).

An advantage of a deep-shaft reactor is the use of gravity to develop the high pressures required for wet air oxidation. As the waste passes down the reactor the pressure rises due to the increase in liquid/gas static head above it [58]. This leads to a significant reduction in power requirements compared with conventional wet air oxidation as the feed pumps are only sized to overcome frictional pressure drop losses [59]. The reactor is designed for turbulent flow of waste and oxygen in the downcomer giving excellent mass transfer between the gas and liquid phases and efficient heat transfer. The waste and oxygen pass through the reactor in a plug flow regime taking advantage of superior reaction kinetics [58]. However, although this configuration attains a higher conversion per unit volume (plug flow), there is a trade off in that increasing the fluid velocity requires a longer reactor for a given residence time.

The pressure in the reactor depends on the depth of the shaft and fluid density, which varies with temperature and gas content [58]. Typically the depth of the shaft is between 1200 and 1500 m leading to a pressure at the bottom of the reactor of approximately 8.5 to 11 MPa. The reactor heat exchange system is used to control the temperature at the bottom of the reactor at 550 K [59]. The residence time within the reactor is approximately 1 h, with about 30 to 40 min of this time spent in the reaction zone [58].

A schematic of the VerTech reaction vessel is shown in Fig. 5. The reactor comprises two concentric tubes, the inner tube called the downcomer and the outer tube called the upcomer, these are enveloped by a heat exchange system. As the influent progresses in the downcomer its pressure increases with depth and its temperature also increases due to efficient heat exchange with the hot effluent in the upcomer. At a temperature of approximately 450 K the oxidation process starts, with the heat of oxidation further increasing the influent temperature. As the waste mixture now passes to the upcomer and rises to the surface, pressure decreases and temperature drops due to heat transfer to both the influent and heat exchanger coolant. The temperature of the effluent on exit from the reactor is approximately 320 K [59]. This concentric tube arrangement requires a relatively small surface area which has significant space advantages compared with above ground systems.

The heat exchanger system that surrounds the reactor is used during normal operation to recover heat from the effluent. A heat exchange medium is passed down the surrounding tube returning to the surface via a separate insulated tube. From this now hot heat exchange medium, energy can be recovered in the form of electricity. During start-up the flow is reversed and the pre-heated heat exchange medium is passed down the insulated tube to heat the mixture at the base of the reactor. This design ensures good temperature control and thermal efficiency [59].

There are significant environmental concerns with deep-shaft reactors regarding the possible contamination of drinking water aquifers from subsurface failures, especially if toxic materials are being processed. A number of safeguards are taken to prevent contamination including extensive geological surveys with only stable sites being selected. In addition where there are drinking aquifers at the top of the reactor the casing is double cement lined. Another drawback is the build-up of scale on the reactor walls which periodically has to be removed using a nitric acid wash [58]. The frequency of the washing process depends on the feed composition, but typically is undertaken once every 10 days taking some 8 h to complete [51,60]. In order to reduce scale formation an inhibitor can be added to the feed [58].

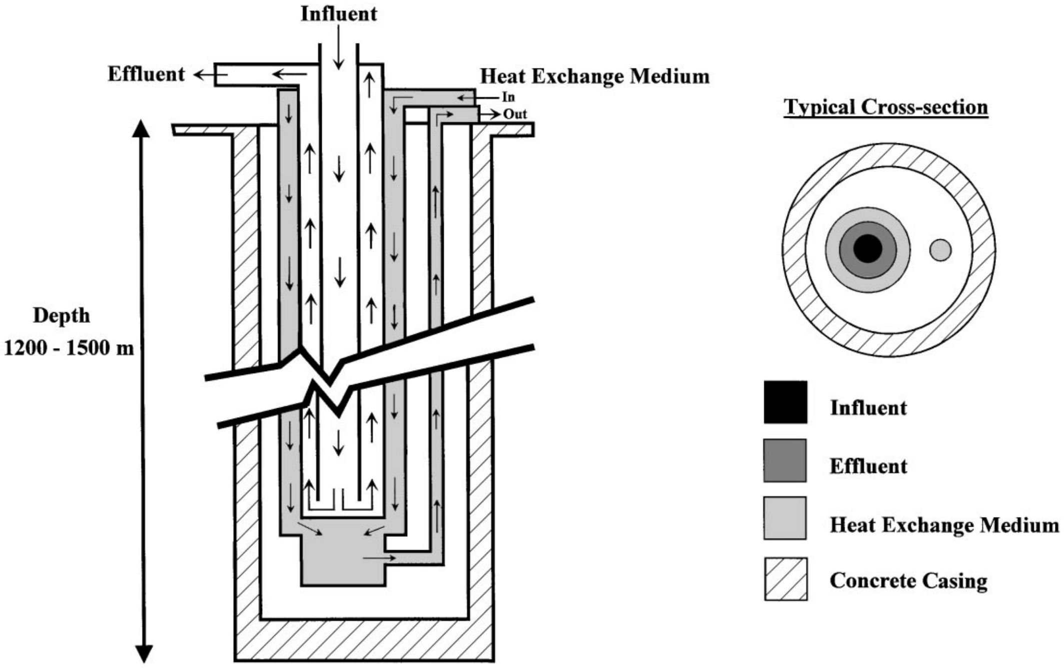

Fig. 5. VerTech reaction vessel (adapted from Bekker and Berg [59]).

The first commercial scale facility was commissioned in 1993 at Appeldorn, Netherlands. The plant has a design capacity of 23 000 ton dry solids per year with the reactor having an inner diameter of 216 mm, an outer tube diameter of 343 mm and a depth of 1200 m. The reactor is suspended in a deep concrete well of 950 mm diameter [59,61]. The plant has experienced a number of operating difficulties, including scaling and corrosion of the shaft and heat exchangers, though these problems have since been overcome [62].

4.4. Kenox process

The main feature of the Kenox wet oxidation process is the recirculation reactor which incorporates a number of novel features, notably static mixing and ultrasonic energy. Developed in the 1980s by the Kenox Corporation of Canada, the first commercial sized demonstration unit was installed in 1986 at a drum re-conditioning plant in Mississauga, ON [63,64]. The claimed advantages of the system are a significant reduction in capital cost coupled with higher yields in COD reduction including acetic acid destruction.

The Kenox reactor consists of two concentric shells with waste and air flowing down through the inner cylinder and then flowing upward through the space between the inner and outer cylinders. At the bottom of the reactor are the vanes of the pump unit, which circulates the waste and air mixture around the reactor. A static mixing device located in the inner cylinder facilitates intimate contact of air and liquid. As the liquid waste and gases pass over the vanes of the static mixer, they are subdivided to expose fresh surfaces of the organic matter to the oxygen and further oxidize the organic compounds. In addition heterogeneous catalysts can be impregnated onto the surface of the static mixer to further enhance oxidation. An ultrasonic probe is located in the upper region of the reactor. Ultrasonic waves are then passed through the waste dissolving any suspended solids and in addition creating microscopic regions of high temperature and pressure to significantly accelerate chemical reactions [64]. A disadvantage of the use of a pump unit within the Kenox reactor is the energy consumption, maintenance requirement and the need for a high pressure seal.

A typical flow scheme for the Kenox process is detailed in Fig. 6. The reactor typically operates at temperatures and pressures between 473 K and 513 K and 4.1 to 4.7 MPa respectively. For most applications a residence time of around forty minutes is acceptable [64]. Prior to entering the first reactor the wastewater pH is lowered to a value of around four by the addition of waste acid and then heated to the required inlet temperature [65]. The Kenox reactor system is modularized, with additional modules being required as the wastewater flowrate increases [64]. On leaving the final reactor module the effluent is cooled and separated into a vapour and liquid phase. The vapour phase is scrubbed to remove any volatile organics while the liquid phase is biologically treated [65].

4.5. Oxyjet reactor system

Researchers at the Universidad Politecnica de Catalunya, Spain and the Universite de Sherbrooke, Canada, have developed a compact technology known as OXYJET, based on the combination of jet-mixers and tubular reactors. The

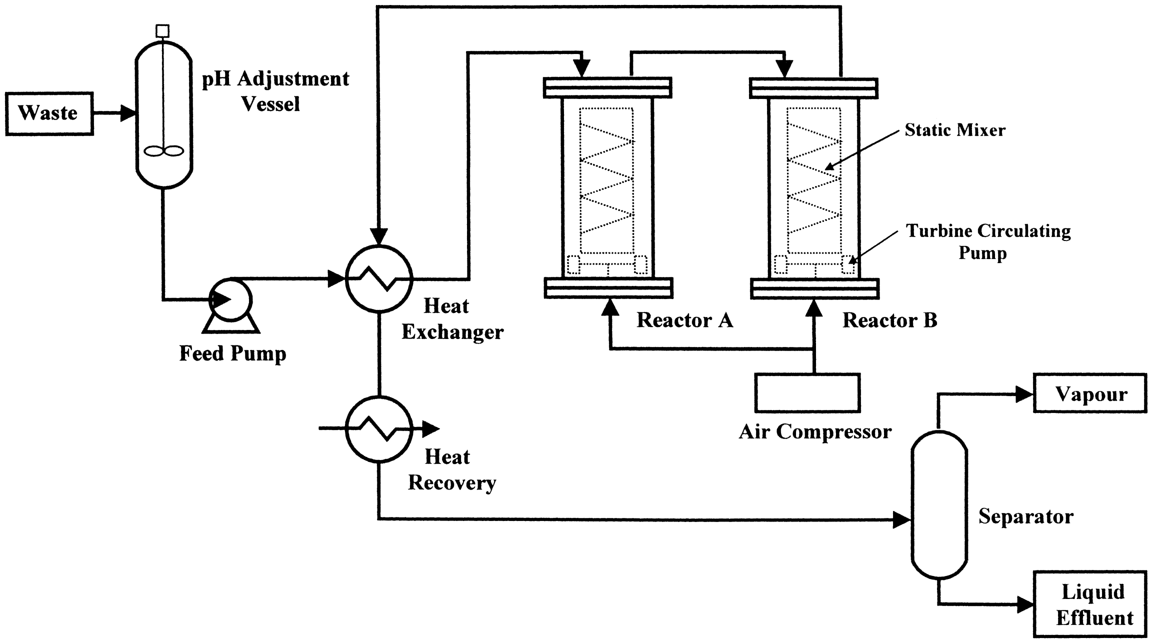

Fig. 6. Kenox process schematic (adapted from Kenox [64]).

strategy behind the oxyjet system is the creation of a high interfacial area flow regime which maximizes oxygen mass transfer to the liquid phase leading to kinetic control over a wider range of operating conditions. In the system, gas and liquid are supplied to a jet mixer which disperses the liquid into fine droplets creating a two-phase mist, see reaction flowscheme Fig. 7. The mean diameter of the drops is estimated to be only a few microns, giving a large interfacial area for mass transfer and no contact with metal surfaces. Following the mixer the two phase mist flows through a tubular reactor where rapid oxidation of the organic compounds occurs in a kinetically controlled regime [66]. In the oxyjet process the oxidation rate is fully governed by reaction kinetics reducing the residence time required in the system compared with conventional bubble technology [67]. Following the tubular reactor there is an option to include a jet reactor. In the jet reactor the two phase flow enters a mixed nozzle assembly where any coalesced liquid is again atomized [67]. In addition it is possible to add a catalyst and/or another oxidant to complete the oxidation.

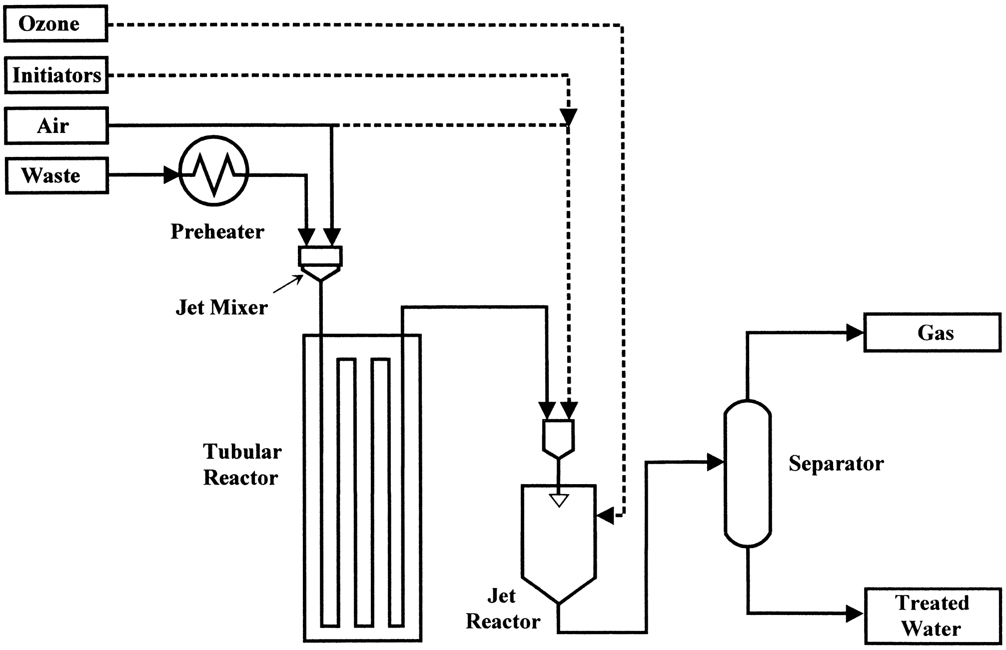

Fig. 7. Oxyjet process development unit (adapted from Gasso et al. [67]).

Jaulin and Chornet [68] used a jet mixer followed by a tubular reactor (1.25 cm I.D., length 7 m) for the oxidation of aqueous phenol solutions. Operating at temperatures in the range of 413 K to 453 K and a residence time of two and a half minutes, they achieved phenol conversions of between 20% and 50%. The addition of a CuO/Cr_2O_3 catalyst to the tubular reactor did not improve reactor performance, possibly due to the decrease in interfacial area caused by rapid coalescence of the mist when in contact with the catalyst bed. However, addition of hydrogen peroxide to the liquid feed solution did improve phenol conversion.

Gasso et al. [66] investigated the use of a jet mixer/tubular reactor system (1.021 cm I.D., length 29 m) followed by a secondary reaction chamber where supplementary oxidant could be added. Operating at temperatures as high as 573 K and residence times of 2 to 3 min, Gasso et al. achieved a reduction in total organic carbon of 99% for both pure phenol and pure ethylene glycol solutions. They were also successful in treating industrial waste from both an olive processing plant and a wood processing plant. Further work showed the suitability of the process to treat pharmaceutical waste, phenolic chemical waste and wood preservation liquor [67].

5. Catalytic systems

In comparison with non-catalytic operation, the presence of a catalyst enhances the reaction rate or attains an acceptable overall reaction rate at a lower operating temperature. In each case this can result in a reduction in the capital cost of the process. In addition, the use of an appropriate catalyst can result in a higher degree of oxidation for organic material refractory to non-catalytic wet oxidation. The catalytic process can, therefore, be used for either effluent pre-treatment prior to a biological step or as a complete destruction process [69].

6. Homogeneous catalysts

The use of homogeneous transition metal catalysts has been shown to enhance the reaction rate in wet air oxidation processes, with homogeneous copper salts being the most active [1,7,26,70,71]. The presence of the homogeneous catalyst in the same liquid phase as the reactants simplifies reactor operation compared with heterogeneous catalysts as it avoids the need for an additional third phase. The interaction of mass transfer and reaction kinetics are therefore similar to the non-catalytic system. The main disadvantage is that this requires the catalyst to be either recovered from the treated effluent or discarded. For example, in the Ciba–Geigy process, cupric salt is used as a homogeneous catalyst which is then recovered as cupric sulphide and recycled to the reactor [27]. The need for an additional processing step to recover the catalyst, especially if it is toxic, has an adverse effect on capital costs.

The addition of other co-oxidants together with a catalyst can have a positive effect on the effectiveness of the process. For example, Kulkarni and Dixit [72] used sodium sulphite in the presence of cupric ions for phenol destruction in aqueous solutions, while the use of nitric acid (HNO_3) has been suggested for reducing the severity of required reaction conditions [1].

Alternatively, the use of radical promoters in combination with transition metals has been used to enhance the wet air oxidation process. Typically hydrogen peroxide has been used as a source of radicals and found to be especially effective in the presence of iron or copper salts. A positive synergistic effect has also been observed when two or more metals are used in combination with hydrogen peroxide [27,73].

6.1. Wet peroxide oxidation process

The Wet Peroxide Oxidation (WPO) process has been developed in France by the Institut National des Sciences Appliquees and the IDE Environnement SA [74–76]. The wet peroxide oxidation process uses a liquid oxidizing agent (hydrogen peroxide) instead of a gaseous one (oxygen), eliminating mass transfer limitations. This process is an adaptation of the classical Fenton's reagent (combination of hydrogen peroxide and Fe^{2+}), but uses temperatures and pressures of around 373 K and 0.5 MPa respectively. Use of metal salt combinations in conjunction with hydrogen peroxide has been shown to enhance significantly total organic carbon (TOC) removal, even for refractory low molecular weight organic acids. For example at a temperature of 373 K, Falcon et al. [74] achieved a 89% reduction in TOC conversion after 60 min of treating a mixture of acetic, oxalic, succinic and malonic acids using hydrogen peroxide and a combination of Fe^{2+}, Cu^{2+} and Mn^{2+} (23 : 50 : 27 by weight respectively).

6.2. Bayer Loprox process

The Bayer Loprox (low pressure wet oxidation) process is especially suited to the conditioning of wastewater streams prior to biological treatment. In the 1970s, research conducted by Bayer found that wastewater containing compounds difficult to treat biologically could be pre-treated at mild conditions in a wet air oxidation process. These mild conditions would partially oxidize organic substances in the wastewater producing a final effluent better suited to subsequent biological treatment. This pre-treatment at mild conditions became the basis for the development of the Loprox process [77].

The Bayer Loprox process operates at temperatures below 473 K and at pressures between 5 and 20 MPa. Typically the process is suitable for wastes with a chemical oxygen demand of between 5 and 100 $g\,l^{-1}$ with reactor residence times of between 1 to 3 h. In the process the oxidation reaction is catalyzed by the addition of Fe^{2+} ions

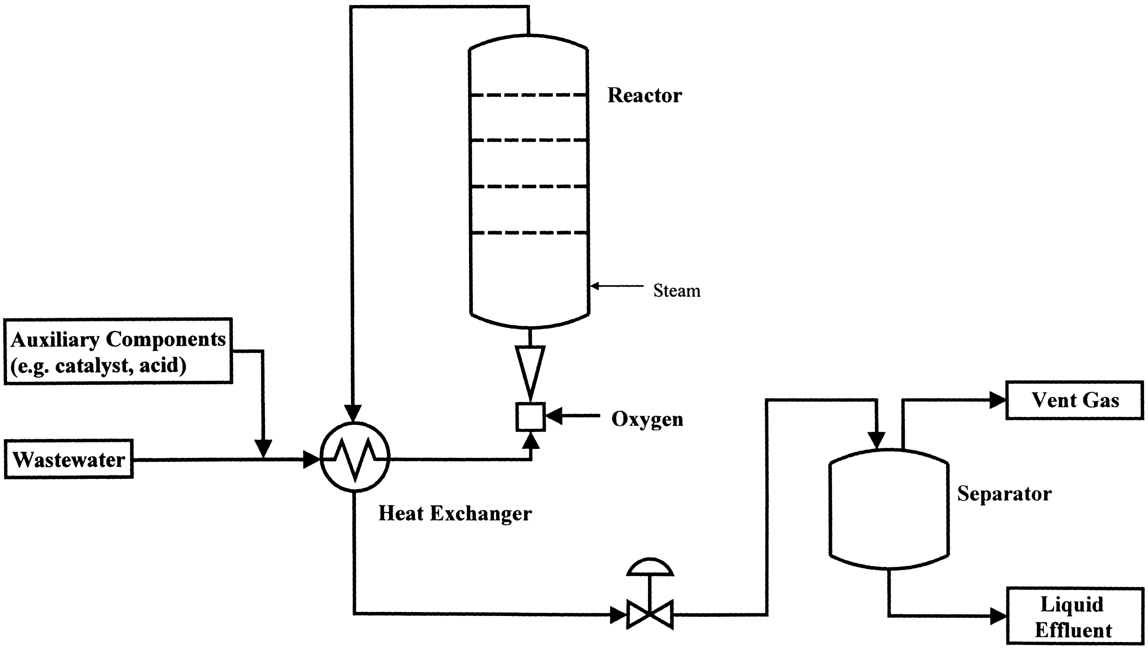

Fig. 8. Bayer Loprox Process Schematic (adapted from Holsar and Horak [78]).

and organic quinone forming substances [77]. It is assumed that during quinone formation hydrogen peroxide is produced as a reaction intermediate [78]. The combination of hydrogen peroxide and Fe^{2+} is a powerful oxidant system with the hydrogen peroxide decomposing to form the hydroxyl radical which can react with organic compounds [77,79].

A schematic of the Loprox process is detailed in Fig. 8. In this process, wastewater feed is initially pre-heated in a counter-current exchanger where heat is recovered from the reactor effluent. The feed then passes through the reactor which is a single or multi-stage bubble column depending on wastewater characteristics such as solids content. Pure oxygen is injected into the waste and distributed as fine bubbles. Following the reactor, the hot effluent is cooled in the heat exchanger before pressure let-down across the control valve. The effluent is then separated into liquid and gas phases before further downstream processing. For temperatures of up to 433 K, equipment in the hot section of the plant is constructed of material lined with PTFE or glass. For higher temperatures, titanium or titanium/palladium alloys are selected as they are resistant to temperatures of up to 473 K even at high chloride concentrations [77,78].

The Bayer Loprox process has successfully treated a variety of wastes including paper mill waste streams, wastewater from landfill sites and municipal sewage sludge. There are a number of industrial scale units in operation, including four at Bayer's Leverkusen factory in Germany, which are used to pre-treat waste streams of flowrate 6 to 60 $m^3 h^{-1}$ [77,78]. Bertrams AG secured the worldwide exclusive license for Loprox in 1995.

6.3. IT Enviroscience catalytic process

The IT Enviroscience process uses a water soluble homogeneous co-catalyst system. The catalyst, which originally consisted of bromide and nitrate anions in an acidic aqueous solution, was patented in 1972 [80] and assigned to the Dow Chemical Company [81]. IT Enviroscience subsequently obtained the rights to the co-catalyst system and developed a more effective catalyst, consisting of bromide, nitrate and manganese ions in acidic solution, for which they were assigned a new patent in 1981 [82,83]. It is postulated that the catalyst performs three roles that enhance the wet oxidation process, these being oxygen fixation, radical generation and organic oxidation [84]. In oxygen fixation the catalyst increases the transfer of oxygen to the aqueous solution via gas and liquid phase reactions of catalyst components with organic material in the reactor [85]. The generation of radicals is believed to be facilitated by the catalyst increasing the rate of reaction [86]. Finally, it is postulated that the bromine anion radical is formed, which is a strong oxidant capable of abstracting hydrogen from organic molecules increasing the organic destruction rate [84].

7. Heterogeneous catalysts

7.1. Introduction

The use of a heterogeneous catalyst has an advantage over homogeneous systems in that the additional catalyst removal step is not required. However, as well as being effective, the heterogeneous catalyst must show satisfactory stability and durability in the severe operating conditions and acidic environments found in wet air oxidation systems. Catalyst deactivation can occur due to sintering, poisoning of active sites or fouling of the catalyst surface following deposition of reaction intermediates. In the reaction conditions typical of wet air oxidation, catalyst deactivation can also occur due to the dissolution of active component into the hot acidic liquid phase.

Catalyst deactivation due to leaching has been demonstrated in laboratory experiments investigating the use of commercially supported copper oxide catalysts for the oxidation of aqueous phenol solutions. Sadana and Katzer [87,88], Njribeako et al. [89], Ohta et al. [90] and Fortuny et al. [91] have all investigated the catalytic oxidation of phenol using Harshaw Cu 0803 T, 10% CuO on γ-alumina catalyst. In semi-batch reactor studies Sadana and Katzer [87] found the oxidation rate to exhibit a pronounced induction period followed by a rapid reaction step. If the catalyst was re-used for a further run, the induction period was shorter and catalytic activity increased in the rapid reaction phase. Sadana and Katzer [88] proposed a heterogeneous–homogeneous free radical mechanism with initiation on the catalyst surface, propagation in the homogeneous phase and termination in both. Although the concentration of copper in the aqueous phase was not measured in their original work, in later correspondence [92] it was reported that the dissolution of copper from commercially available catalysts resulted in cupric ion concentrations of as high as $100\ \mathrm{mg\ l^{-1}}$. In studies completed in a semi-batch spinning basket reactor, Ohta et al. [90] also observed a significant induction period for the fresh catalyst, though there was almost no induction period for the second run with all subsequent experiments being between the two. For ten consecutive experiments completed with cylindrical pellets (equivalent spherical diameter 0.318 cm) consistent catalytic activity was observed from the third run onwards. When a series of experiments was completed with granular particles (average equivalent spherical diameter 0.019 cm), however, catalyst activity was not stable, with progressive deactivation of the catalyst being observed from the fourth run onwards. Fortuny et al. [91] investigated catalyst performance in a continuous trickle bed reactor. For an experiment completed at 413 K, the Harshaw catalyst reached a phenol conversion of 80%, but after 48 h operation this had declined to a value of 40%. The activity of the Harshaw catalyst then slowly declined to reach a conversion of approximately 32% after 216 h of continuous operation. In the work of both Ohta et al. [90] and Fortuny et al. [91], the cupric ion concentration was not measured, so the extent and significance of catalyst deactivation due to leached copper was not known. However, at an operating temperature of 423 K, Njribeako et al. [89] found that copper was leached from the Harshaw catalyst, with the homogeneous catalytic component of the reaction attributable to cupric ion being approximately 20% of the total reaction rate.

Catalyst deactivation due to product adsorption was found to occur by Pintar and Levec [93] when investigating the catalytic oxidation of phenol in a semi-batch slurry reactor. They used a commercially available catalyst which was pre-treated to give a catalyst containing approximately 16 wt.% of $ZnAl_2O_4$, 60 wt.% of CuO and 24 wt.% of ZnO. In their studies a polymeric product was formed which was strongly adsorbed to the catalyst surface. The activity of the catalyst was consistent for two consecutive runs, but in the third, catalyst deactivation occurred primarily due to polymer formation on the catalyst surface. In addition, the catalyst was deactivated due to the leaching of copper which reached a concentration in the liquid of $75\ \mathrm{mg\ l^{-1}}$. A polymeric product was also found on the catalyst surface when aqueous solutions of pure 2,5-cyclohexadiene-1,4-dione and pure glyoxale were oxidized.

The inclusion of a heterogeneous catalyst in a wet air oxidation reactor raises a number of additional operational factors to be considered in the reactor design. These include pressure drop across the catalyst, risk of catalyst fouling and plugging, and avoidance of interparticle and intraparticle mass transport limitations.

In a fixed bed system, an excessively large pressure drop across the bed may occur if the catalyst pellets are too small. Although the use of larger diameter pellets will reduce the pressure drop across the bed, the rate of reaction may become diffusion limited in the porous structure with a significant proportion of the catalyst pellet not being utilized. In addition, the presence of suspended solid materials in the waste stream can result in the clogging of the bed. This will eventually result in an increase in pressure drop across the bed making long term uninterrupted operation of the system impracticable. To protect the catalyst against solid loading, a two stage process can be utilized, where the suspended material is initially dissolved in a non-catalytic reactor before being oxidized in a catalytic reactor [94].

In catalytic wet air oxidation reactors there are three steps of reactant mass transfer. In the first step oxygen transfers from the gas to the liquid phase, in the second reactants diffuse through the main body of the liquid to the catalysts exterior surface (interparticle) and in the final third step reactants diffuse through the catalyst pores to the interior surface of the pellet (intraparticle). Contrary to results found for bubble columns, the gas–liquid interfacial area (a) for mass transfer in a packed column has been found to be unaffected by pressure over the range 0.25 to 1.5 MPa [45].

A number of previous researchers have identified mass transfer limitations when using a heterogeneous catalyst in a wet air oxidation system. Sadana and Katzer [87] investigated the wet air oxidation of phenol in a slurry reactor using a 10% CuO on γ-alumina catalyst. They observed a slower reaction rate for large catalyst particles ($d_p = 0.4$ mm) compared with that for the smaller catalyst particles ($d_p < 0.06$ mm). This was assumed to be due to oxygen intraparticle diffusion limitations in the larger pellets, which was supported by the measurement of different activation energies in each case. Theoretically the observed activation energy for reactions influenced by strong pore resistance is approximately half that of the true value [23]. The results of Sadana and Katzer [87] were consistent with those expected for pore diffusion limitations as they found the activation energy for the large particles to be half that of the smaller ones. Njribeako et al. [95] also investigated the wet air oxidation of phenol, but in a spinning basket reactor using a 10% CuO catalyst on a silica carrier. They investigated the reaction rate for three catalyst pellet sizes ($d_p = 0.2$, 0.43 and 4.0 mm) and found a trend of decreasing reaction rate with increasing size. Further theoretical calculations estimated that even for the smallest particle size intraparticle diffusion of phenol was offering some impediment to oxidation. Baldi et al. [96] and Goto and Smith [97,98] used a commercial CuO-ZnO catalyst to oxidize formic acid over a temperature range of 473 K to 513 K. In a liquid full differential catalytic reactor (particle size d_p 0.038, 0.0541, 0.291 and 0.477 cm), Baldi et al. [96] observed oxygen intraparticle mass transfer limitations for the larger catalyst sizes. In a trickle bed reactor, Goto and Smith [97,98] also experienced mass transfer limitations with gas to liquid being the most significant, followed by intraparticle and interparticle resistance. Levec and Smith [99] used an iron oxide catalyst to oxidize acetic acid in a trickle bed reactor, temperature range 525–560 K, d_p 0.0541 to 0.238 cm. Gas–liquid-particle resistances were again significant, with gas to liquid mass transfer being the most important. For the examples above using copper based catalysts, caution must be taken when assessing the results due to the possible influence of leached cupric ions present in the aqueous phase. As copper is known to be an effective homogeneous catalyst its displacement from the solid support to the solution has an effect on reaction rate which must be accounted for in the analysis.

An alternative method of incorporating the catalyst into the reactor is to use a support moulded into a monolithic structure. The monolithic structure is normally a cylindrical solid support with a number of parallel channels running through the centre. The reactants flow through these channels with the catalyst being located on the walls. The cross-sectional shape of the channels can have various forms including circular, rectangular, hexagonal or sinusoidal. In addition to channel shape, monolith structures can be manufactured to have a specified channel size, cell density and wall thickness and hence a known free cross-sectional area. If particulates are present in the waste they can pass easily through the reactor provided the diameter of the channel is greater than that of the particles. The incorporation of an effective monolithic catalyst therefore increases reaction rate while reducing pressure losses and plugging of the catalyst [100]. In addition, by operating the vertical monolith system in the slug flow regime (segmented gas–liquid flow) a re-circulation pattern within each liquid plug is developed improving mass transfer. In the slug flow regime a thin liquid film is formed between the gas and the monolith wall which allows high mass transfer rates and keeps the catalyst continuously wetted [101].

There are a number of commercial enterprises working on the development of heterogeneous wet air oxidation catalysts. The following sections describes the work of two such companies, which serve as examples of both catalyst effectiveness and methods employed to improve catalyst durability.

7.2. Nippon Shokubai Kagaku process

The Nippon Shokubai Kagaku Company Limited had installed ten catalytic systems by 1996 and developed numerous heterogeneous catalysts in both pellet and honeycomb form for use in wet air oxidation processes [50]. For example their European Patent [100] covers a heterogeneous catalyst capable of converting organic and inorganic substances present in the wastewater to nitrogen, carbon dioxide and water. The catalyst is comprised of titanium dioxide, an oxide of an element of the lanthanide series and one metal from the group consisting of manganese, iron, cobalt, nickel, tungsten, copper, silver, gold, platinum, palladium, rhodium, ruthenium and iridium or a water insoluble or sparingly water soluble compound of the metal [100]. Although the use of titania or zirconia as carriers increased catalyst strength compared with alumina supports, both their catalytic activity and durability was not satisfactory. In contrast to this, oxides of elements of the lanthanide series were found to exhibit catalytic activity, but could not be easily moulded and in the long term degraded in physical strength. In the Nippon Shokubai catalyst the combination of titanium dioxide with oxides of elements of the lanthanide series resulted in a mouldable, physically stable catalyst, exhibiting only a slight loss in strength and catalytic activity, while being capable of withstanding long term use [100]. The Nippon Shokubai process operates over a temperature range of 433 K to 543 K and at pressures of between 0.9 to 8.0 MPa, with typical residence times in the region of about 1 h [50,100]. The effectiveness of the catalyst to remove compounds refractory to non-catalytic oxidation was illustrated by the treatment of a waste containing acetic acid and ammonia at a temperature of 503 K and a pressure of 5.0 MPa [100].

A further catalyst from Nippon Shokubai contains a main ‘A component’ comprising an oxide of iron together with an oxide from at least one of titanium, silicon and zirconium, plus an active ‘B component’ consisting of one or more of cobalt, nickel, cerium, silver, gold, platinum, rhodium, ruthenium and iridium. The A component makes up 90% to 99.95% by weight of the catalyst with the B component making up the balance. The catalyst is capable of treating organic wastes including compounds containing nitrogen, sulphur or halogens. The catalyst maintains activity for a long period and decomposes any elemental nitrogen in a compound to nitrogen gas. It is preferable to operate in the alkaline pH region for the treatment of sulphur and halogen containing compounds as the avoidance of acidic conditions improves the durability of the apparatus [102].

7.3. Osaka gas process

The patented Osaka Gas Process is similar to the Zimpro process except for the inclusion of a heterogeneous catalyst in the reactor, supplied in the form of spheres or a honeycomb support. The catalyst uses titania, zirconia or the like (as either a one-element or two-element system) as the carrier together with a mixture of two or more precious or base metals such as iron, cobalt, nickel, ruthenium, palladium, platinum, copper, gold, tungsten and compounds thereof [69,94].

The operating conditions including temperature, pressure and initial pH vary depending on the composition of the waste and required destruction efficiency, with the catalyst retaining activity for a long service life. For example, in the treatment of gas liquor wastewater from coke ovens over 11 000 h of continuous operation was obtained at 523 K and 6.86 MPa, with no change in catalytic activity. After a residence time of 24 min the waste was decomposed from an initial chemical oxygen demand (COD) of 5870 g l^{-1} to a value of less than 10 mg l^{-1} [69]. Further, the process can be used to destroy a variety of wastewaters and sludge including sewage sludge, ammonium nitrate wastewater, domestic wastes and pharmaceutical waste. In addition, catalysts used for the treatment of various nitrogen containing compounds (e.g. ammonia, ammonium salts and nitrates) will achieve a virtually complete conversion of nitrogen content to nitrogen gas [100,103,104].

8. Conclusions

Wet air oxidation appears to be a promising technology for wastewater treatment. However, there is a lack of fundamental data at the operating conditions of both high temperature and pressure, for the basic stages of the process (i.e. reaction kinetics, mass transfer). As detailed kinetics studies into the wet air oxidation of industrial wastewater are not available, reactor design is typically based on empirical methods and global rate expressions. Although such techniques are adequate over the range of operating conditions investigated, they lack predictive power and provide only a limited insight into the function and nature of reaction chemistry. Due to the radical nature of the process and the significance of both mass transfer and reaction kinetics on the overall reaction rate, difficulty can be experienced when using empirical laboratory studies as a basis for reactor scale-up. It should be noted that kinetic constants involving the wall of the reactor (radical termination, hydrogen peroxide decomposition) are specific for each case and should only coincide for reactors made of the same material and with the same ratio of surface to volume. Studies should be completed to investigate the mechanism, giving full consideration to the influence of operating parameters (e.g. influence of specific radical species, reactor geometry, operating conditions, non-oxidation pathways, composition of the waste stream, etc.) on the observed reaction rate and intermediate selectivity. Further work is required to investigate the influence of reactor materials of construction and geometry on reaction rates and to separate their effects from that of bulk liquid reaction kinetics. Such work is required in order to achieve a better understanding of the reaction process and aid reactor design.

There are similarly only a few correlations available for the estimation of mass transfer parameters at high temperature and high pressure, and these are not applicable over the entire operating range of wet air oxidation systems. Although laboratory studies for ideal systems (e.g. air–water) have shown that operating conditions influence overall gas–liquid mass transfer (e.g. influence on bubble size distribution), there is a lack of studies specifically investigating their influence on mass transfer in wet air oxidation systems. The description of mass transfer in heterogeneous systems also demands the knowledge of backmixing phenomena for high pressure conditions, in order to estimate a reliable residence time distribution in the reactor. This lack of accurate information for key operational parameters hinders the development of mathematical techniques to model the performance of the system. There is a need to develop predictive mathematical models to facilitate optimization of reactor design and operating conditions, with minimal laboratory screening studies.

The scarcity of fundamental information for wet air oxidation is equally applicable to both homogeneous and heterogeneous catalytic systems. In addition to considering the effectiveness of heterogeneous catalytic systems, further attention should be given towards gaining a deeper understanding of catalyst action (reaction mechanisms). This will allow development of appropriate kinetic equations for mathematical modeling. In parallel to this, experimental studies need to consider the stability of the catalyst and the mechanisms of catalyst deactivation (long term catalyst performance). An understanding is required of the processes of catalyst leaching, fouling and poisoning, and their dependence on operating parameters. This can have a significant impact on the development of novel reactor designs, which ameliorate the above problems. Reactor design should also address operational issues (e.g. mass transfer, pressure drop, solid loading, etc.) regarding catalyst incorporation into the reactor, which can have an impact on observed reaction rate and selectivity. For homogeneous catalysts systems there is a need to develop a more effective integrated technique for wet air oxidation and simultaneous recovery and recycle of the metal catalyst from the treated effluent.

Concluding, the challenge facing the further development of wet air oxidation technology is the acquisition of a deeper understanding of all the mechanisms occurring within the process. Only then can predictive modeling techniques be developed to reliably optimize the process.

9. Nomenclature

A	pre-exponential factor, $\text{kmol}^{1-m-n}\,(\text{m}^{-3})^{m+n+1}\,\text{s}^{-1}$
a	gas–liquid interfacial area, m^{-1}
$C_{\text{O}_2,\text{L}}$	oxygen concentration in the bulk liquid, kmol m^{-3}
$C^*_{\text{O}_2}$	saturated oxygen concentration, kmol m^{-3}
C_P	pollutant concentration, kmol m^{-3}
d_b	individual bubble diameter, m
d_vs	mean bubble diameter, m
D	molecular diffusivity of solute in liquid phase, $\text{m}^2\,\text{s}^{-1}$
E	activation energy, J mol^{-1}
g	gravitational acceleration, m s^{-2}
k_L	liquid side mass transfer coefficient, m s^{-1}
m, n	orders of reaction
P	pressure, MPa
R	gas constant, $\text{J mol}^{-1}\,\text{K}^{-1}$
r_m	oxygen mass transfer rate, $\text{kmol m}^{-3}\,\text{s}^{-1}$
r_r	reaction rate, $\text{kmol m}^{-3}\,\text{s}^{-1}$
T	temperature, K
V	volume, m^3

Greek symbols

ε	gas hold-up
ρ	density, kg m^{-3}
σ	surface tension, mN m^{-1}
ν	superficial velocity, m s^{-1}

Subscripts

G	gas
L	liquid

Abbreviations

BOD	biochemical oxygen demand
COD	chemical oxygen demand
TOC	total organic carbon
WAO	wet air oxidation

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