INNSPUB

Journal of Biodiversity and Environmental Sciences (JBES)
ISSN: 2220-6663 (Print) 2222-3045 (Online)
Vol. 14, No. 5, p. 53-70, 2019
http://www.innspub.net

RESEARCH PAPER
OPEN ACCESS

Supercritical water oxidation (Scwo) technology

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Article published on May 30, 2019

Key words: Population, Generation, Organics, Oxidation, Environment.

Abstract

As the World's population continues to grow, technology must be developed to treat wastes of all kinds, and at the same time the energy demand of this increasing population must be met. In both cases waste treatment and energy conversion must be performed with increasing attention to air and water quality on the Earth. Supercritical water oxidation (SCWO) systems have the potential to address these problems in an environmentally sound way. Supercritical water oxidation (SCWO) is a promising technology for destroying highly toxic organic compounds present in aqueous waste streams. Capitalizing on the properties of water in the supercritical, spontaneous and rapid oxidation of hydrocarbons is obtained with a very high efficiency, forming water, carbon dioxide, and depending on the species of heteroatom present in the organic wasteone or more acids. The extreme operating conditions (i.e., the presence of acids under highly oxidizing conditions in SCWO feeds, high temperatures and high pressures), however, require identification and development of constructional materials that are capable of withstanding such an environment. By capitalizing on the properties of water above its critical point (374°C and 22.4 MPa for pure water), supercritical water technology can potentially be exploited for both waste destruction and energy generation. In the first case, supercritical water oxidation (SCWO) provides rapid and complete oxidation of organics, including chemical nerve agent, with high destruction efficiencies at typical operating temperatures.

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Introduction

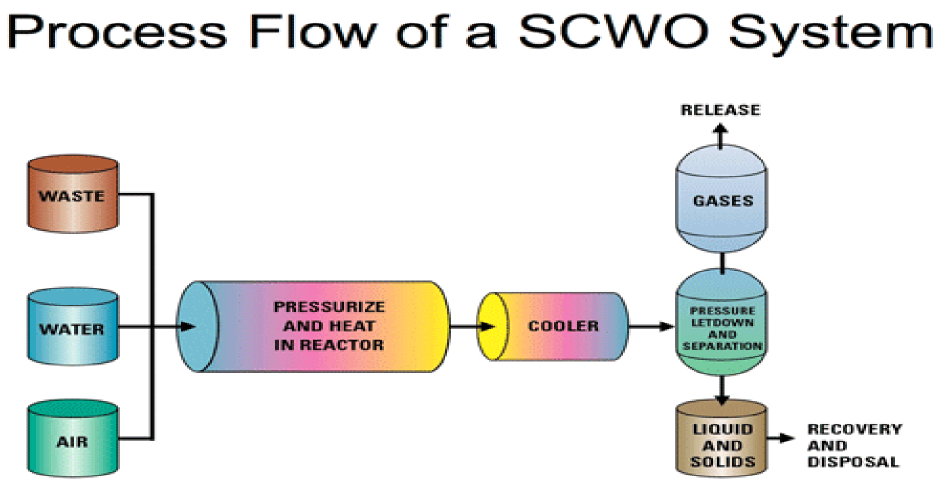
Treatment of toxic and dangerous wastes has become a very important topic for environmental protection. It is necessary to combine chemistry and environmental engineering for searching new technologies for the disposal of toxic wastes. An important part of these wastes are composed of water and are indexed as aqueous wastes. Many aqueous waste products cannot be destroyed by biological treatment, and several industrial waste waters containing highly toxic substances are difficult to dispose of. When their organic content is more than 1%, they are too concentrated to undergo a biological treatment, while, when it is less than 10%, their treatment by incineration is too expensive because it requires extra-gas (Foucault *et al.*, 2009).

New processes have to be found for the treatment of effluents containing up to 10% waste chemicals. Supercritical water oxidation (SCWO) is such an end-of-pipe process in which the organic chemicals in waste waters or sludges could be completely destroyed or converted into harmless product.

With the development of the modem industry, there is in excess of 400 billion tons of sullage, 3 billion tons of solid contamination that are drained into the environment every year. So it is an urgent need to search for an efficient and safe waste handling method. Supercritical water oxidation (SCWO) is an emerging technology to process many organic wastes and has been shown to have several benefits to handling dilute wastes in the range 1 wt%-20 wt% which are not suitable for disposal by either incineration or landfill.

Supercritical water oxidation

Supercritical water oxidation (SCWO) is a high temperature and pressure technology that uses the properties of supercritical water in the destruction of organic compounds and toxic wastes. Under supercritical conditions, carbon is converted to carbon dioxide; hydrogen to water; chlorine atoms derived from chlorinated organic compounds to chloride ions; nitro-compounds to nitrates; sulfur to sulfates; and phosphorus to phosphate (Foucault *et al.*, 2009).



For many toxic and hazardous wastes, the alternatives for safe disposal are becoming very limited. Deep well injection, open burning, and incineration are either restricted or completely unavailable in many areas and have become costly where they are still options. Supercritical water oxidation (SCWO) presents an economic alternative to these methods for many waste disposal applications (Environment Australia, 1997).

Technology description

Supercritical water oxidation (SCWO) is a high temperature and pressure technology that uses the properties of supercritical water in the destruction of organic compounds and toxic wastes. Under supercritical conditions, carbon is converted to carbon dioxide; hydrogen to water; chlorine atoms derived from chlorinated organic compounds to chloride ions;

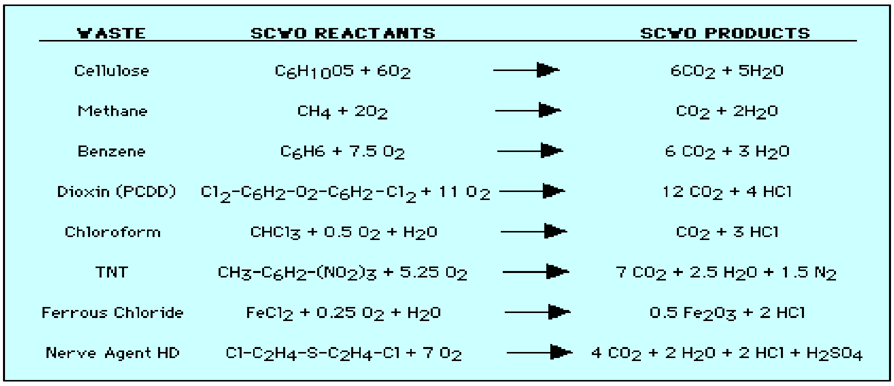
nitro-compounds to nitrates; sulfur to sulfates; and phosphorus to phosphate (Environment Australia, 1997; Foucault *et al.*, 2009). The unique properties of super critical water are the key to the operation of this process. Gases including oxygen and organic substances are completely soluble in super critical water, whereas inorganic salts exhibit greatly reduced solubility under process conditions. Organic substances dissolve in the super critical water, and oxygen and the organic substances are brought into intimate single phase contact at temperatures and molecular densities that allow the conventional oxidation reactions to proceed rapidly to completion. Process residues are contained and consist of water, gas and solids if the waste contains inorganic salts or organics with halogens, sulfur or phosphorous. The effluent gases contain no oxides of nitrogen or acid gases such as hydrogen chloride or sulfur oxide. The process generates no particulates and less than 10 ppm carbon monoxide has been measured (Environment Australia, 1997).

Chemistry of supercritical water oxidation

Chemical reactions in supercritical water oxidation (SCWO) processing systems obey the laws of mass, charge, energy and elemental conservation.

At supercritical conditions, the reactions proceed as gas-phase free-radical reactions involving the formation of a variety of intermediary species and related sub reactions as the reaction proceeds to completion. The following global stoichiometric relationships apply to complete oxidation of the listed waste compounds.

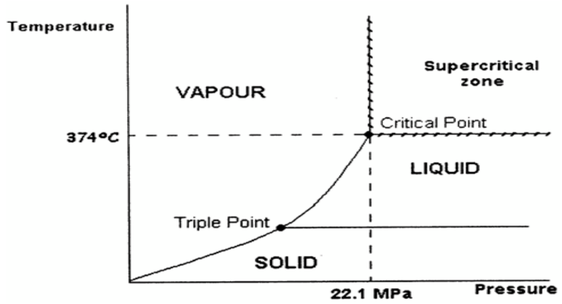
Oxidation of halogenated or sulfur-bearing compounds results in the formation of hydrochloric acid and sulfuric acid, respectively, which can cause corrosion of the reactor and processing system unless steps are taken to mitigate these effects. Base neutralization of these acids produces salts which can form solid precipitates under supercritical conditions (Environment Australia, 1997).



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

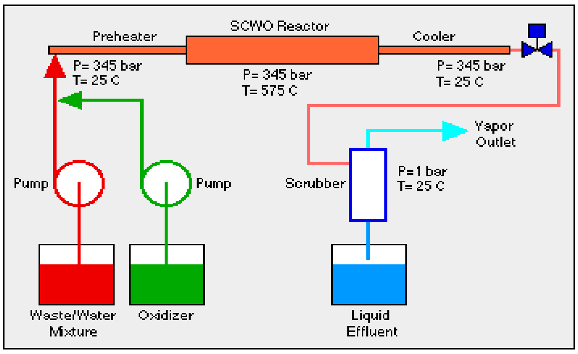
The properties of water in the supercritical regime

The properties of pure water change dramatically as its critical point (647K, 22.1 MPa) is approached. At the critical pressure, there is no constant-temperature vaporization process. The critical point implies that the saturated liquid and saturated vapor states are identical (i.e., at pressures above the critical pressure we never have a liquid and vapor phase of a pure substance existing in equilibrium). Under supercritical (SC) conditions, the density of water is approximately 100kg m-3, between that of liquid (1000kg m-3) and low-pressure vapor (<1kg m-3) water. Near the critical point, these drastic changes in the density of water correlate directly with drastic changes in its solvation properties. Waters ability to shield charge diminishes as its dielectric constant decreases from 80 at ambient conditions to ~2 at 25MPa and 673K. At the same time, the ionic dissociation constant decreases from 10 -14 at room temperature to 10-23 at SC conditions. Consequently, low-density SCW acts as a non-polar dense gas with solvation properties approaching those of a low-polarity organic. Hence, supercritical water (SCW) exhibits high solubility's for non-polar organic compounds and non-condensable gases. For example, benzene (C6 H6) is completely miscible in water above 573 K and 25MPa over all concentrations, Gases such as oxygen (O2), nitrogen (N2), carbon dioxide(CO_2) and methane (CH_4) are also completely miscible in supercritical water (SCW). Conversely, the solubility of inorganic salts is very low in supercritical water (SCW). For example, the solubility of NaCl in water at 25MPa drops from about 37 wt% at 298K to only 120 ppm at 823K (Eliaz *et al.,* 2003).



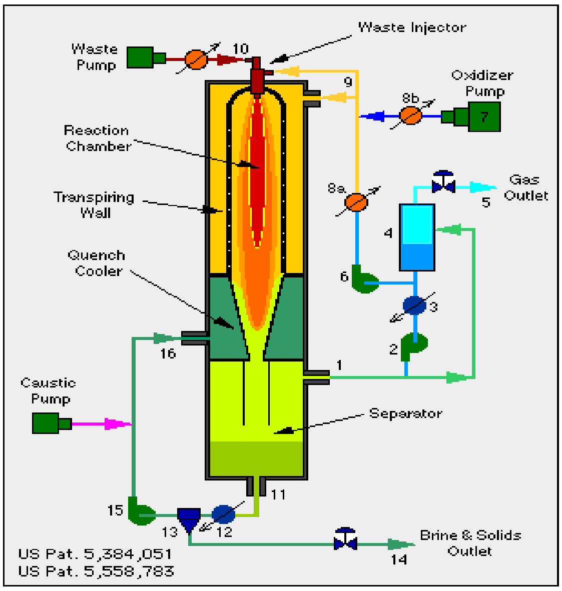
Special engineering requirement of supercritical water oxidation (scwo) processing systems

Unless catered for by careful engineering design, the high-temperature environment within supercritical water oxidation (SCWO) reactors and processing systems can present significant reliability and performance problems. 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 supercritical water oxidation (SCWO) systems. In recent years, supercritical water oxidation (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 temperatures 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 supercritical water oxidation (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 supercritical water oxidation (SCWO) waste treatment systems and most other waste treatment technologies. Traditional tubular or vat-type supercritical water oxidation (SCWO) reactors have been incapable of addressing these problems in realistic plant applications (Shaw *et al.,* 1991).



Summit research has developed a novel supercritical water oxidation (SCWO) reactor designed to handle corrosive species and solids in a straight-forward manner utilizing proven engineering principles (Transpiring-Wall Supercritical Water Oxidation Reactor (SCWOR) (Shaw *et al.*, 1991).

In traditional supercritical water oxidation (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 as shown below. (Closed-Cycle SCWO Process) Traditional supercritical water oxidation (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 by products. 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 (Shaw *et al.*, 1991).

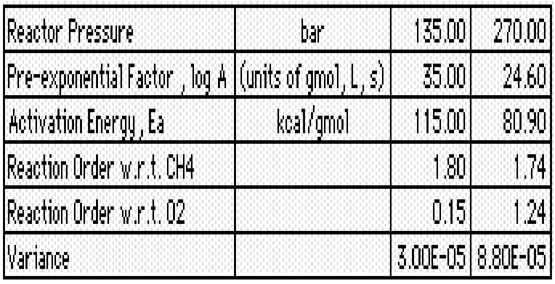


Operating pressure for supercritical water oxidatio (scwo) processing

Traditional supercritical water oxidation (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 by products 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 (Steeper *et al.*, 1996) 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 supercritical water oxidation (SCWO) Reactor to lower pressures, Sandia National Laboratory (Steeper *et al.*, 1996) has observed diffusion-type hydrothermal oxidation reactions to pressures as low as 15 bar.

The Transpiring-wall supercritical water oxidation (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.



Reactor Pressure	bar	135.00	270.00
Pre-exponential Factor , log A	(units of gmol, L, s)	35.00	24.60
Activation Energy, Ea	kcal/gmol	115.00	80.90
Reaction Order w.r.t. CH4		1.80	1.74
Reaction Order w.r.t. O2		0.15	1.24
Variance		3.00E-05	8.80E-05

Characteristic of the supercritical water oxidation (scwo) process

This is a promising technology applicable to many dilute organic wastes (Tester *et al.*, 1993; Frank, 1976) As the critical point is approached, the density of water changes rapidly as a function of changes in either temperature or pressure. In this regime, the density is intermediate between that of liquid water (1g cm-3) and low-pressure water vapor (<0.001g cm-3). Typically at supercritical water oxidation (SCWO) conditions, the water density is approximately 0.1g cm-3 and, consequently, the properties of supercritical water are significantly different from those of liquid water at ambient conditions. The dielectric constant of water at 25 MPa drops from approximately 80 at room temperature to 2 at 450°C, and the ionization constant decreases from 10-14 at room temperature to 10-23 at supercritical conditions. These changes result in supercritical water acting essentially as a nonpolar dense gas with solvation properties approaching those of a low-polarity organic. Under these conditions, hydrocarbons generally exhibit high solubility in supercritical water and conversely the solubility of inorganic salts is very low. The solubility of NaCl, for example, drops from about 37 wt% at 300°C to only 120 ppm at 550°C. The combination of the solvation and physical properties makes supercritical water an ideal medium for the oxidation of organics. When organic compounds and oxygen are dissolved in water above the critical point, kinetics are fast and the oxidation reaction proceeds rapidly to completion. While the products of hydrocarbon oxidation are CO_2 and H_2O, heteroatoms are converted to inorganic compounds (usually acids, salts, or oxides in high oxidation states). As a result of the relatively low temperature of operation, NOx and SO_2 are not produced (Tester *et al.,* 1993). The latter may be particularly important during the destruction of explosives, which produce nitrogen oxides during incineration (lajeunesse *et at*., 1994).

Advantages of supercritical water oxidation (scwo) technology

Advantages of supercritical water oxidation (SCWO) technology are following (jay, 2004).

- Complete destruction of harmful organic chemicals (toxic materials, waste water, sludge)
- High space-time yield (rapid oxidation in homogeneous phase)
- Oxidation produces carbon dioxide and water
- No production of nitrogen oxides, NOxB : low temperature incineration B
- Hetero-atoms are mineralized
- TWR can handle solids and salts containing waste streams

Corrosion problem in supercritical water oxidation (scwo) system

The major disadvantages of supercritical water oxidation (SCWO) revolve around high pressure (P > 23 MPa), potential solids handling problems and for some waste streams, corrosion (Tester *et al.*, 1994). Although supercritical water oxidation (SCWO) is technologically able to destroy hazardous wastes, the process must be carried out in a reactor capable of accommodating elevated temperatures, pressures and potentially, a very aggressive environment. The degradation behavior of various potential materials of fabrication is covered within this section.

The formation of acids may lead to corrosion (Schacht *et al.*, 1998; Kritzer *et al.,* 1998), the formation or the presence of salts to plugging (Abeln *et al.*, 2000) and many attempts have been made to solve the corrosion problem, e.g. by engineering, constructive or material means or by process control, also documented in the recent patent literature (Hong, 1999). At ITC-CPV, R&D is focused to the most promising engineering solution of the salt problem, the transpiring wall reactor concept, first developed in the US (Ahluwalia, 1996).

Iron –base alloys

In general, except for innocuous feed streams, alloys such as 316-L is unlikely to be employed during fabrication of a supercritical water oxidation (SCWO) waste treatment unit. Such alloys have generally been included in a test matrix as a baseline material. Nevertheless, recent results suggest that a high chromium iron-base material (50% Cr) may exhibit reasonable behavior even for an acidic chlorinated influent. Results are however, of a preliminary nature and a significant amount of research would need to be done in order to confirm this trend. Although selected feed streams may be innocuous enough to permit the use of AISI 316-L stainless steel, processing would need to be restricted to low halogen, moderate pH influents (Tebbal and Kane 1998) When exposed to deionized water with in the temperature range 300-500°C, 316-L may reveal general corrosion and excel lent overall per formance (Tebbal and Kane 1998) or, alternatively, localized effects such as pitting (Boukis *et al.*, 1997). Inter granular bcorrosion (300°C) or crevice corrosion (500°C) (Kim *et al.*,2000) may be seen. Within a restricted pH range (˜2-11) and for an influent with minimal Cl, 316-L may exhibit reasonable performance (Tebbal and Kane 1998) and a uniform corrosion rate as low as 0.035 mmpy (Boukis *et al.*, 1997).

However, even for a restricted Cl feed, SCC may be observed at higher pH values (pH>12) (Tebbal and Kane 1998). When exposed to sludge, to a maximum test temperature of 425°C, 316L exhibited pitting and crevice corrosion in both the subcritical and supercritical regions. For the same conditions, Alloy 20CB3 also displayed a high susceptibility to pitting, while Alloy 2205 reportedly exhibited good resistance except at attachment points, which revealed crevice corrosion (Thomas and Gloyna 1991). When exposed to a highly chlorinated organic feed stream (0.3 wt % chloride) at 600°C, weight loss data indicate a corrosion rate on the order of 50 mmpy and SCC for both stressed (U-bend) and While these data apparently agree with the general concept that corrosion resistance improves with increasing Cr content,results are preliminary and need to be confirmed by further testingnon-stresses 316-L samples. Ferralium 255 revealed a much lower corrosion rate (18 mmpy) (Mitton *et al.*, 1996); however, degradation was an isotropic and more pronounced in the ferrite phase (Mitton *et al.*, 1999). When tested in chlorinated acidic conditions a new Cr-Fe alloy, Ducrolloy (50% Cr, 44% Fe), apparently exhibited good corrosion resistance for exposure times up to 400 hours (Konys *et al.,* 1999).

Nickel-base alloys

There tends to be a more extensive database for this class of alloys than for others. This likely results as high-nickel materials are frequently recommended for severe service applications (ASM Handbook, 1987) and have, therefore, been utilized during fabrication for a number of bench-scale and pilot plant reactors. Not with standing this, the current database suggests that these materials may not be able to handle very aggressive supercritical water oxidation SCWO feed streams (Downey *et al.*, 1995; Latanision and Shaw 1993; Tebbal and Kane 1998; Kim *et al.*, 2000; Orzalli, 1994; Mitton *et al.,* 2000) as they may exhibit significant weight loss and localized effects including pitting, stress corrosion cracking (SCC) and dealloying in aggressive environments.

In deionized water at elevated temperatures (˜450-500°C),the general trend, even after extended exposure (˜150-240 hours), is toward the formation of a potentially protective film for both alloy-625 (Boukis *et al.*, 1997; Kim *et al.*, 2000) and C-276 (Kim *et al.*, 2000). Nevertheless, even for such innocuous conditions, both minor pit development (Kim *et al.*, 2000) and grain boundary carbide formation (Wozaldo and Pearl 1965) have been observed for alloy 625. As early as 1990 (Bramlette *et al.,* 1990), dealloying of Cr and Mo (I-625) or Cr, Mo and W (C-276) was recognized as a potential contributor to degradation within supercritical water oxidation (SCWO) systems. Based on effluent analysis, results suggested loss of chromium for no chlorinated feeds, while selective dissolution of the main alloying element, Ni, was apparent for chlorinated feeds (Rice and steeper 1998). Corroboration was subsequently provided (Latanision, 1995; Mitton *et al.,* 1996) by metallographic examination during analysis of a failed C-276 supercritical water oxidation (SCWO) preheater tube, which, for acidic chlorinated conditions, revealed severe depletion of Ni. Interestingly, this analysis also indicated that the most severe corrosion was associated with a high subcritical temperature (Mitton *et al.,* 1996) and that, at supercritical conditions, in the absence of salt precipitates, corrosion may actually be minimal for alloys such as C-276 (Mitton *et al.*, 1998). Recently the concentration of Ni, Cr and Mo in the effluent was experimentally determined at three ambient pH values: 1.3, 7.0 and 12.7 at a high subcritical maximum test temperature (Tmax ˜350°C) and tabulated in the literature (Kritzer *et al.,* 1998). The tabulated data and presents the relative concentration of Ni, Cr and Mo in the effluent for an Inconel 625 reactor exposed to various feed pH values.

The nominal amount of each of the three elements is indicated on the right-hand ordinate. For an acidic chlorinated feed (ambient pH 1.3), the nickel concentration in the effluent was determined to be appreciably higher than the nominal Ni value for the alloy. Conversely, the Cr and Mo effluent concentrations were both significantly lower than their respective nominal values. This suggests selective dissolution of Ni and the probability of conditions associated with the thermodynamic stability of Ni2+ and CrOOH. For a neutral chlorinated feed (ambient pH 7), the shift in pH from acidic to more neutral conditions resulted in a significant decrease in the relative concentration of Ni and an appreciable increase in Cr and Mo in the effluent, suggesting conditions favorable to selective Cr dissolution. A further increase in pH (ambient pH 12.7) results in data that again reveal selective dissolution of Cr. At supercritical temperatures for an untreated acidic chlorinated feed (Mitton *et al.*, 2000), high-nickel alloys I-625, C-22 and I- 686 apparently follow a general trend in which the corrosion rate decreases between 400 and 600°C; however, a significant increase was recorded above 600°C. Conversely, within the same temperature range, the corrosion rate of C-276 increased with increasing temperature. While one report suggests no apparent pattern in the location of localized corrosion for alloy 625 (Norby, 1995), there is significant evidence to suggest that the potential for corrosion of Ni alloys exposed to supercritical water oxidation (SCWO) conditions is more pronounced in the high subcritical regime (Latanision, 1995; Kim *et al.*,2000; Kritzer *et al.,* 1998) and that the aggressiveness of the solution may decrease above the critical point (Huang *et al.*, 1989; Kriksunov and Macdonald 1995), Care is, however, necessary in extrapolating such behavior as cracking has also been reported at supercritical temperatures after extended exposure times (Latanision and Shaw 1993). In addition, to some extent, the upper temperature limit for severe corrosion depends on the pressure and, thus, density of the solution, with higher densities favoring corrosion (Kritzer *et al.,* 1998). While an Inconel 625 tube exposed to an aqueous feed stream containing 1800 ppm HCl without the addition of oxygen, revealed only general corrosion (Boukis *et al.*, 1997).

A 10-fold increase in the concentration (18000 ppm) resulted in transgranular SCC within the subcritical temperature zone (300°C) after exposure for only 46 hours. Under more complex low pH conditions, others (Mitton *et al.*, 2000) report both transgranular and intergranular cracking of I-625 at subcritical, but not at supercritical, temperatures. Mitton has previously reported, however, observing SCC and pitting of I-625 exposed to a mixed methylene chloride isopropyl alcohol feed neutralized with NaOH after extended times at supercritical temperatures (300 hours at 580°C) (Latanision and Shaw 1993). In general, when tested in acidic chemical agent simulant feeds, corrosion of the nickel alloys (C-22, C-276, 625, 825 and HR-160) was unacceptably high for both chlorinated and non-chlorinated stimulants. When exposed to a highly chlorinated feed at 600°C for a short duration (66.2 hours), HR-160 (30% Co) exhibited reasonable performance based on weight loss data; however, in regions where the surface oxide layer was locally disrupted severe grain boundary corrosion was apparent (Mitton *et al.*, 1999). There is some evidence for a correlation between Cr content and corrosion resistance for Ni alloys in supercritical water oxidation (SCWO) systems (Garcia and Mizia 1993). Certainly the high Cr alloys such as G-30 (˜30% Cr) exhibit reasonable corrosion resistance (Mitton *et al.*, 1999; Thamas and Gloyna 1991; Fodi *et al.,* 1998). Recent research exposing G-30 to an acidic chlorinated feed with a maximum temperature of 350°C indicated a corrosion rate of approximately 4 mmpy (Konys *et al.,* 1999). The authors suggest this is too high to permit the use of G-30 as a reactor material; however, as presented in a subsequent section of this paper, 4 mmpy is on the same order as rates found for Pt and its alloys, suggesting that G-30 should not yet be omitted from testing.

Ceramics and ceramic/alloy combinations

The problem associated with the corrosion of various alloys has prompted research into ceramic materials; however, results are not encouraging. With the possible exception of monolithic alumina and PSZ (partially stabilized zirconia) (Boukis *et al.*, 1997), ceramics have, generally, exhibited poor resistance to chlorinated waste streams over a wide pH (2-12) and temperature (350-500°C) range. The general behavior for the ceramic materials tested (Al2O3, AlN, Sapphire, Si3N4, SiC and ZrO2) in both chlorinated and non-chlorinated acidic chemical agent simulant feeds was found to be very poor (Downey *et al.*, 1995) in aqueous sulfuric acid feeds, zirconia ceramics also exhibit poor resistance (Schacht *et al.*, 2000). Plasma sprayed multilayered ceramics on Ni or Ti substrates were exposed to a highly chlorinated feed and while none of the coatings was able to protect the alloy 625 substrate, a titania multilayered ceramic system sprayed onto a titanium base showed promise (Garcia and Mizia 1993).

Noble metals and alloys

The use of noble metals or their alloys would significantly increase the initial cost of system fabrication. Nevertheless, for some very aggressive waste streams, they have been viewed as a possible solution to severe corrosion problems. An experiment carried out in a non-neutralized chlorinated feed stream with low level additions of Zn, Pb and Ce to assess materials suitability for supercritical water oxidation (SCWO) included platinum and two platinum alloys (Pt-10Ir, Pt-30Rh) (Mitton *et al.*, 2000), These materials were exposed for periods between 60 and 240 hours at two temperatures (400 and 610°C). At the higher temperature all three materials revealed excellent corrosion resistance with rates on the order of 0.03-0.08 mmpy. At the lower temperature, however, corrosion rates for Pt, Pt-10 Ir and Pt- 30 Rh were 1.14, 2.34 and 4.83 mmpy respectively. While these rates may be acceptable for the normal engineering alloys, the high replacement cost associated with Pt or its alloys needs to be considered. Even at 1.14 mmpy, platinum losses could be on the order of hundreds of thousands of dollars a year. While the behavior of Pt is good at higher temperatures, in acidic chlorinated feeds it exhibits high rates of degradation at subcritical temperatures (Downey *et al.*, 1995).

For such feeds, this would necessitate a potentially troublesome transition between Pt and a second material. Deposition of a thin gold layer on coupons during testing of various alloys and metals in a gold-lined vessel has been reported, and when exposed to a chlorinated acidified influent gold was found to be unsuitable for use in supercritical water oxidation (SCWO) reactors (Baker and Wood 2000). Experiments were, however, carried out in a static system and may, therefore, not be representative of conditions associated with a dynamic environment. An Inconel-625 tubecoated with a 30 µm gold layer exhibited inter granular SCC and failed within 34 hours. Conversely, under the same conditions, the uncoated tube did not fail even after 150 hours (Boukis *et al.*, 1997). The latter suggests a potential danger in the use of noble liners. Loss of liner integrity could potentially lead to catastrophic failure as a result of enhanced and unexpected degradation of the pressure bearing wall.

Titanium-base alloys

Preliminary tests of Ti indicated poor resistance to the non chlorinated acidic chemical agent simulant feeds; however, resistance to the chlorinated feed was found to be acceptable (Downey *et al.*, 1995). When exposed to chlorinated feeds, titanium (grade 2) apparently exhibits a corrosion rate of less than 3.5 mmpy (Kritzer *et al.*, 1998). Reportedly Ti provides outstanding performance at subcritical and is as resistant as the Ni alloys at supercritical temperatures (Mitton *et al.*, 2000), In addition, good performance (grades 9 and 12) is observed during exposure to sludge (Thomas and Gloyna 1991). More recently, (Foy *et. al.,* 1996) reported on the oxidative hydrothermal destruction of chlorinated organics in a “corrosion-resistant” titanium-lined 316 stainless steel reactor. They monitored corrosion by analyzing for dissolved Ti concentrations that were found to represent a uniform degradation rate on the order of 0.038-0.356 mmpy (1.5-14 mpy). From this, they conclude that titanium appears to be sufficiently protective; nevertheless, they recommend additional long-term testing. It is important to note that the majority of these experiments were carried out in a feed stream treated to achieve neutral pH.

In addition, although they were unable to quantify the amount, the authors report observing, on several occasions, solid titanium (probably TiO_2) particulates filtered from the effluent. As the corrosion rate calculated by the authors is based on soluble Ti, and as the TiO_2 particulates indicate that not all titanium was soluble, the degradation rate would, of necessity, be higher than indicated. Further, although the corrosion rate calculation was based on the assumption that degradation was uniform, this was not established, and localized penetration rates would be significantly higher. Others have experienced problems with titanium. (Garcia, 1996) reported through-wall pitting of liners during destruction efficiency testing of a chlorinated waste. Another group reported Ti coupons were unaffected during expose to a static acidic chlorinated feed; however, a Ti autoclave suffered significant corrosion damage during similar tests on other metals and alloys. In some cases pitting as deep as 1cm was reported (Baker and Wood 2000). Certainly, during exposure to the same environmental conditions, it is possible for titanium to exhibit substantially different corrosion behavior, depending on the presence or absence of occluded regions (McKay and Mitton 1985) and, to some extent this may explain the apparently anomalous behavior of this material. Although one group has suggested titanium liners as a potential solution to corrosion problems in chlorinated organic feed streams (Hazlebeck *et al.,* 1995), further testing is clearly required before a definitive answer will be found regarding the applicability of titanium alloys to these systems.

Potential methodologies for reducing corrosion damage

Recognition of materials degradation as one of the central challenges to the ultimate commercialization of this technology has precipitated a number of potential methodologies for corrosion mitigation.

Corrosion-resistant liners and coatings

One potential methodology for reducing corrosion damage during the destruction of aggressive feeds would involve the use of a corrosion-resistant liner in conjunction with a pressure bearing wall. Although some progress has been made in circumventing corrosion problems in this way, liners have not been extensively tested in these systems. In addition, the liner materials (titanium and platinum) most frequently suggested for aggressive feed streams tend to be expensive. Although the use of such a liner may be promising, as previously mentioned, there are conflicting reports on corrosion of basic materials (Environment Australia, 1997).

Feed modification

Although liners manufactured from materials such as platinum have been promoted as a solution to corrosion problems for some aggressive supercritical water oxidation (SCWO) conditions, one possible alternative would be to adjust the feed stream chemistry such that serious degradation is minimized. It may be possible to accomplish this by reducing the chloride concentration, or by altering the pH and oxidizing conditions such that the most favorable thermodynamics are obtained. Dilution - sufficient dilution of an aggressive feed can potentially reduce the risk of corrosion by lowering the chloride concentration and thus permit processing by supercritical water oxidation (SCWO). The required dilution may, however be so large as to make such a procedure economically unattractive. For example a dilution of 1000-10000 for wastes high in solvents such as carbon tetrachloride may be required to reduce feeds to acceptable levels (Barnes *et al.,* 1993).

Reactor design

The two main difficulties that must be overcome in supercritical water oxidation (SCWO) systems are salt precipitation and corrosion. Over the years, in order, primarily to deal with these problems a number of reactor designs have emerged. In its simplest form, design modification may involve the use of a liner with deionized water between the vessel wall and the liner (Mitton *et al.*, 2000). More complex designs have included, the dual shell pressure balanced vessel (DSPBV) (Fassbender *et al.,* 1995) and the reactor concept of a film cooled coaxial hydrothermal burner (FCHB) (La Roche *et al.*, 1995). In the latter case, while the authors were initially optimistic about the design, subsequent experiments revealed problems including corrosion of the core tube tip and coaxial tubes (Weber *et al.*, 1999). The most commondesigns involve (i) Down-flow vertical vessels, (ii) the tube configuration and (iii) the transpiring wall reactor (McGuinness, 1995). The latter permits pure water to enter through apertures in the cylindrical reactor wall. This clean transpiration water maintains a boundary layer free of corrosive species or solids deposited on the inner reactor surface.

Application of supercritical oxidation water technology

With the development of the modem industry, there is in excess of 400 billion tons of sullage, 3 billion tons of solid contamination that are drained into the environment every year. So it is an urgent need to search for an efficient and safe waste handling method. Supercritical water oxidation (SCWO) is an emerging technology to process many organic wastes and has been shown to have several benefits to handling dilute wastes in the range 1 wt%-20 wt% which are not suitable for disposal by either incineration or landfill. Typical destruction and removal efficiencies can exceed 99.99% for normal operating conditions of 25 MPa, 600°C, and residence times of 60s or less. At normal operating conditions, hydrocarbons are converted to CO_2 and water. Heteroatoms such as phosphorus and sulfur are converted to phosphate and sulfate anions, which, depending on pH control, will remain as their respective acids, or if neutralized may precipitate out as salts. Nitrogen heteroatoms are abstracted to form primarily N_2 ~-3 (Zhang *et al.*, 2001).

Incombustible" waste (1.17 kl) which includes more than 5% water, 1.38 kl of "combustible" waste, and 0.40 kl of "halogenated organic" waste were completely and successfully treated without the formation of dioxins and problems with corrosion have not been reported so far. The total number of operation days of the treatment process was 74, excluding the days used for the analysis of waste, pretreatment, and treatment of inorganic waste water. Furthermore, the treatment process was operated continuously to reduce the load to supercritical water oxidation (SCWO) equipment at the start up and shut down, and the maximum operation period was 8 days. These achievements imply that supercritical water oxidation (SCWO) is a promising technology applicable to the treatment of laboratory waste; however, there are several problems still remaining to be solved. One problem is the high capital and running cost of the technology.

The percentage of labor cost to the total running cost is high, which may be partly due to the legal requirement of licensed laborers to operate such a large-scale high-pressure plant. Another problem is salt formation in the reactor. We have experienced a sudden pressure increase during the operation due to the clogging of the tubing at the exit of the reactor caused by salt precipitation. We found from the ICP analysis that the major components of the precipitate were alkaline metals such as Na and K, and Cl. These elements were initially present as dissolving salts in the original solution and were presumed to form mixed precipitates under the reaction conditions of supercritical water oxidation (SCWO). Those inorganic salts such as NaCl and Na_2 SO_4 are sticky and tenaciously adhere to solid surfaces with which they come in contact in the supercritical water oxidation (SCWO) process.

We measured the melting point of the precipitated salt, and found it to be approximately 630°C. This value is far lower than the melting points of pure inorganic salts such as NaCl (801°C) and Na 2C O3 (850°C). We also observed experimentally that the plugging due to the salt formation does not take place when the original solution contains only NaCl. From these observations, it is suggested that the plugging problem in the supercritical water oxidation (SCWO) treatment of laboratory waste water will be more serious if the original waste contains multiple types of inorganic salt, because of the formation of mixed-salt precipitates that possess low melting points and high adhesiveness's. In laboratory waste, the concentration of inorganic salt in most organic waste water is usually on the order of hundreds of ppm or less; however, the obstruction in the reactor may be caused by a very small amount of salt contamination from the waste. Therefore, a thorough identification of the chemical components of the waste water before supercritical water oxidation (SCWO) treatment is necessary to avoid the plugging problem caused by salt formation in the reactor (Yoshito *et al.*, 2006).

Despite the potential of supercritical water oxidation (SCWO) as a viable technology for organic waste destruction, its commercial development has been hindered by the problems of corrosion and salt precipitation/solids buildup. The extremely low solubility of polar inorganic salts in the supercritical water environment causes salts present in the feed or formed during reaction, to precipitate inside the reactor. If left unchecked, these salts can rapidly accumulate on reactor walls or process surfaces and form plugs, causing expensive and frequent downtime of the supercritical water oxidation (SCWO) system. Other solids such as oxides exhibit low solubility in water over the range from ambient to supercritical conditions and although they have much less tendency to adhere to process surfaces, may still hinder operations if not accommodated. Many wastes will have a combination of salt-type and oxide-type solids, and may have an intermediate tendency to stick to process surfaces. Many of the companies that have attempted to commercialize the SCWO technology over the past two decades have developed innovative approaches to dealing with the corrosion and salt precipitation/solids buildup problems. These are often the distinguishing features of each company's SCWO process.

This paper objectively reviews several commercial approaches that have been developed and used to control salt precipitation and solids buildup in supercritical water oxidation (SCWO) systems. The approaches reviewed consist of specific reactor designs and operating techniques and include the following: reverse flow tank reactor with brine pool, transpiring wall reactor, adsorption/ reaction on a fluidized solid phase, reverse flow tubular reactor, centrifuge reactor, high velocity flow, mechanical brushing, rotating scraper, reactor flushing, additives, low turbulence/ homogeneous precipitation, cross flow filtration, density separation, and extreme pressure operation. Recent commercial SCWO applications utilizing these approaches are also discussed (Marrone *et al.*, 2004).

The pilot plant studies, shows that the supercritical water oxidation (SCWO) technology is ready for commercialization. Furthermore for wastes like de-inking sludge, containing valuable inorganic, supercritical water oxidation (SCWO) treatment offer, besides an extremely clean effluent, the possibility to recover these compounds. The extremely clean inorganic material recovered ought to increase the interest in SCWO treatment. This type of waste may very well be the breakthrough of supercritical water oxidation (SCWO). Supercritical water oxidation (SCWO) has two major limitations with respect to substances present in the water, dissolved salts and acids formed of chlorine, sulphur etc. There are simply two ways of treating such wastes: 1. Makingthe waste treatable in an “ordinary” supercritical water oxidation (SCWO) unit, i.e. remove halogens and dissolved salts. 2. Making the supercritical water oxidation (SCWO) unit able to handle the difficulties in the waste, e.g. halogens. It is not probable that there will be a general supercritical water oxidation (SCWO) system suitable for all such waste from both economical and technical point of view. It has to be reviewed from case to case which solution should be preferred (Ander *et al.,* 2001).

The environmental impacts of waste water treatment processes on global warming are mainly an effect of produced greenhouse gases such as carbon dioxide, which can be reduced by saving fossil fuel through energy recovery. By maximizing the amount of organic material of the waste water that is transferred to the sludge and utilized for energy recovery, the impact of global warming from sewage handling can be minimized. With use of supercritical water oxidation (SCWO) all the potential energy of the organic material or biogas production half of potential energy of the organic material, can be recovered from sewage sludge and organic waste and by utilization of the energy there will be less contribution to the global warming potential from the sewage handling. A large need of energy for district heating makes utilization of the heat energy produced by supercritical water oxidation (SCWO) of sludge and organic waste possible (Levlin, 2003).

The effects of the addition of NaOH on the decomposition of 2-chlorophenol (2CP) and phenol in supercritical water (SCW) and under supercritical water oxidation (SCWO) conditions were investigated. The experiments were conducted in a plug-flow reactor at 713K and 26 MPa. The reactor residence times ranged from 0.13 to 0.51s.

The initial concentrations of 2CP and phenol were 3.89×10^{-3} and 5.3×10^{-3} mol/l, respectively. Experiments were conducted in the presence and absence of H_2O_2 or NaOH in SCW. Under the experimental conditions, the addition of NaOH accelerated the decomposition of 2CP in SCW, but had little effect on that of phenol. On the other hand, the addition of NaOH accelerated the decomposition of both compounds under supercritical water oxidation (SCWO) conditions. From 2CP and phenol supercritical water oxidation (SCWO), many dimers were identified with a GC/MS. The addition of NaOH to 2CP and phenol SCWO reduced the generation of these dimers, and promoted the dechlorination of 2CP in SCW and under SCWO conditions. These results show that the effects of NaOH on the decomposition of 2CP and phenol SCWO are not negligible, and the effects of NaOH on the decomposition of other organic compounds under SCWO conditions should be considered for determining optimum operating conditions and reactor designs (Lee *et al.,* 2002).

using formaldehyde and methanol as a co-oxidant which showed that the increase in MPA conversion was much greater than the increase in methane carbon fraction, which indicates that the increase in HO2 concentration was much greater than the increase in OH concentration, thus confirming the co-oxidation model predictions (Jason *et al.*, 2006).

Oxidation of chemical warfare agents (CWAs) such as sulfur oxidation of chemical warfare agents (CWAs) such as sulfur mustard (HD) and soman (GD) and their simulants 2-chloroethyl ethyl sulfide (2-CEES) and dimethyl methyl phosphonate (DMMP) in supercritical water were studied by a batch reactor. Results showed that HD, GD and their simulants 2-CEES and DMMP could be effectively destroyed into their corresponding mineral compounds by supercritical water oxidation (SCWO). The mineral ratio was a function of reaction temperature, reaction time and oxidant concentration. But reaction temperature seemed to have more important effect on the mineral ratio than other two factors. Sulfur compounds 2-CEES and HD could easily be mineralized under 475℃ and the inorganic products were mainly SO32- and SO42-, while complete oxidation of organic phosphorus reactants GD and DMMP needed a high temperature of >600℃. And under relatively low temperature, DMMP tended to form a white organic phosphorus polymer with P-C and P-O-P bonds. Results also indicated that P-F bond was more easily broken than P-C bond (Lian *et al.*, 2001).

Supercritical water oxidation has become a well-known treatment technology for conversion of aqueous wastes. By introducing a catalyst, higher conversion and selectivity to carbon dioxide can be achieved at a lower temperature and at shorter residence times. The stability of chromium oxide in supercritical water was studied to determine the feasibility of using catalysts during supercritical water oxidation. Various process variables, including oxygen and water concentrations, fluid flow rate, and temperature were found to affect the reactivity of the chromium oxide catalyst. Under these conditions, chromium was present in the reactor effluent as chromic acid, H2CrO4. The visual observation of the catalyst after the completion of the experiments suggested that a reaction front moved along the length of the reactor. A rate expression, based on Langmuir–Hinshelwood kinetics, with dissociative chemisorption of oxygen on a hydrated chromium oxide surface, was proposed. The model, developed based on this rate expression and the continuity equation for the fluid phase, was consistent with the experimental results (Sudhir *et al.*, 1996).

Disappearance kinetics of 2,4-dichlorophenol (DCP) oxidation in supercritical water was investigated. The experimental data reveal that the reaction is 0.97 order for DCP and 1.16 order for oxygen. The activation energy and the Arrhenius pre-exponential constant are 13.6 kcal/mol and 72.9M-’ 13s-‘, respectively. Several condensation by-products, such as trichlorophenols and dibenzo-p-dioxin, from supercritical water oxidation (SCWO) of DCP at 673K were determined. We also found experimentally that the presence of sodium or iron cations in oxidation of DCP in supercritical water suppressed the formation rate of condensation by- products and enhanced the reaction conversion (Lin *et al.*,1998).

Supercritical water oxidation (SCWO), also referred to as hydrothermal oxidation (HTO), is a developing technology for the destruction of hazardous and nonhazardous wastes. SCWO destroys combustible materials using an oxidant in water at temperatures in the range of 350°C (662°F) to 600°C (1112°F) and pressures of 17 MPa (2500 psi) or greater. General Atomics and its subcontractors are currently conducting two comprehensive research and demonstration programs geared toward the destruction of department of defense (DoD) wastes utilizing SCWO technology. Wastes of primary interest include chemical agents and solid propellants. Technical challenges, particularly corrosion and solids handling, were overcome, and the destruction of chemical agents and solid propellants was demonstrated on a bench scale. SCWO results for chemical agents show destruction and removal efficiencies for GB, VX, and mustard agents to be in excess of 99.9999%, limited only by detection capability. supercritical water oxidation (SCWO) results for hydrolyzed Class 1.1 solid propellant show destruction and removal efficiencies for total organic carbon (TOC) of >99.9%. Design and fabrication of a transportable SCWO pilot plant for chemical warfare agents, propellants and other DoD hazardous wastes and a prototype HTO system for solid rocket propellant disposal are complete and demonstration testing is underway (Spritzer *et al.*, 1995).

The aim of this work is to present the application of the hydrothermal oxidation in supercritical conditions, also named supercritical water oxidation (SCWO) to the treatment of two commercial cutting fluids: Biocut® and Servol®. Experiments were carried out in a continuous flow system at a constant pressure of 25 MPa, using pure oxygen as oxidant in excess and different temperatures ranging from 673 to 773K. Both semi-synthetic cutting fluids are a mixture of several compounds so the efficiency of the oxidation process was followed in terms of the reduction in chemical oxygen demand (COD) and total organic carbon (TOC). A comparison of the results obtained in the study showed that it is possible to apply successfully SCWO for both cutting fluids, obtaining more than 95% for both COD and TOC removal at 773K. However, the results also show that different residence times are needed to obtain the same percentage of COD or TOC removal depending on the cutting fluid treated, being in all cases Servol® easier to oxidize than Biocut®. A kinetic model to predict COD and TOC conversion has been proposed for both cutting fluids. A two-parameter mathematical model involving two steps (a fast reaction followed by a slow reaction) was used to describe the Biocut® SCWO kinetics and to calculate the kinetic constants (Oneto *et al.,* 2002).

Supercritical water oxidation (SCWO) can decontaminate hazardous organic wastes, including mixtures whose constituents vary widely in their susceptibility to oxidation. The SCWO kinetics of complex organic wastes are analyzed using a mathematical model that eliminates the substantial input requirements and computationally demanding mathematics of multistep, component-specific rate expressions. The approach assumes that SCWO occurs by an infinite set of independent, parallel, first-order chemical reactions, with a continuous distribution of activation energies. The resulting model, distributed activation energies model (DAEM), was applied by earlier workers to other kinetics problems of comparable complexity, inter alia, decay of molecular defects in solids and coal pyrolysis. A three-parameter DAEM is shown to correlate the SCWO kinetics of eight organic wastes, including several complex mixtures.

These wastes are: JP-5 aviation fuel, Velsicol H537 hydraulic fluid, aqueous methanol solutions, NaOH and NH4OH hydrolysates of solid rocket propellants, an orange military dye marker, municipal sewage sludge, and alcohol distillery waste water. The model was separately parameterized for each waste by best fitting its predictions of conversion as affected by residence time and temperature to experimental data from various investigators.

A satisfying correlation resulted for each case. Illustrative reactor engineering calculations demonstrate DAEM's superiority to a single reaction model in sizing a PFR for SCWO of a complex organic mixture. The times required to achieve 99.99% destruction of different wastes depend strongly on the nature of the waste and differ by about three orders of magnitude from the most labile waste to the most refractory waste (Vogel *et al.,* 2002).

Supercritical water oxidation (SCWO) sometimes referred to as hydrothermal waste processing, uses the solvating traits of water in its supercritical condition to effectively destroy liquid organic wastes.

One major problem in the supercritical water oxidation process is corrosion, because all metallic tubes in the process are exposed to high temperature and high pressure as well as severe corrosive species such as Cl−, F−, S2− and O2−. The presence of Cl− when the pH of a solution is very low and the solution has excess oxygen causes active corrosion and metal loss by metal-chloride and oxygen chloride formation. Chromizing treatment on stainless steel and immersion tests in supercritical water. Weight change of chromized steels and untreated steels was measured, and the chemical state and composition of oxide films on stainless steel were investigated.

On the basis of supercritical water oxidation (SCWO) tests using distilled water, the oxide layer was found to be very thin and homogeneous and weight gain was observed regardless of testing temperature, while the chromizing treatment slightly reduced weight gain. In the case of supercritical water oxidation (SCWO) tests using salt water, weight loss was observed regardless of testing temperature and its corrosion mode was pitting by chloride ion, while chromizing treatment greatly decreased the corrosion rate (Kim *et al.*, 2004).

The fate of nitrogen containing organics has also been investigated. But, except for traces of N2O, nitrous oxides formation has never been observed due to low oxidation temperatures (Killilea *et al.*, 1992; Tiffany *et al.*, 1984).

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