

WET AIR OXIDATION FOR HAZARDOUS WASTE CONTROL*

R.G.W. LAUGHLIN, T. GALLO and H. ROBEY

Ontario Research Foundation, Mississauga, Ontario, L5K 1B3 (Canada)

(Received November 2, 1981; accepted in revised form October 5, 1982)

Summary

The Wetox[®] process has been proven effective on a variety of industrial and municipal waste streams. Many of these streams contained chemicals which could be considered extremely toxic or hazardous. Destruction efficiencies of the compounds of concern were typically greater than 99%.

An advantage of the technology is that elements such as sulphur, chlorine and nitrogen are retained in solution, thus minimizing any potential air pollution problems.

The first commercial Wetox system has been installed at a chemical company in Ontario in the spring of 1982. This unit is being designed to treat about 50,000 litres/day of a wastewater which has a chemical oxygen demand of approximately 7%. The organic contaminants are complex sulphur, nitrogen and chlorine bearing compounds which will be reduced in the process.

Introduction

There is a great need to develop effective control technology for the destruction of toxic and hazardous components in aqueous industrial waste streams. The technology of wet air oxidation described in this paper is particularly effective in the destruction of oxidizable, usually organic, contaminants in concentrations between 1 and 20% by weight in industrial wastewaters. In this range, the concentrations are too high for conventional chemical or biological oxidation, but too low for effective incineration.

Wet air oxidation

Wet air oxidation is a process in which combustible material is oxidized by air or oxygen in the presence of liquid water. Elevated temperatures (150–300°C) are required to achieve useful reaction rates, and, therefore, to maintain a liquid phase, elevated pressures (2.0–15 MPa) are required. The process is operated continuously with respect to both liquid and air or oxygen addition.

A generalized flowsheet for wet air oxidation is shown in Fig. 1. The

*Original version presented at the Second World Congress of Chemical Engineering, Montreal, Canada, October 4–9, 1981.

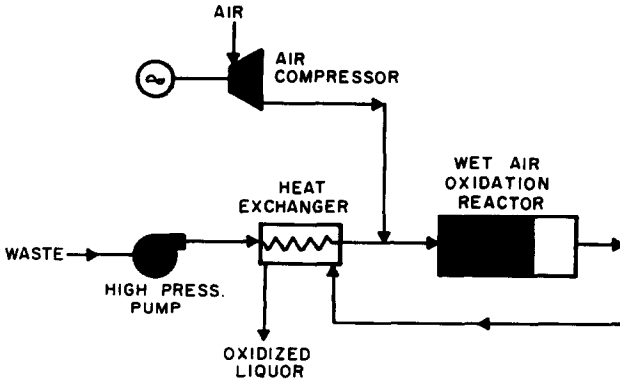


Fig. 1. Wet air oxidation, basic flow sheet.

waste is pumped via a high-pressure pump through a heat exchanger and then into a reactor where compressed air is added. The oxygen in the air reacts with the organic matter in the slurry to produce mainly carbon dioxide and water. Due to the exothermic nature of the reaction, heat is produced which raises the temperature of the reactor contents. The effluent from the wet oxidation reactor is heat exchanged with the incoming waste.

Energy must be supplied to get the reactor up to operating temperature initially, and to provide heated effluent to heat up incoming waste. This can be provided by electrical heaters in the reactor for small installations, or by direct injection of live steam for larger installations.

Almost any combustible material which is in an aqueous medium can be oxidized by this process. Since the products of the oxidation reaction are released in an aqueous environment, they are thoroughly scrubbed. Thus, air and odour pollution problems are minimized.

The wet air oxidation process provides an efficient means for energy recovery from relatively dilute waste streams. The reaction occurs and energy is liberated in the liquid phase with no barrier to transfer. Therefore, energy can be recovered with a high degree of efficiency.

The process is most economical for wastes which have a concentration of oxidizable material between 1 and 20% by weight with water. In this range, sufficient material is available to react with the oxygen to generate enough heat to maintain the desired temperature and pressure in the reactor without an external energy source. Above about 6% concentration, excess heat generally is produced which can be recovered efficiently and economically. Above a 20% concentration of oxidizable material so much heat is produced that there is a danger of boiling the system dry.

The Wetox[®] process

Ontario Research Foundation (ORF) has been working since 1972 on a particular approach to wet air oxidation known as the Wetox process. This

process is now being marketed commercially by WetCom Engineering Ltd. of Toronto, Ontario, Canada. The first commercial installation of a Wetox system has been built and installed in the spring of 1982. This unit is designed to process 50,000 litres/day of an industrial wastewater stream which has a chemical oxygen demand (COD) of approximately 7%. The organic contaminants are complex sulphur, nitrogen and chlorine bearing compounds which are reduced in the process.

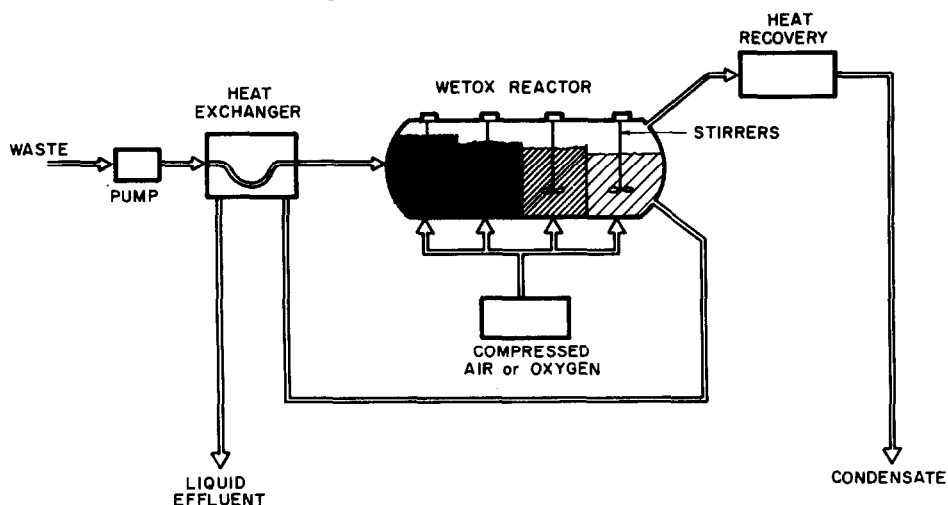


Fig. 2. Wetox® process schematic.

The heart of the Wetox process (see Fig. 2) is the specific reactor design employed to achieve the wet air oxidation reactions. This reactor is a multi-compartmented horizontal autoclave with agitation and oxidant addition in each compartment. This design results in substantially increased reaction rates and makes possible efficient operation at modest temperatures (225–250°C) and pressures (about 4 MPa). The agitation substantially increases the rate of absorption of oxygen into the waste since it

- decreases the size of the air bubbles and hence increases the effective interfacial area for mass transfer;
- creates eddy currents which, by delaying the escape of the air bubbles, effectively increases the contact time for mass transfer;
- causes turbulent shear and hence reduces the thickness of the stagnant liquid film and hence resistance to mass transfer.

The steam and liquid phases are withdrawn separately from the reactor. This feature improves the heat exchanger efficiency, increases the effective retention time for the liquid, and reduces the volume of the liquid effluent for chemical recovery or treatment.

Another wet air oxidation technology is known as the Zimmerman, or Zimpro process. This process has been marketed commercially for many years. Features of the Zimpro hazardous waste destruction system which

differentiate it from Wetox include the following [1–3]:

- temperatures and pressures employed up to 320°C and 150 bar;
- vertical, tower reactor design;
- phase separation is afforded outside of reactor;
- no agitation of the slurry.

Typical efficiencies of the Wetox process for COD reduction are 75–95%. The residual organic species causing the 5–25% COD concentration in the effluent generally are quite different from the original contaminants in the waste stream. They largely are simple low-molecular-weight partially oxidized species such as alcohols, aldehydes and organic acids. Acetic acid is a major contributor to all Wetox effluent COD concentrations. In most cases, it represents 50% or greater of the residual COD, with a further 25% being propionic acid. These low-molecular-weight acids are formed as breakdown products of the oxidation of longer-chained complex organic molecules. They also may be present in the influent waste stream. It has been found that these low-molecular-weight organic acids are comparatively refractory to oxidation by wet air oxidation. Much higher temperatures and pressures than normally are employed would be required to ensure their complete destruction.

These low-molecular-weight organic acids are readily biodegradable. It is more cost effective to consider combining Wetox with a biological oxidation effluent polishing step, than to try to achieve 100% destruction in the Wetox reactor. The two systems are symbiotic. Wetox produces a readily assimilable feed to the biological oxidation system, while it, in turn, destroys the biological sludge which is the rejected by-product of the biological oxidation system.

Other materials which will appear in the Wetox effluent will be any non-oxidizable inorganic materials which were present in the influent waste. These are all contained in the liquid phase effluent, and may, in some cases, be of interest for recovery. An example of this would be the recovery of

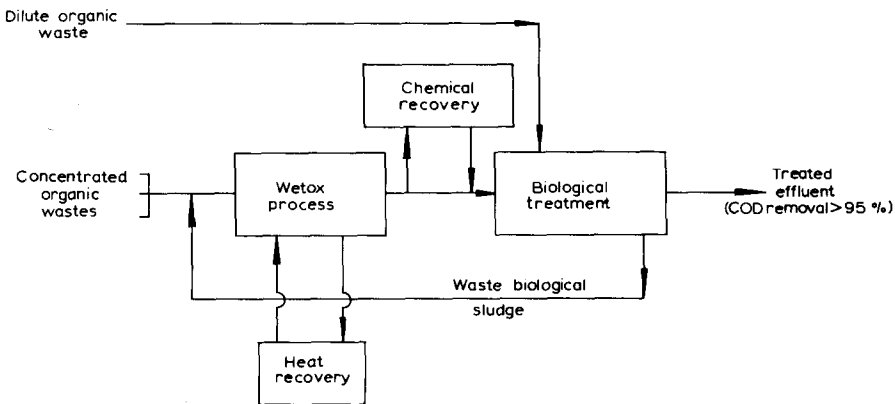


Fig. 3. Wetox process with biological treatment and chemical recovery.

clay filler from paper mill sludges. The dyes, fibers, and other organic materials in these paper mill sludges are destroyed, thereby cleaning up the residual clay fillers for reuse in the papermaking process. Figure 3 shows a flowsheet incorporating an integrated Wetox, biological treatment and chemical recovery process.

Three elemental substances which are of concern when wastes are incinerated are sulphur, chlorine and nitrogen. In Wetox, sulphur and chlorine are converted to sulphuric and hydrochloric acids respectively, while nitrogen forms ammonia. All are retained in solution as acid or base, or, if appropriate metal cations are present, salts will be formed.

Wet air oxidation for hazardous waste control

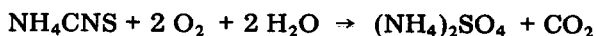
The Wetox process is particularly applicable to wastes which are considered hazardous or toxic, and cannot be readily treated by other means. Typical destruction efficiencies for the Wetox process operating at about 230°C and 4 MPa when measured by parameters such as chemical oxygen demand are 75–95% destruction of COD. As was discussed previously, the nature of the organic species remaining in the effluent from the Wetox system is quite different from the nature of the influent contaminants, particularly when those materials have complex chemical structures.

The precise nature of the chemical reactions occurring in the wet oxidation process are not understood. It is believed to be a combination of both oxidation and hydrolysis occurring in the reactor, with hydrolysis tending to favour the formation of refractory compounds such as acetic acid. Much of our work in developing the Wetox reactor has been directed towards optimum rapid dispersion of oxygen to try to encourage complete oxidation to occur.

Over the past several years, the applicability of the Wetox process to some 60 different industrial waste streams has been examined. A number of these wastes have contained chemicals which could be considered to be extremely toxic. In the sections that follow, the fate of these components in the Wetox process are discussed briefly.

Coke oven gas scrubber liquor

The major component of this waste stream of concern is ammonium thiocyanate, NH_4CNS . Test work at Ontario Research using 2-litre batch, 10-litre semi-batch autoclaves and a 50-litre continuous flow integrated Wetox pilot plant, showed that the ammonium thiocyanate could be destroyed to a level in excess of 99% according to the reaction



A temperature of 240°C and a pressure of 4.3 MPa was required with a one hour residence time in the Wetox reactor.

Coal gasification condensate waste

In the test work done on this waste stream, phenolics were the component of particular concern. Table 1 below illustrates the inequity between the apparent ineffectiveness of the process as measured by COD (reduction ~ 50%) with the destruction rate for phenolics 99.8%.

TABLE 1

	Feed concentration (mg/litre)	Effluent concentration (mg/litre)
COD	15,000	7,500
Phenolics	3,000	7
Methanol	800	40
Propionaldehyde	25	trace
Acetone	1,000	100
Acetic acid	500	1,600
Propionic acid	200	150
Isobutyric acid	300	0

Sulphidic refinery spent caustic

Using typical conditions of 230°C, 4 MPa and one hour retention time, 88% destruction of chemical oxygen demand was achieved after wet oxidation of a sulphidic refinery spent caustic. The reduced sulphur compounds in the waste were oxidized completely to sulphate, thus eliminating the odour associated with this waste product. The odour was not present in samples taken as early as 5 minutes after the start of reaction. This waste is illustrative of the fact that, in the wet oxidation system, carbon-sulphur or sulphur-hydrogen bonds appear to be broken preferentially, and sulphur more readily oxidized than either carbon or hydrogen.

Advantage of this fact is taken in applying wet oxidation techniques to the problem of chemical desulphurization of coal.

Chlorinated hydrocarbon pesticide residues

In this test a 90% COD reduction was achieved after one hour's residence time. One particular component of concern in this residue was DDT. A destruction efficiency of greater than 98% was measured for DDT.

Cyanide wastes from electroplating operations

A number of different plating wastes containing up to 50,000 mg/litre of cyanide were oxidized. Oxidation occurs quite readily for all but the most resistant ferricyanides. Residual cyanide levels of less than 1 mg/litre or destruction efficiencies of greater than 99.998% were achieved.

Since the nitrogen in the cyanide appears in the effluent as ammonia, much of the cyanide destruction must, in fact, be a hydrolysis reaction. In subsequent experiments, it was shown that the reaction could be achieved with no addition of oxygen or air to the system, but just by heating the reactor up to about 230°C and maintaining that temperature for 1–2 hours. This hydrolysis process is being developed [4] and is presently the subject of a commercial demonstration being supported by the American Electroplaters' Society [5].

Wood preservative liquor

Many wood preservative liquors contain pentachlorophenol which is a toxic compound of some concern to environmental regulatory agencies around the world. Earlier work undertaken by ORF showed a reduction of 99.99% in pentachlorophenol with an equivalent overall COD reduction in the stream of 76%. In a recent study [3] we have examined both a wood preservative waste containing pentachlorophenol (PCP) and pure PCP. In this study, the effluent streams from the oxidation were examined to try to determine the nature of any breakdown product. PCP destructions of up to 99.96% were observed. Of this, 99.4% of the chlorine was accounted for as inorganic chloride ion. Trace quantities of other chlorinated organic materials were observed in GC–mass spectrometry analysis of these effluents.

PCP destruction via wet air oxidation has also been investigated in a Zimpro high-temperature, high-pressure system [2, 3]. At 320°C and 275°C, PCP removal efficiencies of 99.88% and 81.96% respectively were achieved. At 275°C, and employing a copper catalyst, PCP removal efficiency was increased to 97.30%.

Other sulphur and nitrogen containing chemicals

In addition to the work on PCP described above, work was recently undertaken on two other pure compounds as examples of organic compounds containing nitrogen and sulphur. The compounds chosen were mercaptobenzothiazole (MBT) and diphenylamine (DPA).

With mercaptobenzothiazole, a destruction efficiency of >99.99% was observed. The major by-product observed in the oxidized effluent of batch testing of MBT was nitrobenzene at a concentration of 0.03% of the original MBT. Traces of azobenzene, aniline and azoxybenzene were also observed.

In tests run in the continuous-flow pilot plant, rather high concentrations of aniline and nitrobenzene were observed in the vapour phase effluent from the reactor. These compounds are steam strippable, and it would suggest that, since only trace quantities of aniline were observed in the batch reactor effluent, had the aniline not been stripped from the reactor, it would have further oxidized to nitrobenzene and other products.

The wet oxidation of pure diphenylamine indicated a >99.99% reduction

in DPA. Traces of aniline, nitrobenzene, azobenzene, dimethylazobenzene and chloro-aniline were detected by GC/MS in the effluent from the batch oxidation tests. In the continuous flow tests carried out on DPA, aniline and nitrobenzene were again detected in the vapour phase effluent from the reactor in quantities equivalent to $\sim 20\%$ of the original DPA in the influent to the reactor.

In a programme to be undertaken later, Ontario Research will be examining vapour phase catalysis as a means of "polishing" the destruction of steam strippable components in the vapour phase effluent from a continuous flow Wetox reactor.

Commercial installation

As was mentioned previously, a first commercial Wetox system has been installed in 1982 at a chemical company in Ontario. This treats a number of different waste streams, many of which contain compounds which would be regarded as hazardous or toxic. There are many different effluent streams from the plant, only some of which are treated by Wetox. Figure 4 shows a simplified diagram of how Wetox fits the overall treatment process for this plant, or more generally to any plant with a wide variety of waste streams containing different types of concentrations of contaminants. All concentrated waste streams are processed by Wetox. The effluent from the Wetox reactor may be combined with dilute plant waste streams which contain low concentrations of toxic contaminants. This combined waste stream may then be treated by activated carbon. The effluent from the activated carbon treatment is combined with any other dilute waste streams which do not

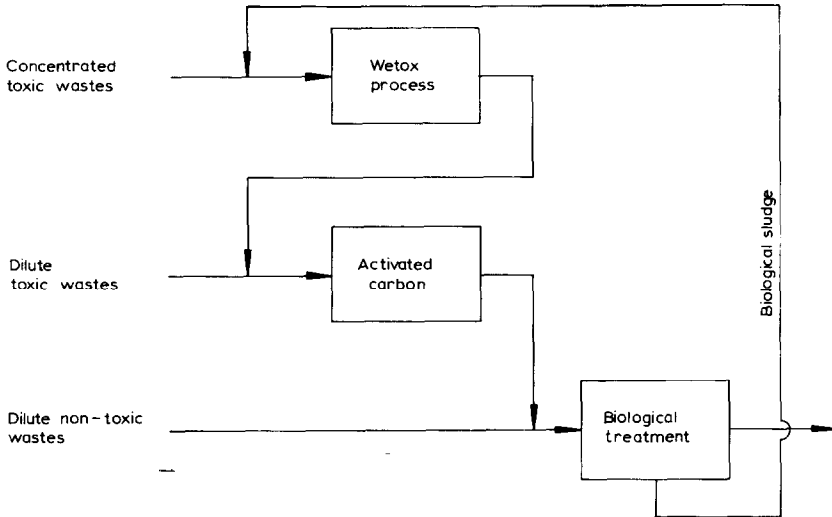


Fig. 4. Toxic waste treatment system.

contain toxic contaminants, and these are either seweraged or treated biologically on site as illustrated in Fig. 4. If the biological treatment process is located on site, the excess sludge produced can be returned for processing through the Wetox reactor.

Acknowledgment

The financial support of Environment Canada for the work on PCP, MBT and DPA is gratefully acknowledged.

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