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Supercritical Water Oxidation: A Technical Review

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Supercritical water oxidation (SCWO) technology presents important environmental advantages for the treatment of industrial wastes and sludges. The homogeneous reaction that takes place between the oxidizable materials and oxygen, at temperatures and pressures above the critical point of the water (647.3 K and 22.12 MPa), is well known. Specific equations of state for water and aqueous mixtures, gases, and organics have been developed. The process is not having the expected industrial development. Some new plants have been closed by corrosion and operational problems related with high temperature, high pressure, and oxidative atmosphere inside of the equipments. To overcome these technical difficulties more research focused on solving operational problems is necessary. This article presents an overview of the technical aspects of the supercritical water oxidation process. Reactors design, construction materials, corrosion, salts precipitation problems, and industrial applications are discussed. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 3933–3951, 2006
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Introduction

In general, taking a mixture of liquid and gas at equilibrium conditions, when pressure and temperature increase, thermal expansion causes the liquid to become less dense. At the same time, the gas becomes denser as the pressure rises. At the critical point, the densities of the two phases become identical and the distinction between them disappears. Thus, above the critical temperature T_c, the system is simply described as a fluid, called a *supercritical fluid* (SCF).

Technically, a SCF is a gas but not a vapor. The term “gas” refers to any phase that “conforms in volume to the space available.” The SCFs share physical properties with gases and liquids. In the gas-to-liquid transition region, SCFs present a combination of properties that make them very suitable for the development of new processes that cannot be carried out with conventional liquids or gaseous solvents. The solubility of a product in a supercritical fluid is a function of its density, making SCFs tunable solvents. Some processes such as extraction, crystallization, or even reaction have taken advantage of the special properties of the SCFs. The most frequently used SCFs are carbon dioxide and water.

The polarity of water changes with pressure and temperature. At supercritical conditions water is a nonpolar solvent completely miscible with organics. Supercritical water (SCW) also presents complete miscibility with oxygen, creating a homogeneous reaction medium, which makes SCW a very suitable medium for the oxidation of organics. The process known as *supercritical water oxidation* (SCWO) or *hydrothermal oxidation* (HTO) consists of the homogeneous oxidation of chemical compounds in an aqueous medium using oxygen or hydrogen peroxide as the oxidizing agent, at temperatures and pressures above the critical point of water (647.3 K and 22.12 MPa). The reaction of SCWO can also be heterogeneous when the organic material is a solid or in the case of heterogeneous catalytic SCWO. In this review only noncatalytic SCWO will

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be considered. Extensive information about catalytic SCWO can be found elsewhere.[1]

The main application of the SCWO is the destruction of wastewaters and sludges, especially those containing recalcitrant, xenobiotic, and nonbiodegradable pollutants. As a consequence, the SCWO competes with other processes, mainly the wet air oxidation (WAO) and incineration.

From the environmental perspective, SCWO is a process that achieves the complete elimination of oxidizable material. With the appropriate reaction temperatures, pressures, and residence times almost any pollutant can be completely destroyed by SCWO, with residence times < 1 min. Up to the present, a wide range of organic and inorganic substances susceptible of oxidation, such as ammonia or cyanides, have been converted into CO_2, water, and N_2 using the SCWO. Partial oxidation products, such as dioxins, NO_x, or CO, have not been detected. Thus, the resulting effluent complies with the most severe environmental regulations and can be disposed without further treatment.[2] From the perspective of sustainability, considering "Sustainable Development Progress Metrics," environmental, economics, and social metrics are more favorable for the SCWO process than for WAO or incineration.[3]

The SCWO process consists of four main steps: (1) pressurization of the reagents, (2) reaction, (3) salt separation, and (4) depressurization and heat recovery. The SCWO process consumes a massive quantity of energy in pressurizing and preheating the reagents, but the integration of the process allows recovery of energy from the hot pressurized product stream for preheating or even to produce electricity.[4] Companies involved in the development of the SCWO process are thus presented with favorable economical balances by use of the SCWO.[5,6]

From a technical perspective, the SCWO has the advantage of presenting simple and fast reaction rates and of being a homogeneous reaction without the limitations of mass transfer. Nevertheless, it also presents some limitations related to the harsh operational conditions and their effect on the facilities' construction materials that must still be overcome before the generalized industrial use of the process. The two main challenges of SCWO—corrosion and salt deposition—are being solving through technical solutions such as the use of special construction materials and the development of new reactor designs able to soften the conditions that the materials must support.[7]

Nowadays, some industrial applications of the SCWO have been developed, such as the oxidation of sludges[5] and chemical weapons,[8] to mention only a few. To develop new industrial applications of the supercritical water, research focused on the development of equipment that support the drastic operation conditions reducing the costs should be performed. This would allow joining the environmental advantages with the economic viability of the process.

This article presents an overview of the technical aspects of the supercritical water oxidation process. Topics such as reactor design, construction materials, corrosion, salt precipitation problems, and industrial applications are discussed.

Properties of Supercritical Water

Supercritical water (SCW) acts as a nonpolar dense gas and its solvation properties resemble those of a low-polarity organic solvent.[9,10] SCW shows complete miscibility with "permanent" gases, such as nitrogen, oxygen, and carbon dioxide.[11,12-14] In contrast, inorganic salts are almost insoluble in SCW.[2,15]

SCW also presents high diffusivities and low viscosities. In the region above the critical point these properties are only slightly affected by temperature and can be predicted.[10] Extensive works about SCW properties can be found elsewhere.[16-21] For the modeling of industrial SCWO process working with high fuel concentrations, interest is focused on knowing the properties of aqueous mixtures. When energy balances are necessary, a good estimation of the thermophysical properties is required, so the interest in an equation of state (EoS) that is able to describe the SCWO systems is growing. When a detailed CFD modeling is performed a good knowledge of the transport properties is also needed. Sometimes experimental measurements of the SCW properties are difficult to gather, so molecular simulation methods are used. In the next sections these subjects of growing interest for the current development of the SCWO technology are considered.

Calculation of the thermophysical properties of the supercritical aqueous medium: EoS used to describe the SCWO systems

In recent years interest in modeling of the SCWO process has been increasing. With the scaling of the processes and the interest in the heat integration,[4,22,23] models taking into account mass and energy balances[24,25,26] were developed. To obtain accurate results of this kind of models, precise values of densities, enthalpies, and heat capacities are needed, for both water and aqueous mixtures.

Calculating the properties of aqueous systems in the surroundings of the critical point of water is a difficult task. Conventional cubic EoS are not very accurate in this region, although the Peng–Robinson EoS with the volume translation correction[27] is able to reproduce densities of the water–air system quite accurately and to reproduce the behavior of real SCWO reactors.[28,29] Kutney et al.[30,31]developed an EoS able to calculate thermodynamic properties of several substances involved in the SCWO and of its mixture in conditions of up to 40 MPa and 500°C. This EoS couples a volume translation to a pressure-explicit equation in volume and temperature that combines a Carnahan–Starling hard-sphere repulsive term b and a simple van der Waals attraction term a. Densities and residual properties can be predicted with average errors of 5 and 7%, respectively, for which the maximum errors are 13 and 32%, respectively.

The presence of salts in the mixture modifies the liquid–vapor (LV) equilibrium and can generate a two-phase reaction mixture.[32] In addition, if salts are present in the system, more complicated EoS are necessary. Anderko et al.[33] summarized several EoS developed for modeling high-temperature and supercritical aqueous systems.[34-37] Among them he describes the Anderko and Pitzer[38] EoS. It is a comprehensive EoS for representing LV and solid–liquid (SL) equilibria as well as volumetric properties. It is based on a reference term that describes the properties of a system containing dipolar ion pairs and solvent molecules. The equation consists of a reference and a perturbation contribution. The reference part represents the properties of a mixture of hard-sphere ion-pair and dipolar solvent molecules. This EoS considers a fully ion-paired molecular basis for the salt. This basis is satisfactory for concentrated solutions and for diluted solutions at vapor-like densities, and precludes accuracy in the dilute region when the dielectric constant is large enough to allow substantial dissociation.

In the Anderko and Pitzer[38] model, the EoS parameters were fitted to an extensive amount of experimental data of the water–NaCl system in the temperature range from 573 to 773 K and to a more limited amount of data above 773 K and pressures up to 500 MPa. In both temperature regions, the EoS reproduces the LV equilibrium, volumetric properties, and solubility of solid NaCl within experimental uncertainty. Anderko and Pitzer also used their EoS for fitting water–KCl data and water–NaCl–KCl data in the same pressure and temperature (PT) range.[39] Jiang and Pitzer used the EoS for the water–$CaCl_2$ system.[40] Later Duan et al. used the EoS for the H_2O–CO_2–NaCl,[41] H_2O–CH_4–NaCl, and H_2O–CO_2–CH_4–NaCl[42] systems. In 2001, Kosinski and Anderko extended the EoS to multicomponent water–salt–nonelectrolyte systems and developed a corresponding-states methodology for systems for which very little experimental information is available. In addition, they readjusted water and salt parameters for temperatures < 573 K.[43]

Transport properties calculation in SCWO systems

The development of more complex reactor designs, such as the reverse flow reactor vessel or the transpiring wall reactor, and the awareness of the importance of the reagents mixing[44] have opened the way to more complicated models using computational fluid dynamics (CFD) tools,[28,45,46] to accurately describe the flow pattern inside the reactor. To do so, the momentum balance must be solved and accurate values of the transport properties such as viscosity and heat conductivity of diffusivity are needed.

Viscosity. The prediction equation proposed by Sengers and Kamgar-Parsi[47] is recommended by the International Association for Properties of Water and Steam (IAPWS),[48] for calculating water viscosity. This equation computes viscosity as a function of reduced temperature and density. This equation can be applied for pressures up to 500 MPa and temperatures up to 900°C in some conditions.

In 1999, Marcus[49] developed a correlation fitted with an expression taking into account the relative void volume, the enthalpy of vaporization, and the hydrogen bonding.

Thermal Conductivity. The equation proposed by Sengers et al.[50] for the calculation of the thermal conductivity of a supercritical steam as a function of the temperature and the density is able to predict thermal conductivities values with a deviation $< 3\%$ with respect to the experimental values.

In his modeling, Lieball[28] used the correlations proposed by Chung[51,52] refitted to experimental data for calculating both viscosity and thermal conductivity. Vielcazals et al.[53] modeled the SCWO process considering the whole mixture with water properties using the transport properties recommended by the IAPWS.[54]

Diffusion Coefficient. In CFD modeling, the diffusion is calculated as the sum of the molecular and the turbulent diffusion coefficients. In the main part of the reactor the diffusion process is dominated by turbulence, in which molecular diffusion is the dominant factor at only some locations. The diffusion coefficient depends on both the diffusing compound and the composition of the mixture, although it can be simplified, considering the mixture as pure water.[28]

Most correlations for the molecular diffusion coefficient found in the literature are valid for only the liquid or the gas state but not for both. For all species but water, Lieball[28] suggests the correlation of He.[55] For the self-diffusion coefficient of water the correlation by Liu and Macedo[56] or by Marcus[49] can be used.

Computational calculation of SCW properties by molecular simulation

The calculation of several properties of supercritical water by numerical methods, such as molecular simulation, is becoming frequent. This is useful to estimate water properties that are unknown and sometimes difficult to obtain experimentally, and also to provide an explanation about its behavior. To mention only a few:

- In 1993, Kalinichev[57] calculated a self-diffusion coefficient of SCWO using methods of molecular dynamics simulation.
- In 1996, Mizan et al.[58] calculated several water properties including dielectric constants and self-diffusivity coefficients by molecular dynamic simulation.
- In 2003, Harvey and Mountain[59] used molecular dynamics simulation to calculate the diffusivity of sodium chloride at infinite dilution in high-temperature steam.
- In 2004, Nieto-Draghi et al.[60] computed a self-diffusion coefficient and Maxwell–Stefan coefficients as well as the shear viscosity for the water–benzene mixture at supercritical conditions.

Oxidation Reactions in Supercritical Water

The combination of the solvation and physical properties makes supercritical water an ideal medium for the reaction of organics. In recent years a growing interest in the reaction of organics in supercritical water or near-critical water has been developing. A number of works that study in depth the organic reactions in SCW, focusing on the influence of the properties of water and in the kinetics modeling, has been developed over the last few years.[61-64] Thus, in this work, only a few remarks about the SCWO reactions and their kinetics modeling from an engineering perspective are presented.

When organic compounds and oxygen are dissolved in water above the critical point they are immediately brought into intimate molecular contact in a single homogeneous phase, with no interface transport limitations and, for sufficiently high temperatures, the kinetics is fast and the oxidation reaction proceeds rapidly to completion.

The kinetics of the SCWO of organics is frequently considered as a first-order or pseudo-first-order kinetics with respect to the concentration of the organic compounds.[65-68] The oxidation rate is frequently considered independent or weakly dependent on the oxidant concentration.[65-68]

In 1991, Li et al.[65] proposed a generalized kinetics model for wet oxidation and SCWO of organic compounds. They considered that the oxidation kinetics is controlled by the formation and destruction of rate controlling intermediates: some organics compounds are directly destroyed into the final oxidation products, whereas others are transformed into stable intermediates. By-product analyses have indicated that short-

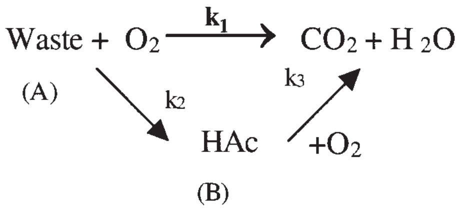

Figure 1. Kinetic model scheme.

chain carboxylic acids, ketones, aldehydes, and alcohols are the main oxidation intermediates, of which the most frequent are acetic acid and ammonia for nitrogen-containing reagents. These intermediates are more stable and their oxidation rate is slower. In Figure 1, the general reaction mechanism for hydrocarbon oxidation is shown.

This mechanism has been successfully used to model the SCWO oxidation of isopropyl alcohol and acetic acid in pilot-plant scale.[26,25]

In 2005, Vogel et al.[69] made a complete review of the existing kinetics data of the oxidation of methanol in supercritical water. They proposed a reaction model able to explain the apparent divergences among different measured data sets. They explain the SCWO of methanol as a free-radical chain mechanism, similar to others formerly proposed.[70-75] This mechanism yields an S-shaped conversion vs. time curve as opposed to the exponential curve observed with first-order kinetics. In the beginning of the reaction an induction time is observed. During the induction period negligible conversion of methanol occurs, and a critical concentration of radicals is built up (initiation phase). Once this critical concentration has been reached, the methanol is consumed rapidly by reactions with these radicals (quasi-steady propagation phase). When most of the methanol and/or oxygen have been converted, termination reactions between radicals, which yield stable products, start to dominate and methanol conversion is slowed down (termination phase). Whereas the propagation regime alone can be satisfactorily described by first-order kinetics, the whole regime including the initiation phase and the termination phase cannot. In general, the induction period is shortened with high temperatures and high reagent concentrations, but is also strongly affected by traces of metal ions, oxidation inhibitors, stabilizers, metal surfaces, and also the pH. From this analysis we can conclude that a first-order representation of apparent kinetics is adequate when induction times are negligible and up to a certain conversion. This is a very frequent situation in SCWO so first-order models are convenient for modeling.

Although there are a great number of studies about oxidation kinetics in supercritical water, the influence on pressure in the oxidation rate is still not clear. Some works indicated that oxidation efficiency increases when density, that is pressure, is elevated[76-79]; others concluded that high pressure is detrimental for the oxidation rate[80] and there are authors who indicated that pressure has no effect on the SCWO rate.[81] All these experiments were performed in the temperature range from 370 to 480°C and pressure range from 18.7 to 28.2 MPa.

Li et al.[65] indicated that pressure influence in SCWO was very small compared to that of temperature and it could be neglected. When necessary to take it into account, these authors suggest considering the rate constant as a function of the pressure, using the concept of volume of activation, that is, the excess of partial volume of the transition state over partial volume of the initial species.[82] The expression is

$$(\partial \ln k/\partial P)_T = -\Delta V^\circ/RT \qquad (1)$$

where k is the rate constant, ΔV° is the volume of activation at cm^3/mol, R is the gas constant (82.05 $atm{\cdot}cm^3/mol{\cdot}K$), T is the temperature in K, and P is the pressure in atm. Typical values for the volume of activation in liquid reactions are between 30 and 50 cm^3/mol, but in supercritical fluids, especially in the surroundings of the critical point, the volume of activation reaches values greater than -1000 cm^3/mol.[83,84] Strictly, volume of activation is variable with pressure and temperature, but for small intervals it can be taken as a constant.[82]

Some authors[77,79] explained the influence of pressure, considering that water concentration plays a role in the oxidation mechanism, and introducing the concentration of water in the kinetic expression as

$$r = k \cdot \text{Fuel}^a \cdot O_2{}^b \cdot H_2O^c \qquad (2)$$

Recently Henrikson et al.[85,86] reinterpreted former data of phenol SCWO[76-81] and, together with new experimental data, an inhibition and acceleration effect of the concentration of water in the SCWO, independent of the pressure effect, has been found. At lower water concentrations (about 1–7 M) the SCWO reaction is inhibited, whereas at higher concentrations it is accelerated. Plausible explanations of this phenomenon are that, at low water densities, the rate-controlling process is limited diffusion or by a decrease in polarity as the reactants form the transition state.

SCWO Process

In general, the SCWO for the destruction of organic wastes consists of four main steps as shown in Figure 2.

1. Feed preparation and pressurization
2. Reaction
3. Salt separation
4. Heat recovery and depressurization

Feed preparation and pressurization

The feed of a SCWO reactor consists of the oxidant and the wastewater streams. Because oxidant hydrogen peroxide, oxygen from the air, or liquid oxygen can be used, the efficiency of the process is independent of the oxidant.[44] The choice of air

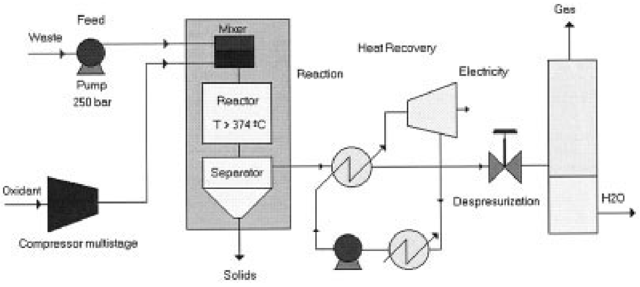

Figure 2. SCWO process.

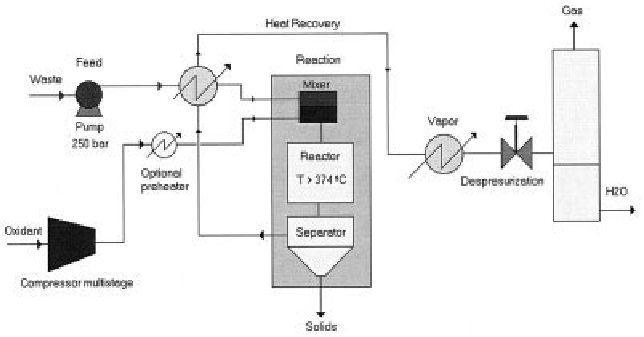

Figure 3. SCWO process with a heat exchanger for preheating the feed.

or oxygen as oxidant is dictated by economics. Oxygen compression costs are considerably lower than those from air (on equivalent oxygen basis), but they represent an additional raw material cost. Using hydrogen peroxide may be advantageous in bench-scale facilities, but the commercial applicability of this oxidant is limited because of its high cost.

Organic materials in an aqueous medium are pumped up to the working pressure ($P > 22.1$ MPa) into the reactor. The heating value of the feed is limited to an appropriate upper oxidation temperature limit of about 700–750°C (around 4500 kJ/kg) by diluting with water or adding fuel if the heating value of the waste is low. If the heating value of the aqueous waste is too low, the feed could be preheated by heat exchange with the hot effluent leaving the reactor, as shown in Figure 3.

Reaction

When the oxidant and the organic waste streams are mixed with the hot reagents they react exothermically. The heat released by the oxidation reaction is sufficient to heat the reagents up to the operation temperature, at which all the organic matter is rapidly oxidized.

The reactor is designed to support the harsh operational conditions and the oxidative atmosphere. The main operational parameters are reaction temperature, residence time, concentration of oxidant, and pressure.

Reaction Temperature. When the reaction temperature is increased, the efficiency of the process is higher and the residence time necessary for the total oxidation of the reagents is lower. At reaction temperatures around 650°C, residence times necessary for complete conversion are <50 s, with independence of the pollutants treated.[87]

Residence Time. Residence times can vary from a few seconds to 1 min depending on the reaction temperature.

Concentration of Oxidant. Total removals are obtained working with the stoichiometric amount of oxidant.[88]

Operation Pressure. When the pressure is above the critical pressure of water (22.1 MPa), conversion is not improved by elevating the pressure. At lower pressures,[89] the conversions decrease, but if the reaction temperature is high enough the detrimental effect of pressure can be compensated.[90]

Salt separation

Because of reduced salt solubility, eventually stable solid particles (both precipitated sticky salts and nonsticky solids completely insoluble in SCW) are present in SCWO processes. These particles can cause equipment fouling, plugging, and erosion.

Nevertheless, the low solubility of salts in supercritical water allows them, in theory, to be removed by a solid–fluid separation, for instance, by means of hydrocyclons or filtration systems, making possible the recovery of valuable products. Microfiltration systems are appropriated when a high purity of the filtrate is necessary, although it presents disadvantages such as mechanical placement, corrosion, erosion, fouling, and process control.[91] All these methods of recovering solids at the outlet of the reactor are effective only when the solids do not tend to stick to the wall of the reactor. This can happen if the solid is not sticky or if a system for removing the solids from the walls is implemented in the reactor (such as transpiring wall reactor).

Heat recovery and depressurization

The gaseous products of the reaction (CO_2 and N_2 if air is used as oxidant), along with the supercritical water, leave the reactor at a temperature around 650°C and a pressure > 23 MPa. This stream must be cooled and depressurized down to room conditions, then separated into a liquid aqueous phase and a gas phase.

For dilute aqueous wastes, with low heat of reaction, it is possible to use the heat content of the products to preheat the waste up to the operation conditions, using a heat exchanger. The minimum organic matter content necessary depends on the heat exchanged. Feeds with a heating value of 930 kJ/kg (equivalent to $2\%_{ww}$ hexane) can generate an effluent with an energy content sufficient to preheat the feed from room temperature to 400°C and to generate electric power equivalent to that consumed by the high-pressure pump and the air compressor can be released.[4] Lavric et al.[22] obtained similar results working with a $5\%_{ww}$ of hexane and using different ways of producing electricity. Excess thermal energy contained in the effluent can be used to generate steam for external consumption, to produce electricity or for heating needs of industrial processes at high temperature.[4,92,93] The plant for the SCWO of sludges, developed by Hydroprocessing LLC (located in Harlingen, TX), is presented as more profitable than other processes for sludge treatment, as a result of the selling of the excess thermal energy as hot water and the use of the produced CO_2 for the neutralization of industrial effluents.[5]

For larger-scale systems energy recovery may potentially take the form of power generation by direct expansion of the reactor products through a supercritical steam turbine. Such a system would be capable of generating an amount of power much greater than that required for air compression, or oxygen pumping, and feed pumping. In a theoretical study of power generation from oxidation of coal by SCWO, energetic efficiencies of 37% with steam at 650°C and 30 MPa are achieved.[23] Fujie et al.[94] studied the combustion behavior of brown coal in SCW obtaining a complete destruction at 600°C and 30 MPa during a residence time <1 min and without production of NO_x or SO_x, suggesting that the exhaust gas processing would be unnecessary, and thus making the possibility of a power station working with the SCWO of coal more attractive.

Design Considerations

Because of the harsh operational conditions of the SCWO process, particularly high temperature and high pressure, special attention to the reactor's design and to construction materials must be paid. Corrosion and salt deposition are the main challenges of the SCWO process and they should be taken into account in the design of reactors for the SCWO process.

Corrosion

SCWOs have a number of characteristics that make them especially favorable to the corrosion process.[95] The main ones are elevated temperatures and high concentrations of dissolved oxygen, along with the extreme pH values, high concentrations of ionic species (at subcritical conditions), and sharp pressure changes.

Corrosion in the SCWO environment depends both on parameters related to the aqueous solutions and on parameters related to the material (alloy composition, surface condition, material purity, and heat treatment).[96]

Typical Forms of Corrosion in the SCWO Process. The main forms of what corrosion may appear in the SCWO process are the following: pitting corrosion, general corrosion, intergranular corrosion [intercrystalline corrosion (IC)], and stress corrosion cracking (SCC).[96]

- Pitting corrosion

Pitting corrosion is a localized form of corrosion occurring in the passive state of the metal, produced by aggressive anions such as chloride or bromide that can penetrate into the protecting oxide film and destroy it locally. Typical initiation points are inclusions or grain boundaries. The small pits formed in the first step lead to the oxidation and dissolution of metal components (such as nickel and/or chromium ions) that react as Lewis acids with the water producing a strong acidification of the solution inside the pits. Because of migration processes from the bulk solution, the concentration of aggressive anions increases. Thus, the solution becomes increasingly corrosive inside the pits and corrosion progresses. Pit growth generally occurs in high rates. High temperature additionally weakens the oxide film, favoring pitting corrosion.

- General corrosion

General corrosion is ascribed to a general instability of the oxide film and thus corrosion attacks the entire surface of the metal. It occurs when none of the alloy components is able to form a protective layer. The absolute material loss caused by general corrosion might be high, but because of the diffusion-controlled character, the corrosion rates are linear and thus they can be predicted and considered in the calculations of wall thickness.

- Intergranullar corrosion [intercrystalline corrosion (IC)]

Grain boundaries and their surroundings are chemically different compared to the bulk grains themselves. This fact makes possible the formation of new phases at the grain boundaries, such as metal carbides or nitrides. Further, an enrichment or segregation, respectively, of trace elements at the grain boundaries leads to detrimental conditions. Different corrosion mechanisms are observed, so IC can be observed under nearly all conditions, but in general, the penetration depth and amount of dissolved material are low. Therefore, IC is not as critical as the other forms of corrosion. However, whole grains may be dissolved at longer times and by the influence of mechanic stress, IC may lead to the dangerous stress corrosion cracking (SCC).

- Stress corrosion cracking (SCC)

SCC is an extremely dangerous form of corrosion, given that its nature and its occurrence are stochastic. Thus, failures can be catastrophic. SCC is commonly present in the transition ranges between the active and the passive, or the passive and the transpassive potential, respectively. Thus, SCC was observed in high-temperature water in the presence of either hydrogen (active region) or oxygen (transpassive region). Most detrimental anions are chloride, bromide, and sulfide.

SCC needs both a chemical and a mechanical component. At higher mechanical stress of the material, the chemical aggressiveness of the solution does not need to be so high. On the other hand, in highly aggressive environments, relatively low values of stress can cause SCC. SCC commonly leads to a failure of the entire reactor arising from leakage.

Influence of the Aqueous Solution Properties on Corrosion. In the work range of SCWO corrosion may be produced by ionic or radical reactions pathways,[96] either of which is more prominent depending on the specific properties of the aqueous solution in the concrete area. The first one is produced by ionic reactions and is thus favored by the polarity of water. Liquid water is polar, but the polarity of supercritical water as well as that of its ionic product depend on its density, so water is very polar at high densities and nonpolar at low densities. Radical reactions are favored by low-density high-temperature water, that is, in the supercritical region.

In general, at room temperature the corrosion process is controlled by the kinetics of the oxidation reactions of the material. On the contrary, at high temperatures, the dissolution process of the protective oxide layer controls the corrosion process. In high-temperature water, this protective layer has a different composition from that formed at room temperature because the thermodynamically metastable components that form the layer at room temperature are rapidly dissolved. Thermodynamically stable products form the layer produced in high-temperature water. This is why the corrosion rate is higher when the inner part of the reactor is exposed to the atmosphere, that is, the reactors working in batch. This is what Hayward et al. call the "hide out" effect.[97]

The corrosion rate in water usually increases with temperature, but in the case of the supercritical water, the behavior is different. Corrosion experiments in supercritical aqueous solutions show that the corrosion at supercritical temperatures of 500°C was lower by orders of magnitude than at subcritical temperatures of 300°C.[95,97-99] This fact is explained by the sharp change of the thermophysical properties of water in the surroundings of the critical point such as density and dielectric constant.

At temperatures > 600–700°C, another corrosion mechanism, called high temperature corrosion (creeping) can occur. At these temperatures, most commonly used metals, such as iron, nickel, and chromium begin to form volatile corrosion products, which are easily retired from the surface of the metal, or in some cases melt the material, leading to fast general corrosion.

As mentioned earlier, corrosion in the SCWO environment is controlled by the dissolution of the protecting oxide layer to the primary corrosion products. That is, the higher the salt solubility (which depends on the density of the solution), the

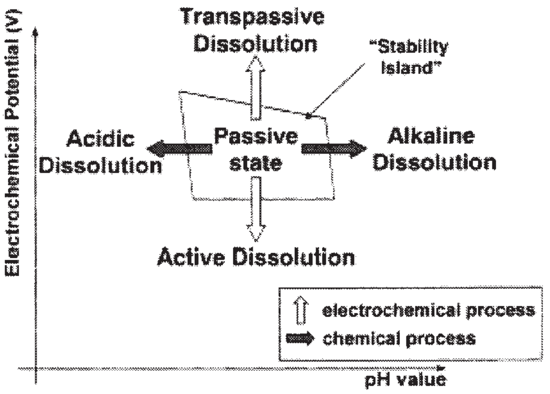

Figure 4. Stability region of the protecting oxide layer and main dissolution mechanisms (from Kritzer[96]).

faster the corrosion rate. This dissolution of the salts can be carried out by electrochemical process, which is a function of the electrochemical potential, or by a chemical process that depends mainly on the pH of the solution. This behavior is schematically shown in Figure 4.

- Chemical dissolution process

As generally known, the pH value is based on the equilibrium reaction of the self-dissociation of water:

$$H_2O \Leftrightarrow H^+ + OH^-$$

This reaction is endothermic in character and thus, at high temperatures, the equilibrium shifts toward the right side, that is, at a pressure of 25 MPa and high temperatures, the concentrations of both H^+ and OH^- are about three orders of magnitude above the values in ambient water, reaching a maximum at temperatures about 300°C, so that water can be considered to be both acidic and alkaline. Higher temperatures at constant pressure lead to a reduction of the number of hydrogen bonds and thus favor the nonpolar character of water. Consequently, self-dissociation drastically decreases above a certain temperature. The dissociation of mineral acids follows the course of density of the solvent, reducing when increasing temperature at a constant pressure, and increasing when elevating pressure, as Frantz proved for HCl.[100]

The pH value is one of the factors that has more influence on corrosion in high-temperature water because extreme values of pH lead to a chemical dissolution, which is described as dissolution of the protecting oxide at constant electrochemical potential, and indicated as the horizontal direction in Figure 4. This form of dissolution is caused by the amphoteric character of most oxides; they can be dissolved either in acidic or in alkaline solutions. The pH region of highest stability depends on the isoelectrical point of the oxide, which is a function of temperature. Of the oxides formed by the most common materials used in the SCWO process, chromium oxide is the least soluble and nickel oxide is the most soluble in supercritical water. This explains why chromium alloys present the best resistance to corrosion. Kritzer presents an exhaustive review about corrosion in high-temperature water, making special emphasis on this phenomenon.[96]

- Electrochemical dissolution process

The protective oxide layer formed when the metal is passivated can also be dissolved through an electrochemical process, as indicated in the vertical direction of Figure 4. The explanation of this phenomenon is the following: because most of the reactions responsible for corrosion are oxidation reactions, they are highly sensitive to changes in the electrochemical potential. For the formation of the oxide film, a minimum electrochemical potential is necessary. Below that potential, the metal might undergo a so-called *active dissolution*. Increasing the electrochemical potential above that of the passive range might lead again to a high dissolution of the metal or alloy, what is known as *transpassive dissolution*.

Kritzer explains this phenomenon using the case of chromium as an example. Chromium is the metal that forms the protective oxide layer in most Ni alloys and stainless steels, the most widely used materials in the SCWO process. In the passive state chromium oxides to Cr(III), insoluble, that perfectly protects the material. Below the minimum electrochemical potential Cr(III) transforms into Cr(II), which is soluble, and is thus unable to protect the material ("active dissolution"). Increasing the electrochemical potential above that of the passive range, Cr(III) passes to Cr(VI), also soluble ("active dissolution"). This process in chromium is disfavored by high temperature because the maximum potential of the passive range decreases with increasing temperature.

The transpassive process has not been observed at room temperature in materials such as titanium, niobium, or tantalum up to very high electrochemical potentials, but as the properties of the oxide layer change in supercritical medium, it does not mean that this process does not occur at high pressures and temperatures.

As the solubility of oxygen in water increases, the oxidizing power of the solution increases, too, and electrochemical processes become more important (in a typical SCWO environment oxygen partial pressure is nearly two orders of magnitude above the corresponding value for applications in air at ambient pressures). Even though Cr at high temperatures and oxygen concentrations tend to transform into soluble Cr(VI), Ni alloys can resist this condition because of the NiO protective layer, except in the presence of Cl^-, when the protective layer rapidly dissolves. In summary, Ni alloy corrodes rapidly at high temperatures and acid conditions because Fe and Ni dissolve chemically, whereas Cr dissolves electrochemically.

- Influence of anions

Anions can promote or inhibit the rates of different corrosion processes, according to how they interact with the protective oxide film layer of the metal. Their main influences are:

(1) *Oxide-film destruction*. Some anions such as halides (chloride, bromide, and iodide, but not fluoride) in high-temperature water and also sulfide or sulfite under harsher conditions may lead to a localized destruction of the oxide layer (such as pitting corrosion, SCC).

(2) *Corrosion product dissolution rate*. For example, the general corrosion of nickel-base alloy 625 at high subcritical temperatures in oxidizing solutions of HCl and HNO_3 occurs in the same temperature range, but the corrosion rates differ by an order of magnitude because of the higher solubility of $Ni(NO_3)_2$ compared with that of $NiCl_2$.

(3) *Anions as oxidizing agents*. Nitrate and sulfate in high-temperature water can also corrode metals in the absence of oxygen.

(4) *Oxide-film supporting by incorporation*. Several anions are incorporated in oxide film, drastically reducing the solubility of the layer. This positive behavior was proved experimentally for carbonate, phosphate, fluoride, and hydroxide at high temperatures.

Construction materials

Influence of the Characteristics of the Construction Materials in the Corrosion

- Alloy composition

It seems obvious that the alloy composition has a great influence on its resistance to corrosion.

Chromium, as an element in an alloy, enhances the protection of that alloy against pitting in acid and an oxidizing environment. Nevertheless, at high temperature it has a tendency to form chromates and loses its protective effect.

Nickel is able to enhance corrosion resistance in alkaline, oxidizing agents and at high temperatures, but in acid conditions at high temperature both Ni alloys and Fe alloys with high nickel content present high corrosion rates.

Alloys with elements such as Nb, Ta, Al, Zr, and Y are supposed to be completely stable in high-temperature water and in the presence of an oxidizing agent, but these alloys are still not tested at these conditions.

- Heat treatment and surface conditions

The most widely used materials in SCWO are Ni alloys and stainless steel. In these alloys, the following parameters related to general corrosion and pitting corrosion are of great importance[96]:

(1) *Nonmetallic inclusions in the grain boundaries*. Depending on the heat treatment applied to the material, the concentration of certain elements in the grain boundaries can be lower that in the rest of the alloy, that is, when the concentration of chromium in the grain boundaries is 50% lower than that in other parts of the material, chromium carbide can be formed, with a detrimental effect on the resistance of the material.

(2) *Strong enrichment of nonmetallic contaminants in a small area that can lead to intergranular attack and stress corrosion cracking*. At temperatures $> 900°C$, the solubility of these contaminants in the metal is high enough to avoid the formation of two phases, and at temperatures $< 600°C$, the migration velocity of impurities toward the grain boundaries is too slow. Thus to avoid this phenomenon, the most detrimental temperature region is between 600 and 900°C.

(3) *Surface condition*. Polished surfaces are known to be more resistant to corrosion than nonpolished ones. However, after corrosion has once started, the corrosion rate of polished surfaces might be significantly higher.

Most Widely Used Materials in SCWO Process. As a result of the corrosion processes described before, and of the necessity for working at high pressures and temperatures, both reactors and heat exchangers of the SCWO process should be constructed in materials appropriated for their resistance to corrosion and high temperatures. Russel[101] studied the "top" materials appropriated for the SCWO process.

- Stainless steel (AISI 316) is adequate for working at temperatures between 300 and 500°C, low concentrations of Cl^-, and values of pH between 2 and 11.
- Titanium alloys (Ti-Gr2, Ti-Gr9, and Ti-Gr12) present high resistance to strongly oxidative environments. Nevertheless, at high temperatures their mechanical resistance is low (creeping). It could be a good solution to use it as coating of another material.
- Al- or Si-based ceramics, such as alumina, silicium carbide, or nitride, are good options for working below $pH = 12$. At higher pH values these materials are dissolved.
- The most promising and commonly used solutions to obtain high resistance to corrosion at high temperatures are Ni alloys 625 and C-276.
- New alloys, with better properties, are currently being developed, but they have not been tested in SCW. Some proposals to enhance the existent alloys are the following:

(1) Test whether chromium is really necessary in Ni alloys because of the detrimental behavior of chromium in high-temperature oxidizing conditions.[96]

(2) Develop Co alloys that could present better resistances than Ni alloys in oxidizing and high-temperature environments. Until now, these alloys have been tested in water with high sulfide and chloride concentrations at temperatures $< 200°C$, obtaining bad results, possibly arising from the lower Cr and Mo contents than other Ni alloys designed specifically to withstand corrosion in environments with Cl^- at high temperatures.[101]

At the moment, it is accepted that there is not a unique material able to withstand all the possible conditions. The SCWO process is a very versatile technology and its development should not be dependent on the available construction materials.

Table 1. Solubility Data of Key System H_2O–Inorganic Salts in the Surroundings of the Critical Points of Water

System	Reference(s)
$NaCl–H_2O$	103–108
$KCl–H_2O$	107
$Na_2SO_4–H_2O$	103, 109
$NaCl–Na_2SO_4–H_2O$	103, 110
$Na_2CO_3–H_2O$	109, 110, 111
$Na_2CO_3–Na_2SO_4–H_2O$	110, 111
H_2O–nitrates	112

Avoiding salt precipitation problems in SCWO process

As mentioned earlier, liquid water at room conditions is a good solvent for inorganic salts (100 g/L), but the solubility of inorganic salts in water decreases drastically near the critical point of water (1–100 ppm). Thus, in supercritical water the presence of precipitated solids can lead to fouling, plugging, and erosion of equipment. These solids can be present in the feed or be produced during the reaction. They can even be produced by adding an acid solution for neutralization to the system. In fact, the plugging of reactors produced by the salt precipitation is the main reason for delay of the commercialization of the SCWO process for some applications.[7,102]

Several studies have been carried out to determine the precipitation conditions in the SCWO process. Some papers containing solubility of inorganic salts in SCW are shown in Table 1. Also some models have been developed to calculate the solubilities of inorganic salts in high-temperature–high-pressure steam of supercritical water.[107,113]

NaCl and Na_2SO_4 are considered model salts because they are the most frequent in the SCWO process and because of their different behaviors in the precipitation. The phase diagram of the aqueous solutions of NaCl at 25 MPa presents a LV region between 390 and 450°C, and the solid–vapor (SV) equilibrium region for temperatures $> 450°C$. This means that in the LV area, the salt will precipitate, forming liquid salt droplets that become solids at higher temperatures.[103,107] In the case of Na_2SO_4 there is no LV area, so the salt precipitates, forming nuclei from the homogeneous fluid phase. Thus, NaCl particles will be porous and larger (up to 10 μm), whereas the sulfate rapidly forms a great number of smaller particles (1–3 μm).

A number of studies have been performed to determine how salt deposition affects and is affected by the heat and mass transfer phenomena. In general it is very important in SCW systems because natural convection is affected by temperature and concentration gradients. Given the number of factors related (fluid mechanics, heat and mass transfer, kinetic and phase equilibrium) no general conclusions have been obtained for any feed or type of reactor. In Hodes et al.[102] numerous studies are cited.

Different solutions have been proposed to solve the plugging problem. Marrone et al.[114] summarized some of these solutions:

- Solubilize the salts, by elevating the operation pressure to increase the solution density. The problem of this solution is that the solubility of the protecting oxide layer is also increasing, and thus corrosion is favored.
- Increase the velocity of the fluid, to keep the particles suspended and avoid the deposition. This is the solution adopted by Chematur in its commercial applications.[6,115] On the contrary, it has been proposed to work with low turbulence to achieve a homogeneous nucleation of the particles and reduce their adherence to the equipments walls.
- Use of additives dissolved in the feed. These additives can act in two ways: as a mobile surface (fluidized bed) where the particles can initiate the nucleation (sand, silica), but these particles can produce erosion in the equipment; or changing the chemical properties of the solid mixture, that is, another salt that mixed with the salt present in the solution forms a eutectic of lower melting temperature, to remove the funded salt.
- Introduction of mobile surfaces where the salts can precipitate. For the moment the maximum operation time of these devices is a few hours.
- New reactor designs, such as the transpiring wall reactor and the MODAR reverse flow reactor, where the precipitation of salts on the wall is avoided.

As a conclusion, Kritzer and Dinjus[7] indicated that the best solution to avoid salt precipitation inside the reactor is to reduce the quantity of salt present in the feed. This can be achieved using solid–fluid separation devices. These devices can be used before or after the reaction step. Following, some studies about the solid–fluid separation in SCW are listed:

- *Sedimentation by gravity*. This is the type of separation used in the MODAR or the tubular reactor of concentric tubes.[116] It requires a low fluid velocity and a sufficient density difference. This technique is effective for big particles, but the sedimentation velocity of the particles limits it. A periodical cleaning is necessary.
- *Hydrocyclons*. Dell'Orco et al.[117] studied the used of hydrocyclons to eliminate particles with a known size distribution, under sub- and supercritical conditions. These devices proved to be effective in the elimination of particles of microscopic size and their efficiency is increased with temperature.
- *Microfiltration systems*. Goemans et al.[118] studied the used of cross-flow microfiltration devices for the elimination of inorganic salts in SCWO processes, using $NaNO_3$ as a representative salt, of a large number of low melting point salts. The elimination efficiency increases with temperature, obtaining removal efficiencies up to 85% at 27.6 MPa and 470°C, although it is limited by the salt solubility. The separation efficiency of metal oxides with an average size of 1.6 μm was $>99.9\%$.[91] The main disadvantages of using this kind of facilities for removing salts are the important associated problems of corrosion.

Types of reactors for the SCWO process

The two main disadvantages posed by the use of SCWO are corrosion and salt deposition in the equipments. To overcome these two problems, a number of reactor designs have been developed. Schmieder and Abeln[119] divided them into four reactor concepts.

(1) *Tubular reactor*.

(2) *Tank reactor*, with the reaction zone in the upper part and a cool zone in the lower part of the tank to dissolve the salts.

(3) *Transpiring wall reactor*, with an inner porous pipe, which is rinsed with water to prevent salt deposits at the wall.

(4) *Film-cooled reactor*, which cools the wall by coaxial introduction of large amounts of water.

In this article three types of reactor were chosen to present the evolution of the SCWO reactors design: the tubular reactor, which is the first alternative to high-pressure systems; a cooled-wall reactor; and a transpiring wall reactor, a promising design to overcome salt deposition problems.

Afterward, shorter descriptions of other reactor proposals are shown.

Tubular Reactor. Because of its simplicity, the tubular reactor is the most widely used SCWO reactor, especially in small laboratory facilities such as those dedicated to essay the viability of new SCWO applications[120,121] or to determine kinetic parameters or heats of reaction.[66,68,122-124]

Generally, the kinetics of the SCWO process is pseudo first order with respect to the waste concentration. For this reason, plug flow reactors achieve the highest conversions in a certain residence time. However, tubular reactors also present important disadvantages. In the first place, they tend to plug as a result of the precipitation of salts. Another important inconvenience is that the fast exothermic reactions can produce uncontrolled hot spots inside the reactor. This reactor design makes it impossible to separate the pressure effect from the temperature effect; so even if the inner surface of the reactor is coated with a high-temperature and/or high corrosion resistant material, the temperature in the whole wall will be high, and so a thicker wall reactor will be necessary to withstand the high pressure, obtaining heavier and more expensive reactors than using film-cooled reactors.

To avoid salt deposition in tubular reactors, they are designed with small diameters, to obtain high fluid circulation velocity. However, even when this design avoids the deposition

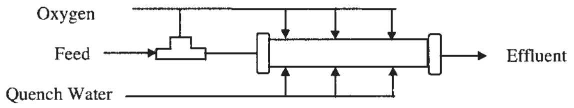

Figure 5. Scheme of the multi-injection tubular reactor (from Cocero[20]).

of solids already present in the feed, precipitated salts formed inside the reactor have a tendency to adhere themselves to reactor walls. Thus this reactor is more appropriate for feeds with low solids content.[125]

When the organic matter concentration in the feed is very high, multi-injection tubular reactors are used to avoid hot spots in the reactor. A scheme of this type of reactor is shown in Figure 5.

Nowadays, tubular reactors are used in industrial applications such as the AquaCat® and AquaCritox® processes of Chematur.[6,115] The plugging problem is solved by the used of two alternating heat exchangers, so when one of them is in the operation step the other can be in a cleaning step. A photograph of the tubular reactor of the AquaCat® process, in the 3000 kg/h capacity plant, located in the Johnson Matthey sites in Brimsdown, UK, is shown in Figure 6.

Cooled-Wall Reactor. The cooled-wall reactor is a film-cooled reactor developed and patented by the High Pressure Process Group of the University of Valladolid (Spain). In this type of reactor, temperature and pressure effects are isolated. This is achieved by using a cooled-wall vessel, which is maintained near 400°C, and a reaction chamber, where reactants are mixed and reaction takes place. This reaction chamber is made of a special material to withstand the oxidant atmosphere of the reactants at a maximum temperature of 800°C and a pressure of 25 MPa. It is enclosed in the main vessel, which is pressurized and cooled down with the feed stream before entering the reaction chamber, so that it works at about 400°C and does not suffer the oxidant atmosphere. This pressure vessel can therefore be made of stainless steel with a relatively low thickness.

Figure 6. View of the tubular reactor of the AquaCat® Process[115] (from Ref. 115).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

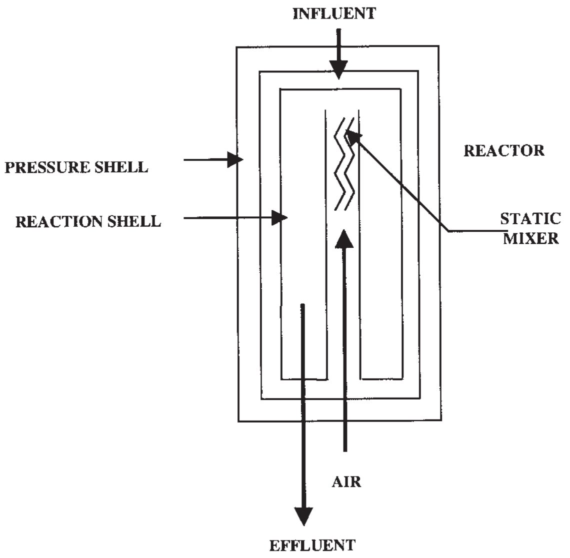

Figure 7. Scheme of the cooled-wall reactor (from Cocero[20]).

Another additional advantage of this reactor design compared to that of other film-cooled reactor designs is that it allows feed preheating inside the reactor, resulting in a compact unit that is very appropriate for mobile units. A scheme of the cooled-wall reactor's behavior is shown in Figure 7.

The cooled-wall reactor was developed in a 30 kg/h pilot plant and tested with industrial wastes such as cutting oils and PET effluents,[20,87,88,126] obtaining excellent results. In 2001, the cooled-wall reactor was scaled-up to work in a demonstration SCWO plant located in the site of the firm CETRANSA in Santovenia de Pisuerga (Valladolid, Spain), with a treatment capacity of 200 kg/h of waste.[117,127,129] Operation with this reactor is limited to low salt concentration wastes, to avoid plugging problems. Images of the reactor and the plant are shown in Figure 8.

Transpiring-Wall Reactor. The transpiring-wall reactor (TWR) consists of a reaction chamber surrounded by a wall through which clean water circulates, forming a cool, protective film against corrosive agents, salt deposition, and scaling, and high temperatures. An alternative design developed by Ahluwalia[130,131] uses a reactor consisting of concentric platelet liners such that the reaction zone is the annular region between the two liners. In recent years, numerous TWR designs have been developed, resulting in a number of patents, listed in Table 2, that are thoroughly analyzed in Bermejo et al.[132]

The main item in the TWRs is the porous wall. There are two types of porous wall. Their working principle is shown in Figure 9.

(1) In the first place, the liner patented by Mueggenburg et al.[134] consists of many thin layers or platelets bonded together. Each platelet is etched with a specific pattern of indentations such that a three-dimensional network of channels is formed when the platelets are combined to form the liner. These platelet liners, supplied by Aerojet, are used in TWRs working for the U.S. Army in Sandia's EER, Pine Bluff Arsenal[135] and in trials for the waste destruction of Blue Grass Chemical weapons.[133] Information about these reactors is shown in Table 3.

Figure 8. SCWO reactor and pilot demonstration plant of the High Pressure Process Group of the University of Valladolid (Spain).

(2) The second type of porous wall consists of a porous tubular element that is a filter element. This element can be made of a sintered metal (stainless steel[136] or Ni-alloy[132,137]) or a ceramic element, such as porous alumina.[138,139] The main characteristics of these reactors are summarized in Table 3.

Currently, some transpiring-wall reactors are in use. Their main characteristics and operational parameters are summarized in Table 3.

All the reactors presented here have a porous element that serves as the wall of the reaction chamber, and have found different technical solutions for reagent preheating, cooling, and flow control though the wall. A complete analysis of these factors is made elsewhere.[132] With regard to the operational results, even when all these reactors have been successful in destroying contaminants, they failed in recovering all the salts introduced with the feed, even though the plugging problem is eliminated.[132]

The main disadvantage of this reactor is the energy recovery: the hot products are cooled and diluted by mixing with the transpiring cold water. To avoid plugging problems it would be convenient if the salts would exit the reactor in a water solution. Thus, the outlet temperature should be under the critical point of water to maximize salt solubility and, as a consequence, the heat recovery is less favorable.

Other Reactor Designs

- *Reverse flow tank reactor with brine pool*

MODAR Inc. (Natick, MA) developed the first tank reactor.[141] It is composed of an elongated, hollow cylindrical pressure vessel, capped at both ends so as to define an interior reaction chamber. Defined within the reaction chamber are a supercritical temperature zone in the upper region of the reactor vessel and a subcritical temperature zone in the lower region of the reactor vessel. Oxidation takes place in the supercritical temperature zone. Dense materials, such as inorganic salts, initially present in the feed or formed by reactions, which are insoluble in the supercritical temperature fluid, fall into the liquid phase present in the lower-temperature subcritical zone of the vessel. A perimeter curtain of downward flowing subcritical water is established about a portion of the interior of the cylindrical wall of the vessel to avoid salt deposits on the walls of the reactor vessel. This reactor design is used in the commercial plant of Nittetsu (Japan) for the destruction of semiconductor-manufactured wastes, with a treatment capacity of 63 kg/h.[114] In 1998, Stone and Webster was contracted by the Defense Advanced Research Projects Agency and the Office of Naval Research to design a very compact, automated shipboard unit, using this reactor design.[142]

Table 2. Main Patents Related to the Transpiring Wall Reactor*

Inventor (Assignee)	Patent Number (Date)	Description
Mc Guinness (Turbosystems)	5384051 (1/25/95)	Transpiring wall reactor to introduce supercritical water and oxidant.
Mueggenburg et al. (Aerojet-General Corp.)	5387398 (2/7/95)	Platelet design for SCWO transpiring wall reactor.
Mc Guinness (Turbosystems)	5558783 (9/24/96)	Transpiring wall reactor to introduce supercritical water and oxidant.
Daman (Foster Wheeler)	5571423 (5/11/96)	SCWO process using a transpiring wall reactor.
Ahluwalia (Foster Wheeler)	5571424 (5/11/96)	SCWO process using a TWR with concentric platelet liners, being the reaction space between the two liners.
Ahluwalia (Foster Wheeler)	5670040 (9/23/97)	SCWO Apparatus using a reactor with two concentric platelet liners being the reaction space between the two liners.
Daman (Foster Wheeler)	5723045 (3/3/98)	SCWO using transpiring wall reactor.

*From Bermejo et al.[132]

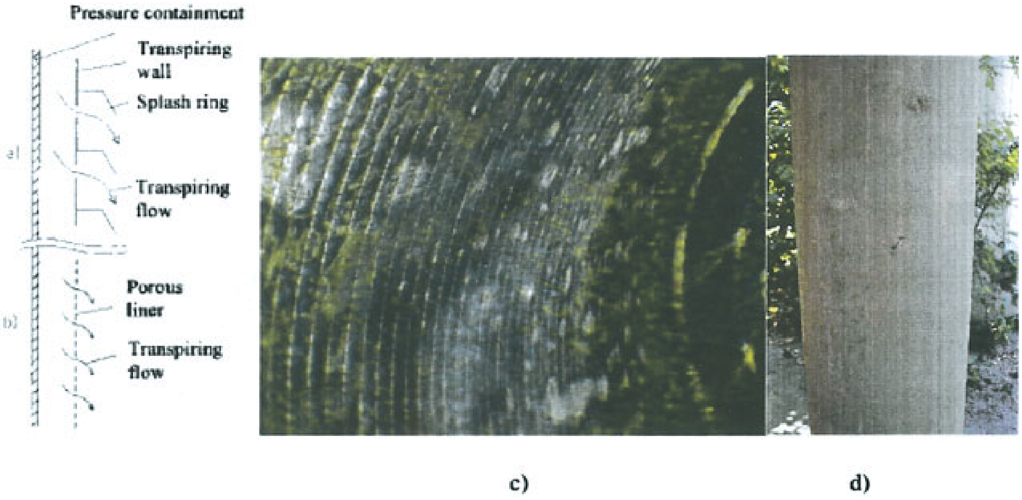

Figure 9. (a) Platelet principle; (b) porous inner type principle (from Schmieder and Abeln[119]); (c) platelet used in the U.S. Navy/Army's Dugway Proving Ground Facility after 100 h operation from Ahluwalia et al.[133]; (d) sintered porous wall of the UVa's reactor after 100 h operation.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

- *Fluidized bed reactor*

Developed by SRI International, this reactor consists of a variant of the SCWO process that uses a bed of fluidized solids functioning as both reactant and adsorptive surface for salt control. The process is referred to as *assisted hydrothermal oxidation* (AHO), and works at lower temperatures and pressures than the conventional SCWO process ($T = 380-420°C$ and $P < 22.1$ MPa).[114]

- *Reverse flow tubular reactor*

Patented by Abitibi-Price, this reactor is composed of a single tube segregated into two different thermal zones, through which process fluid can be fed in either direction. In this way, when passing the subcritical reagents, it is possible to redissolve the salt layer formed when the reactor was operating in the inverse sense, that is, in which the entrance is the outlet, and vice versa.[114]

- *Centrifuge reactor*

This was proposed by Reid and Halff,[143] modifying a centrifugal solids removal device to operate as a reactor.

- *Double-wall stirred reactor*

This reactor, developed by the CEA (Commissariat à l'Energie Atomique, Commission for Atomic Energy, France), has a double wall made of titanium to prevent corrosion and a mechanical stirrer that creates a turbulent flow, avoiding salt precipitation and favoring heat transmission.[144]

- *SUWOX process*

This reactor, developed by a process created at the IKET (Institut für Kern- und Energietechnik, Institute of Nuclear and Energetic Technology, Karlsruhe) and the FZK (Focusing Zentrum Karlsruhe, Germany),[145,146] is a film-cooled reactor. In the external chamber a stream of clean water at the system pressure is circulating; in the inner chamber the reaction takes place at 420–490°C and a pressure up to 70 MPa, having a density high enough to keep salts dissolved.

SCWO for the Destruction of Wastes: Industrial Applications

The main application of SCWO is the destruction of industrial wastes and sludges, especially those that are recalcitrant, xenobiotic, or nonbiodegradable, serving as an alternative for wet air oxidation (WAO) and incineration processes.

The SCWO process can be used for the treatment of a wide range of wastewaters and compounds that can be oxidized. When working with wastes with a low energetic content, fuel can be added to the feed, and when the waste has an elevated heating value it can be diluted down to the organic matter concentration necessary to achieve a certain reaction temperature. At the appropriate pressures, temperatures, and residence times a great variety of organic compounds have been oxidized to CO_2, water, and N_2, without detectable formation of partial oxidation products.

Up to the present, this technology has been applied to the destruction of a wide range of organic compounds nonsoluble in water or inorganic compounds such as ammonia or cyanides. In SCWO the solubility of organic compounds increases, and so does the solubility of the permanent gases as O_2. Thus the oxidation reaction takes place in a single phase, obtaining destruction efficiencies of nearly 100%.

The SCWO process has been applied to contaminants considered as toxic and dangerous, from low molecular weigh compounds to high molecular weight compounds such as aromatic, polycyclic organic compounds.[2] As an example, the following applications can be mentioned: Modell et al.[147] successfully eliminated PCBs and DDTs without formation of dioxins, and it has also been applied to the destruction of dioxins in fly ash.[148] Johnston et al.[149] applied SCWO to the destruction of pharmaceuticals, obtaining efficiencies > 99.99%. SCWO has also been successfully applied to the treatment of solid rocket propellants and synthetic military gases,[150] within the demilitarization program. SCWO has been studied as an alternative for the destruction of military wastes. Both the Department of Defense and the Department of Energy

Table 3. Transpiring Wall Reactors: Main Characteristics and Operational Conditions*

Organism	Construction Characteristics	Operational Conditions	Results	Ref.
ETH Zurich (Switzerland)	Diameter = 22 mm Length = 50 + 325 mm (combustion chamber + porous reaction area) Material: Porous Sintered Alloy 625 (3 μm) Oxidant: O_2 T. Flow: Water	t_R = 50–100 ms (combustion chamber) Feed = 5.4 + 3.6 kg/h (fuel + waste) F_T = 5 kg/h (approx.) T_R = 700°C; P = 250 MPa T_{FT} = 40–250°C	Methanol TOC rem. > 99.9%	137
ITC-CPV Karlsruhe (Germany)	Diameter = 60 mm Length = 950 mm Material: Porous Sintered SS (#1.4404, 30 μm) Oxidant: Air T. Flow: Water	Feed = 5–20 kg/h Air = 40 kg/h F_T = 30 + 50 kg/h (T. Flow + Quench) T_R = 630°C (540°C) P = 32 MPa (30 MPa) T_{FT} = 550°C	Ethanol, Na_2SO_4 Paper mill waste effluents TOC rem. = 99.9%	136
Sandia's EER (USA)	Diameter = 27.9 mm Length = 914 mm Material: Aerojet Platelet AISI SS304 Oxidant: Air T. Flow: Water	Feed = 36 kg/h F_T = 37.8 kg/h = 653 kg/m^{2}h (TP) T_{FT} = 450°C T_R = 550–450°C P = 25.5 MPa	Isopropyl alcohol Military smokes and dye formulations No Na_2SO_4 deposits in the transpiring wall	135
Pine Bluff Arsenal (USA)	Diameter = 121 mm Length = 3000 mm Material: Aerojet Platelet AISI 304 Oxidant: O_2 T. Flow: Water	Feed = 150 kg/h F_T = (TP + Quench) T_R = 400–725°C P = 24.8 MPa T_{FT} = 450°C	Isopropyl alcohol Sugar and Na_2SO_4 solutions Military smokes and dye formulations TOC rem. > 99.9% (TOC < 5 ppm)	135
U.S. Navy/Army's Dugway Proving Ground Facility (Utah, USA)	Material: Aerojet Platelet AISI 304 Oxidant: Air (replaced later by O_2)	Feed = 36–46 kg/h P = 24 MPa	Naval wastes (Cl^- and Fl^- containing) (71 h) Chemical weapons (231 h) TOC rem. > 99.9% (Trials for Blue Grass chemical weapons destruction)	133
CEA (France)	Diameter = 15 mm Length = 500 mm Material: porous α-alumina (0.8 μm and 50 nm) Oxidant: H_2O_2 T. Flow: Water + H_2O_2	Feed = 3 kg/h F_T = 3 kg/h T_R = 450°C P = 25 MPa T_{FT} = 380°C	Methanol > 99.5% Mixtures dodecane/tributylphosphate Na_2SO_4 10% recovery	138
M.E.R&D Institute, Samsung Electro Mechanics Co., Ltd., Suwon Korea University of Seoul (Korea)	Similar to CEA's reactor Oxidant: H_2O_2 (Sprayed into the reactor) T. Flow: Water + water + NaOH (last section)	Feed = 1 kg/h P = 25 MPa	2,4-Dichlorophenol T_R = 340–440°C Elimination (88.9–98.7%) (Problems of back mixing)	139
UVa (Spain)	Diameter = 74 mm Length = 1500 mm Material: Porous Sintered Alloy 600 wall Oxidant: Air T. Flow: New Water	t_R < 1 min Feed = 5–40 kg/h F_T = 10–72 kg/h T_R = 650°C; P = 23 MPa T_{FT} = 25–250°C	Isopropyl alcohol Mixtures isopropyl alcohol/acetic acid/crotonaldehyde TOC rem. > 99%	132 140

*Adapted from Bermejo et al.[132]

of the United States have contributed the most to the development of the SCWO process.[151]

NASA has investigated the SCWO process applied to the destruction of the biomass produced in spatial trips. The study has been extended to other materials such as ion-exchange resin decomposition,[152] biomass, and industrial and urban sludges, with an important energy recovery in the waste destruction.[153] SCWO has also been studied with respect to the destruction of light radioactive wastes.[154]

Recent applications with recovery of valuable solid products are the following. Veriansyaha et al.[120] achieved chromium recoveries > 97% (as Cr_2O_3) from the SCWO of wastewater from a liquid crystal display (LCD). Lee et al.[121] recovered hematite (α-Fe_2O_3) nanoparticles from the SCWO of NaFeEDTA (metal complex ethylenediaminetetraacetic acid). At the industrial scale, the AquaCat® process of Chematur recovers oxidized metals from the SCWO of catalyst,[115] in Johnson Matthey, Brimsdown, UK.

Industrial applications of the SCWO

The SCWO process was developed industrially by MODAR and MODEC. Since 1996 MODAR has been part of the Gen-

Table 4. Main Companies and Commercial Plants of the SCWO Process*

Company Reactor Used	Commercial Plant (Country)	Application (Processing Capacity)	Date	Ref.
Organo Corp (Lis. MODAR) MODAR reverse flow tank reactor	Nittetsu Semiconductor factory (Japan)	Semiconductors manufacture wastes (63 kg/h)	1998 (built) (No longer functioning)	8, 114
	A national Japanese university		In operation since 2002	
MODEC (Horizontal reactor with high velocity and brushing)	Several companies (Germany)	Pharmaceutical wastes, pulp and paper mill waste, sewage sludge (2 tons/day)	Until 1996	114
General Atomics (GA)	U.S. Army, Newport, IN (USA)	Bulk VX nerve gas agent hydrolysis, chemical agents, explosives, dunnage, shipboard wastes, and rocket propellant (949 kg/h)	1999 (Commissioned) 1/10 scale plant tested in 2000–2001	114, 155, 157
Reactor with the inner wall covered by platinum, titanium, or Ni alloy.				
Salt precipitation controlled by additives and periodical cleaning)	U.S. Army, Blue Grass Army Depot, KY (USA)	Chemical agents, aging munitions	Contract awarded at 2003. Expected completion in 2009	8
Foster-Wheeler (Transpiring wall reactor)	U.S. Army (Pine Bluff, AK (USA)	Smokes and dyes, chemical agents, explosives, and shipboard wastes (150 kg/h)	1998 (No longer functioning)	114, 135, 8
Eco Waste Technologies (EWT) (Rights acquired in 1999 by Chematur)	Huntsman Chemical, Austin, TX (USA)	Oxygenated and nitrogen-containing hydrocarbons (such as alcohol, glycols, amines) (1500 kg/h)	1994–1999	114
Chematur	AquaCritox® Process, Karlskoga (Sweden)) (Pilot plant)	Nitrogen-containing wastes (250 kg/h)	1998	114, 115, 6
Tubular reactor, with periodic reactor flushing with nitric acid and/or high velocity	Aqua Cat® Process, Johnson Matthey premises (UK)	Spent catalyst: recover platinum group metals and destroy organic contaminants (3000 kg/h)	Commissioned 2002 Starting up 2004	
	Japan (built by Shinko Pantec)	Municipal sludge (1100 kg/h)	2000 (Built)	
SRI International (AHO process)	Japan (built by Mitsubishi Heavy Industries)	PCBs and chlorinated wastes	Completed in 2005	114
Hydro-Processing	Harlingen, TX	Mixed municipal and industrial wastewater sludge (9.8 tons dry sludge/day)	2001 (Built) Stopped because of corrosion problems	114, 5, 8

*Adapted from Marrone et al.[114]

eral Atomics (GA) group. Other companies such as Foster and Wheeler and Chematur have also played an important role in the commercialization of the SCWO process. In Table 4, the main SCWO supplier companies and their main industrial plants are listed.

The first SCWO industrial plant was built by EcoWaste Technologies in 1994 for the Huntsman Petrochemical plant in Austin, TX, with a processing capacity of 1500 kg/h wastes, mainly oxygenated and nitrogen-containing hydrocarbons (such as alcohol, glycols, amines).[114] In 1999, the Swedish company Chematur acquired the SCWO exclusive rights of EcoWaste Technologies.

GA[155] has designed, fabricated, and installed numerous SCWO systems for the U.S. Government and commercial clients, including systems for the treatment of chemical warfare agents/agent hydrolysates; energetic slurries and hydrolysates; size-reduced wood, plastics, and carbon; municipal sludges; fire suppression fluids; and general hazardous wastes. In support of the Army's Chemical Agent Demilitarization Program, GA is developing a full-scale SCWO disposal system for destruction of hydrolyzed VX nerve agent, with a processing capacity of 949 kg/h waste feed. Previous to the construction of the Newport full-scale SCWO, GA has designed, built, and tested a 1/10th-scale SCWO system to provide design verification and scale-up data for the full-scale SCWO system. The 1/10th-scale SCWO system was relocated to a RCRA hazardous waste treatment facility in Texas, where field tests with over 20 metric tons of VX/NaOH hydrolysate have been successfully carried out. GA, as part of the Bechtel Parsons Blue Grass Team, was awarded in 2003 with a contract for the design and fabrication of multiple SCWO units for the destruction of agent (GB, VX, and mustard) and energetic (propellant and explosives) hydrolysates as well as size-reduced wood and plastic associated with assembled chemical weapons disposal at the Blue Grass Army Depot site in Richmond, KY.

Foster and Wheeler also developed SCWO plants for the

U.S. Army, using the patented design of the transpiring-wall reactor. The TWR of Sandia National Laboratories (Livermore, CA) is the pilot-scale prototype (Feed = 36 kg/h) of the reactor at Pine Bluff Arsenal (Feed = 150 kg/h). Total organic carbon (TOC) removals $> 99.9\%$ (TOC < 5 ppm) have been obtained working with isopropyl alcohol, sugar, and Na_2SO_4 solutions and military smokes and dye formulations.[135] At the moment the plant is inactive because of liner mechanical issues and limited funding.[8]

In April of 2001, the first SCWO plant for the destruction of sludges began its operation in Harlingen, TX, with a processing capacity of 9.8 tons/day of dry sludge. This plant is working according to the Hydrosolids Process, developed by Hydroprocessing LLC.[5] At the moment the plant is inactive because of corrosion issues.[8]

In Europe, Chematur has commercialized its SCWO process under the brand name Aqua Critox®.[6,115] Chematur has also developed two processes.

(1) The AquaReci® process is a joint development of Chematur and Feralco AB. The process can be applied to municipal and drinking water sludges. The Aqua Critox® process is combined with recovery of coagulants and/or phosphorous from the pure, solid inorganic residue resulting from the supercritical oxidation step.[115]

(2) The AquaCat® technology was jointly developed by Chematur and Johnson Matthey for the recovery of precious metals from spent catalysts.[115] In this way transportation of hazardous waste can be eliminated. The first commercial-size unit was built at Johnson Matthey's Brimsdown site, and started up in 2004. The unit is the first commercial unit in Europe based on supercritical water oxidation, and the largest SCWO unit in the world.

The French firm Hydrothermale Oxidation Option (HOO) has recently been commissioned to design two SCWO plants in France. The plant at Ostau is designed for treating industrial wastes with low concentrations of salts and chlorine; it has a tubular reactor with a treatment capacity of 100 kg/h.[156]

Conclusions

In recent years supercritical water and near-critical water have generated increasing interest as reaction media, taking advantage of their special properties. The most developed reaction process in supercritical water is the supercritical water oxidation or SCWO.

SCWO is a versatile technology able to obtain the complete destruction of a great variety of wastes in short residence times. The process runs at temperatures $> 600°C$, pressures > 22.1 MPa, and under an oxidant atmosphere that makes conditions favorable for the corrosion of construction materials. SCW properties make for a favorable homogeneous reaction media but the low solubility of polar compounds causes solids precipitation and plugging. These well-known problems of the SCWO process define the needs of research: new reactors that avoid corrosion and plugging.

Modeling is a necessary tool to develop new reactors. Reactor modeling is able to provide insight into characteristics of the reactor that are difficult to obtain experimentally, and also to furnish a better understanding of the mixing process. To achieve good reactor simulations, it is essential to possess accurate values of the thermodynamic and transport properties of the aqueous mixtures. In this field, much work remains to be done because, even when transport properties of water can be predicted, thermodynamic properties and phase equilibrium of the aqueous system are still a handicap, especially when inorganic salts are present in the mixture.

As an alternative to conventional reactors, the transpiring wall reactor presents a possible solution for corrosion and plugging problems. The transpiring wall reactor presents the disadvantage of the dilution of the hot reaction products by mixing them with the transpiring water. Thus, the reactor effluent temperature is reduced, making the heat recovery less efficient. More research should be done to improve materials construction and the heat recovery of this reactor design, and in developing other reactor designs able to achieve good protection of the materials of the reactor, avoiding corrosion and salt deposition and at the same time maximizing the energy recovery.

The same problems affect other equipment as heat exchanges. Some designs avoid using external heat exchanges by the mixture of feed, oxygen, and fuel. This alternative is less favorable for the energetic balance of the process.

Corrosion and plugging problems continue to cause some existing SCWO industrial plants to stop after a few months of operation. The extreme operational conditions along with the corrosive environment make necessary an extensive study of the materials behavior on duty. A challenge in SCWO is the application of new construction materials able to stand the harsh operational conditions in the main equipment, valves, and fittings.

From the perspective of energetics, SCWO can be performed in an energetically profitable way. Corrosion resistant devices for separation of salts must be developed, to produce electricity by direct expansion of the reaction products. Currently, research conducting the development of turbines able to work at temperatures $> 700°C$ is progressing, which will facilitate a profitable energy recovery from the SCWO effluent.

We are confronted by the challenge to create a technology that is technically and economically viable—without environmental limitations!

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