

## Supercritical Water-A Medium for Chemistry.

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TOC = Total Organic Content

COD = Chemical Oxygen Demand

Punto critico dell'acqua: 374 °C and 22.1 MPa.

As the temperature of a liquid is increased, it becomes less dense due to thermal expansion. Above 380 °C, the density of water decreases very rapidly up to 410 °C. Beyond 410 °C, the rate of decrease of density decreases.

The dielectric constant of water decreases with decreasing density. Supercritical water behaves almost as a nonaqueous fluid dissolving nonpolar compounds like alkanes, aromatics, etc. In general, organics are completely miscible in water under supercritical condition, while inorganics like NaCl are practically insoluble. The residual solubility of NaCl in supercritical water is of the order of 100 mg/L. Strong electrolytes behave as weak electrolytes in supercritical water. Oxygen is also completely miscible in all proportions in supercritical water [Pray et al. (1952) and Japas and Franck (1985)].

The reduced effect of hydrogen bonding is responsible for the change in solubility properties of supercritical water. Hydrogen bonding is a weak force, and its effect decreases with a decrease in the density of water under supercritical conditions. Cochran et al. (1991), on the basis of spectroscopic and computer simulation studies, found that the number of hydrogen bonds per water molecule under supercritical conditions is about one third the number at ambient conditions. At constant density, as the temperature is increased, the dielectric constant decreases due to the breakage of hydrogen bonds. Water is still associated, and the association strongly depends upon pressure and temperature under supercritical conditions. This association influences the solubility phenomena, the reaction chemistry, and the corrosion.

In case of SCWO, the pressure may play a more important role since the density of supercritical water varies greatly with the pressure at a given temperature [Li et al. (1991)]. The pressure effect on the rate constant can be expressed as

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^\ddagger}{RT}$$

where  $k$  = rate constant, unit dependent on the overall reaction order;  $\Delta V^\ddagger$  = volume activation ( $\text{cm}^3/\text{mol}$ );  $R$  = gas constant,  $82.05 \text{ (atm}\cdot\text{cm}^3)/(\text{mol}\cdot\text{K})$ ;  $T$  = temperature (K), and  $P$  = pressure(atm).

Supercritical water is highly corrosive particularly if halogenated compounds are present. This necessitates the use of expensive special alloy reactors. One economic solution is to use a normal carbon steel reactor lined with corrosion-resistant alloy. The problem in that case may be the detection of leaks.

can be solved by the use of a thin insert of corrosion-resistant metal/alloy (such as titanium, zirconium, or Inconel) not fitting to the wall of the carbon steel pressure vessel. The space between the two is filled with a high-temperature heat transfer fluid. The insert is designed so that it can expand toward the pressure vessel wall when pressurized. The heat transfer fluid balances the pressure, while its electrical properties can be monitored to indicate leaks.

Another problem faced is the precipitation of salts formed during the reaction resulting in severe plugging of the reactor system within a few minutes of operation.

Various reactor designs/modifications have been reported to take care of these problems. Huang et al. (1992) describe a vertical cylindrical reactor with internal rotatable scraper blades for supercritical water oxidation of wastewater.

The oxidized effluent is withdrawn from the top while aqueous brine slurry is discharged from the bottom. The scraper blades dislodge solid deposits from the bottom.

Huang et al. (1992) introduced the oxidant and wastewater into the upper region of the reactor to establish the downward flow of subcritical fluid through the supercritical zone along the inside surface of the vessel wall. The downward flow of subcritical fluid prevented the deposition of the precipitate formed during oxidation.

Inorganic salts, insoluble under supercritical conditions, are dissolved in liquid water during the cooling of effluent mixture at the outlet of the reactor. Other insoluble matter can be separated by filtration.

The Modar process is quite similar to the wet air oxidation process. The organic waste (either an aqueous solution or a slurry) is pressurized to the reactor pressure and pumped in the reaction vessel. Oxygen is also pumped to the reactor.

When the waste contains a heteroatom which will produce mineral acid, caustic may be injected as a part of the feed stream to neutralize the acid formed.

In order to ensure rapid completion of the oxidation reaction, part of the effluent from the reactor is mixed with the feed stream to raise its temperature to a sufficiently high value. The remaining part of the effluent is fed to a cyclone. The inorganic salts precipitate out and are separated. The effluent, still at very high temperature and pressure, is used for energy recovery. The gas stream can be expanded through a turbine to extract the available energy as power. The Modar process has been reported to be energetically self-sustaining at 2% organic concentration in the feed, and excess energy can be recovered in the form of steam at higher feed organic concentrations.

In general the destruction efficiencies of pollutants are of the order of 99-99.9% at 400-500 °C in 1-5 min residence time. Higher destruction efficiencies of pollutants (of 99.9999%) are achievable at 600-650 °C even with residence times of the order of seconds. The oxidation end products are CO<sub>2</sub> and simple acids (in the case of halogenated organics), and the final effluent is so innocuous that it can be discharged without any further treatment. The gaseous effluent is also clean. Carbon monoxide is at the most a few parts per million. Nitrogen-containing compounds are converted to N<sub>2</sub> and N<sub>2</sub>O under supercritical water oxidation conditions. Nitrous oxide (N<sub>2</sub>O) can be eliminated by performing the oxidation at higher temperature. If the oxidation temperatures are lower (400-500 °C), ammonia may form as intermediate which has been found to oxidize to N<sub>2</sub> at higher temperature (600 °C).

For this purpose a number of WAO studies have been performed on the aqueous solutions of several pure compounds (important model pollutants) and wastewaters containing toxic and hazardous compounds. Wet air oxidation of aqueous solutions of phenols and carboxylic acids has been studied in great detail with emphasis on the kinetics and mechanism of wet air oxidation.

The slow rate of oxidation of low molecular weight carboxylic acids is a major limitation of the WAO technique. In view of this the understanding of WAO of low molecular weight carboxylic acid achieves great significance.

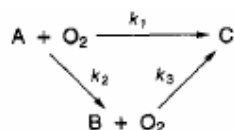
The use of homogeneous and heterogeneous catalysts (particularly copper salts) has received a great attention.

It is important to use catalyst systems which are stable and do not get leached away in the solution by reacting with acids present. This is the case when CuO is used as the catalyst.

Copper sulfate and copper nitrate have been used as homogeneous catalysts for the oxidation of carboxylic acids. The heterogeneous catalysts used include transition as well as noble metals. The various heterogeneous catalysts that have been used are Cu, Pd, CoO/ZnO (6.5: 82.9, Cu:Mn:La oxides (4:2:1) supported on a spinel support (ZnO and Al<sub>2</sub>O<sub>3</sub>, 48.5 and 51.5%, respectively),

copper chromite, iron oxide, Co:Bi (51) complex oxides, RdCe, and Mn/Ce. Of the various catalysts studied, the multicomponent catalyst systems like Co:Bi, Cu:Co, Cu:Co:Bi, and Ru/Ce were considerably more active than other catalysts (except Mn/Ce catalyst). Co:Bi (51) was found to be the most active one [Imamura et al. (1982a,b 1988)]. Activity of Co:Bi catalyst was due to the presence of basic sites on the catalyst surface on which acetic acid is adsorbed. This is followed by a redox reaction between catalyst and adsorbed acetic acid to induce its decomposition.

The organics in the effluent from a WAO system can be divided into three groups [as by Li et al. (1991): all initial and relatively unstable intermediates except acetic acid (group A), refractory intermediates like acetic acid (group B) and oxidation end products (group C). A schematic pathway is given below:

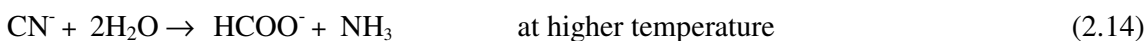


It has been observed by the authors that, in addition to acetic acid and other oxidation end products, significant quantities of solid carbonaceous materials are also formed during WAO of several waste streams. This solid carbonaceous material undergoes oxidation in the same manner as the activated carbon during its wet air oxidative regeneration (section 3.5). This aspect of formation and subsequent oxidation of solid carbonaceous material during WAO of waste streams should be incorporated in the model of Li et al. (1991).

Oxidation of phenol by molecular oxygen has been proposed to be an electrophilic reaction. The reaction between aryloxy radical with oxygen was considered to be the rate-limiting step. They observed the following order of reactivity for the phenols studied:

Phenol and chlorophenols exhibited an induction period, the length of which depended on the oxygen partial pressure, followed by a fast reaction step. In the case of methoxyphenols, the induction period was absent. The methoxyl group favors the formation of aryloxy radical by increasing the electron density on the aryl ring. This results in increased oxidation rate, and thus there is no induction period. Oxidation of alkyl group occurs much more readily compared to that of the ring resulting in the rapid formation of radicals. Due to this, oxidation of alkylphenols is characterized by an initial fast reaction period followed by a slow reaction period.

Decomposition of cyanide ion occurs even in the absence of oxygen as per the following equations



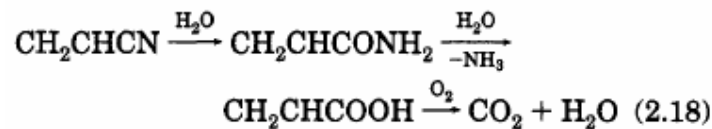
or



Thus under the conditions of high temperature prevailing during WAO, the destruction is mainly by hydrolysis. In the presence of oxygen and even in the presence of traces of Ni or iron oxides, NaCN is oxidized as



Acrylic acid was found to oxidize directly to carbon dioxide and water.



They assumed the sludge to be consisting of (i) solid matter, X, (ii) soluble nonevaporative matter at 120 °C, Y; (iii) soluble evaporative matter at 120 °C, Z; and water. The weight and COD of X, Y, and Z are state variables and the model can be represented as



no corrosion (almost generally) appears in the supercritical region the corrosion is most severe between 270 - 390 °C

SCWO has been applied to a broad range of materials, e.g., aqueous waste streams, sludges, contaminated soils, industrial organic chemicals, plastics, synthetics, paints and allied products, industrial organics, agricultural chemicals, explosives, petroleum and coal products, and rubber and plastic products. It is applicable to the treatment of a range of contaminants

including acrylonitrile wastewater, cyanide wastewater, pesticide wastewater, PCBs, halogenated aliphatics and aromatics, aromatic hydrocarbons, MEK and organic nitrogen compounds [3].

Methods to destroy polychlorinated biphenyls (PCBs) are facing unusually challenging problems due to the very high chemical stability and low water solubility of these compounds

(Hutzinger et al., 1983; Bolgar et al., 1995; D. O. Carpenter, 2000). For example, incineration of PCBs generates very harmful products such as polychlorinated dibenzofurans/dioxins (PCDFs/Ds) and because PCBs themselves result from incineration of chlorinated pollutants and have been used as fire retardant, this method is inappropriate for PCB destruction.

Supercritical water oxidation (SCWO) of organic compounds is drawing much attention due to attractive features such as cleanness, quickness, and the potential to effectively destroy a large variety of industrial and high-risk wastes.

Some stable products of PCB SCWO such as PCDDs/Fs, formed under certain conditions, are more hazardous than the starting material and their formation is a factor to consider in the design of SCWO reactors.

When recycling paper, de-inking sludge is received as a by-product. This sludge contains about 3% organic material, mainly fibres, and 3% inorganic material, mainly paper filler. The ability of SCWO to destroy the organic material in this sludge completely has been proven elsewhere [2,3]. In addition to the destruction of organic matter, the industry has an interest in recycling the paper filler after the SCWO treatment.

wastewater which was produced in a process for amine manufacturing. The waste contains ammonia and short chain amines and gives a nitrogen rich water containing almost as much total nitrogen (Tot-N) as total organic carbon (TOC), about 15 000 to 20 000 mg/l.

Although SCWO has been demonstrated to be effective for the destruction of most organic compounds, little success has been achieved in the complete destruction of ammonia or nitrogen in highly nitrogen containing wastes. However it is known that it is possible to destroy ammonia if the ratio of total organic carbon (TOC) and total nitrogen (Tot-N) in the wastewater is high [11,12]. If this ratio is low it is not possible to destroy all ammonia with oxygen but it is shown elsewhere [13,14,15] that it is feasible to destroy the ammonia using nitric acid for the oxidation.

Effluent from the pulping mill generated after cooking of wood or other suitable raw material is termed as black liquor due to its color. It is highly organic in nature and contains organic matter in the form of suspended solids, colloids, BOD, COD, sulfur compounds, pulping chemicals used, organic acids, chlorinated lignins, resin acids, phenolics, unsaturated fatty acids, terpenes, etc.

Cyanides are present in discharges from the electroplating industry, extraction of metals, coke furnaces, petroleum refineries, etc. Sodium cyanide is used in manufacture of pharmaceutical, agrochemical, and dye intermediates. The effluents from these industries contain unreacted cyanides. Among nitriles, effluent from acrylonitrile manufacturing plant has attracted attention because of its high toxicity due to the presence of acrylonitrile, acetonitrile, acrolein, inorganic cyanides, and ammonium sulfate along with large concentration of other organics.

WASTE	SCWO REACTANTS	→	SCWO PRODUCTS
Cellulose	$C_6H_{10}O_5 + 6O_2$	→	$6CO_2 + 5H_2O$
Methane	$CH_4 + 2O_2$	→	$CO_2 + 2H_2O$
Benzene	$C_6H_6 + 7.5 O_2$	→	$6 CO_2 + 3 H_2O$
Dioxin (PCDD)	$Cl_2-C_6H_2-O_2-C_6H_2-Cl_2 + 11 O_2$	→	$12 CO_2 + 4 HCl$
Chloroform	$CHCl_3 + 0.5 O_2 + H_2O$	→	$CO_2 + 3 HCl$
TNT	$CH_3-C_6H_2-(NO_2)_3 + 5.25 O_2$	→	$7 CO_2 + 2.5 H_2O + 1.5 N_2$
Ferrous Chloride	$FeCl_2 + 0.25 O_2 + H_2O$	→	$0.5 Fe_2O_3 + 2 HCl$
Nerve Agent HD	$Cl-C_2H_4-S-C_2H_4-Cl + 7 O_2$	→	$4 CO_2 + 2 H_2O + 2 HCl + H_2SO_4$

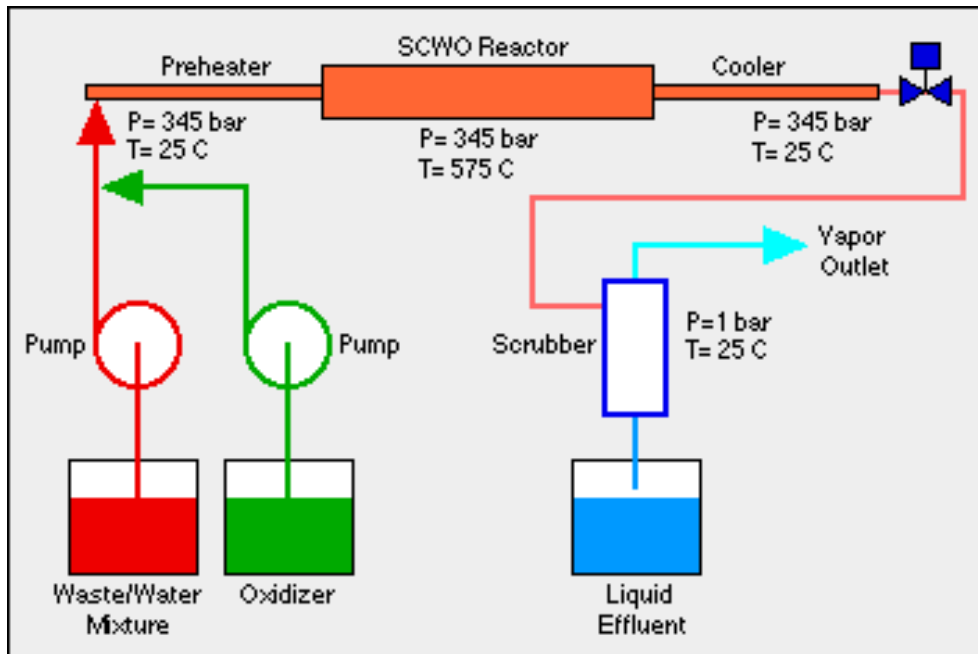
### Special Engineering Requirements of SCWO Processing Systems:

Unless catered for by careful engineering design, the high-temperature environment within SCWO reactors and processing systems can present significant reliability and performance problems, as discussed below.

Experience has shown that corrosion rates can be rapid when treating wastes containing halogens, such as chlorine. Corrosion-resistant alloys such as Hastelloy C-276 and Inconel 625 do not provide adequate protection against chloride attack under the oxidizing conditions found in SCWO systems. In recent years, SCWO reactors have been built using liners fabricated from titanium alloys. These have shown increased resistance to chloride attack. However, these reactors are limited to approximately 650 C maximum reaction temperature due to mechanical strength limitations of the pressure vessel wall.

The aqueous solubility of salt decreases sharply at supercritical pressures when the temperature rises above the critical temperature. If salts are present in the waste feed, or formed during processing, they will precipitate from solution wherever local temperatures exceed the critical temperature. Other relatively insoluble solid compounds, such as carbonates and metal oxides, are also commonly formed during SCWO processing. Undissolved solids are often present in the waste stream. Unless these solids are effectively transported through the supercritical regions or otherwise removed from the process, accumulations will form and total plugging of the reactor can occur. Furthermore, significantly higher corrosion rates have been observed beneath deposited solids. It is essential to control any tendency for solids to accumulate.

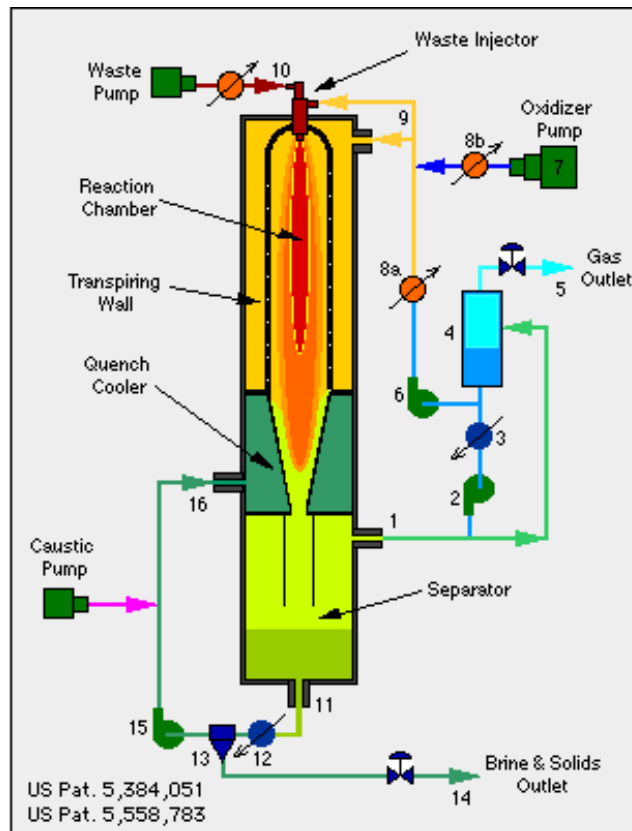
Wastes containing halogenated species and solids are practically a "fact-of-life" for SCWO waste treatment systems and most other waste treatment technologies. Traditional tubular or vat-type SCWO reactors have been incapable of addressing these problems in realistic plant applications.



Summit Research has developed a novel SCWO reactor designed to handle corrosive species and solids in a straight-forward manner utilizing proven engineering principles. (Transpiring-Wall SCWO Reactor)

In traditional SCWO processing systems the entire water effluent stream is depressurized and subsequently disposed of or treated for re-use by the process at ambient pressure. We have developed a proprietary closed-cycle process that separates and recovers water for the process at full system pressure. (Closed-Cycle SCWO Process)

Traditional SCWO processing systems utilize shell & tube type heat exchangers which are prone to plugging and corrosion. Our system utilizes an open quench-cooled heat exchanger where cooling is achieved by directly mixing cooled liquid effluent with the hot reactor byproducts. This ensures that solids are heavily diluted and flushed from the system. It is also a more compact heat exchanger for high latent heat load applications. The cooled liquid effluent can be treated with caustic and other additives to control corrosion, effluent pH, solids, and composition of all effluent streams. (Closed-Cycle SCWO Process)



Closed-Cycle SCWO Processing System

### Operating Pressures for SCWO Processing

Traditional SCWO processing systems are designed to operate at pressures in excess of the critical pressure of water ( $P > 220.55$  bar). Traversing a supercritical isotherm from, say, 250 bar to lower pressure, the corresponding changes in physical properties of the reactants and byproducts are only gradual in nature. This suggests that a continuum of reactor operating points may exist along any supercritical isotherm. Recent investigations at Sandia National Laboratory [1] indicate that methane oxidation rates at 135 bar are significantly faster than at 270 bar, as follows;

As for sustainability of the fundamental reaction mechanism of the Transpiring-Wall SCWO Reactor to lower pressures, Sandia National Laboratory [1] has observed diffusion-type hydrothermal oxidation reactions to pressures as low as 15 bar.

The Transpiring-wall SCWO reactor and Closed-Cycle Processing System is designed to operate and handle solids in a straightforward manner at all pressures, down to densities far below the critical pressure of water. This capability allows exploitation of improved reaction kinetics that may exist for some materials at subcritical pressures.

Obviously, at lower pressures the costs for process equipment and compression is significantly less than at supercritical pressures.