

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Supercritical Water Oxidation for Environmentally Friendly Treatment of Organic Wastes

Yanhui Li and Shuzhong Wang

Abstract

Supercritical water oxidation is a promising, environment-friendly technology to efficiently deal with a wide variety of organic wastes such as wastewaters, industrial and municipal sludge, etc. As for the two key problems, i.e., corrosion and salt plugging, generally encountered in supercritical water oxidation plants, this chapter firstly reported the related mechanism analysis, solutions, research status, and development trends, respectively. From the perspectives of corrosion prevention and control, safety and automatic control, economic improvements, and development of novel reactors, a number of advanced technologies and equipment such as on-line desalination in supercritical water, new operation scheme assisted secondary traditional treatment, produced-gas recovery and oxygen reuse and novel TWM reactor, etc., were introduced systematically. Finally, this chapter summarizes the implementation status of industrial plants and the technological features of several firms being active in the construction of full-scale supercritical water oxidation plants. This chapter will provide very valuable information for the researchers and engineers who are interested in supercritical water oxidation for the harmless treatment of organic pollutants.

Keywords: supercritical water oxidation, waste treatment, corrosion, salt precipitation, technical status, industrial plants

1. Introduction

Supercritical water (SCW) refers to water whose temperature and pressure are above its critical point (374.15°C, 22.1 MPa). The physical properties of SCW such as density, viscosity, dielectric constant, hydrogen bonding, and ionic product is vastly different from those of normal water and steam. The density of SCW is about 1/3 of the normal state, the dielectric constant is reduced from 87.7 at 0°C to 2–30 of SCW, and the ion product is reduced 10^3 to 10^9 times than that of normal water. Supercritical water has a low dielectric constant, and thus is extremely soluble to nonpolar compounds such as organic matter and oxygen. In addition, SCW has a significantly lower viscosity than that of the normal water, the diffusion coefficient is improved, the mass transfer performance is enhanced, and thus it can be completely miscible with nonpolar gases and hydrocarbons. In view of the special properties of SCW, nonpolar molecules such as O_2 and organic matter have strong solubility in supercritical aqueous systems, which can be mutually dissolved in any ratio to form a homogeneous phase, and the mass transfer resistance at the interface

is eliminated. There, SCW can be used as an excellent reaction medium for organic matter and oxygen [1].

Supercritical water oxidation (SCWO), which was firstly proposed by Modell in MIT in the middle of 1980s, is an effective and advanced oxidation technology to destruct organic matters by taking advantage of the unique properties of SCW under the typical operation conditions of 450–600°C, 24–28 MPa. A schematic of a typical SCWO process is displayed in **Figure 1**. In SCWO reactor, organic wastes can be thoroughly oxidized and decomposed into harmlessly small molecules, such as CO_2 , N_2 , water, etc., under excess oxidants in single-phase SCW. Hetero-atoms in organic matters are mineralized into corresponding acids or inorganic salts, and the formation of nitrous oxides is inhibited owing to the low reaction temperature. SCWO is particularly suitable for disposing organic wastewaters with high toxicity, high concentration, and bio-refractory components [2–4]. It can also recover energy and achieve heat self-sufficiency easily to ensure an economic advantage [5]. When a mass concentration of organic matters in feedstock is in the range of 3–4%, the whole reaction process does not require an extra energy input commonly. Furthermore, compared with incineration, SCWO does not have the problems of high cost, public resentment, and secondary pollutants like dioxins [5]. Hence, SCWO has attracted much attention in the past three decades. Brunner [1] has summarized SCWO results of real waste materials including textile wastewater, wastewater from terephthalic acids, food wastes, municipal excess sludge, and alcohol distillery wastewater. Furthermore, Veriansyah and Kim [5] have also systematically introduced SCWO experiments of toxic organic wastes such as pesticide, bacteria and dioxins, chlorophenol and chlorobenzene, pharmaceutical and biopharmaceutical wastes, solid rocket propellants, military wastes, etc. Some other feedstocks, including landfill leachate [6–9], industrial dyeing wastewater [10, 11], polychlorinated biphenyls (PCBs) [12], chlorinated wastes, oily wastes, etc., have also been disposed via SCWO efficiently.

Nowadays, SCWO plants have been commercialized by several famous companies and universities [14–16], such as General Atomics, Chematur AB, HydroProcessing, Supercritical Fluids International (SCFI), SuperWater Solution, Xi'an Jiaotong University (XJTU), etc. In 2001, two commercial-scale SCWO

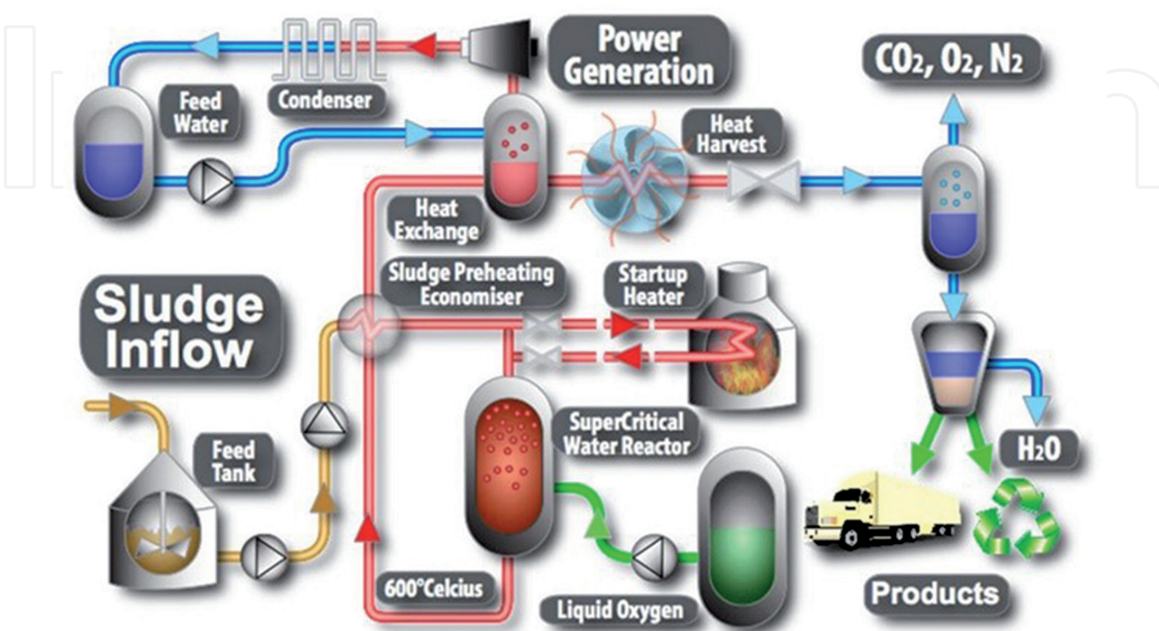


Figure 1.
A schematic of a typical SCWO process for sludge treatment [13].

plants were installed in Harlingen (Texas, USA) to treat sewage sludge with the solid-containing rates of 7–8 wt% [14]. Another SCWO plant with a treatment capacity of 7 m³/h has also been built by Chematur Engineering AB (Sweden) to deal with sewage sludge [17]. From 2009 to 2011, SuperWater Solution installed and successfully tested a 5 dry t/d SCWO system for the Iron Bridge Regional Water Reclamation Facility in Orlando, FL, USA [16]. In 2007, the SCFI Group acquired patented SCWO technology (AquaCritox®) from the Sweden Chematur Engineering AB. Further work directed by the SCFI group has emphasized the reduction of costs. In 2015, the world's first 100 t/d SCWO plants for industrial refractory wastewater treatment was designed and constructed under the guidance of the authors. Besides, there were some other pilots or full-scale SCWO plants for the harmless treatment of sewage sludge and organic wastewaters. Nevertheless, the three key problems concerning corrosion, plugging triggered by salt precipitation, and high running cost still exist [18], even make some commercial scale SCWO plants inactive.

2. Key problems and status

The harsh conditions involved in SCWO process, such as high temperature, high pressure, excessive oxygen, corrosive ions, etc., easily induce severe reactor corrosion problems, meaning a shorter reactor life. On the other hand, inorganic salts will precipitate from SCW due to its extremely low dielectric constant, which may result in reactor plugging triggered by deposited salts and further cause expensive and frequent shutdowns of the whole SCWO plant. These two aspects, to a certain degree, are still not effectively solved and seriously hinder the extensive commercialization of SCWO.

2.1 Corrosion

Corrosion is a key obstacle to limit the commercial application of SCWO, which not only shortens reactor life but also induces a bad treatment effect of feedstock due to the formations of corrosion products. Harsh operation conditions (high concentration of oxidants, extreme pH values, high temperature, and pressure) together with reaction intermediate/ultimate products (high concentrations of ionic species, free radicals, and acids) result in severe corrosion problem in SCWO reactors. Corrosion mainly occurs on reactor's inner wall; it also appears in heat exchanger and cooler on inlet and outlet pipelines of the reactor [19–21].

Materials serving for SCWO include stainless steels, nickel-based alloys, titanium, tantalum, noble metal ceramics, etc. [21–25]. A series of investigations on the corrosion resistances of these materials under supercritical and/or subcritical conditions [20, 24, 26–30], reflected that no one kind of material can withstand corrosion at all conditions, but some exhibit perfect corrosion resistance under specific conditions, as given in **Table 1**. Thus, appropriate reaction conditions such as heteroatom types in feedstock, reaction temperature, and pressure should be optimized in order to minimize corrosion rate for a chosen reactor construction material. Generally speaking, nickel-based alloys show a relatively good corrosion resistance among all the acids listed in **Table 1** under supercritical conditions. Titanium is fit to be employed under subcritical conditions, and is a potential proper liner of preheater and cooler being installed before and after reactor, respectively.

Corrosion in SCWO circumstance also depends on parameters concerning both materials (alloy composition, surface condition, material purity, and heat

Materials	T < T _c ^a ; high density		T > T _c ^a ; low density	
	Good resistance	Poor resistance	Good resistance	Poor resistance
Nickel-based alloys	H ₃ PO ₄ , HF, alkaline solutions	HCl, HBr, H ₂ SO ₄ , HNO ₃	All acids	[H ₃ PO ₄] > 0.1 mol/kg, NaOH
Titanium	All acids	F ⁻	HCl	H ₂ SO ₄ , H ₃ PO ₄

^aThe critical temperature of water.

Table 1.
Corrosion resistance of alloys against various media at subcritical and supercritical temperatures [19].

treatment) and the aqueous solutions (chemical dissolution process, electrochemical dissolution process, and influence of anions) [31]. Under the same condition, various alloys always display different corrosion resistances, which mainly depend on the intrinsic content of alloying elements, especially iron, chromium, nickel, and molybdenum. Iron is usually used to improve economy of iron-based alloys, nickel-based alloys, and titanium-based alloys. In SCW, Fe shows the highest oxidation rates to form stable oxide among the interested metal elements (Fe, Ni, Ti, Mo, and Cr). The corrosion rate of Fe in the oxidizing HCl solution is three times higher than that in SCW without HCl, indicating that the oxidizing acidic chlorinated solution can promote dealloying Fe of alloys in high density systems [32]. Fe always has a faster diffusion velocity than other elements so that the Fe oxides make up the majority of the outer layer of corrosion scales formed on alloys at temperature higher than 400°C [33]. The common Fe oxides includes Fe₂O₃, Fe₃O₄, and α(γ)-FeOOH under the SCWO condition. The mass loss of Fe is higher than that of Mo at 300–350°C and lower than that of Mo at 400–450°C in SCW with NaCl [34].

The Cr is considered as the most important alloying element to improve corrosion resistance [35]. The Cr₂O₃ presented the lowest solubility and the best oxidation resistance among the oxides of chromium, iron, and nickel [29, 32, 35–38]. The higher chromium-containing alloys presented the lower thicknesses of the formed oxide scales. The NiCr₂₅ alloy performed the best corrosion resistance among the interested binary Ni-Cr alloys (0–25 mass% Cr) in an aqueous solution resulting from the oxidation of CH₂Cl₂ at 40 MPa and temperatures of 100–415°C [39]. The cracking susceptibility of nickel-based alloys also decreased with an increase in Cr content of the substrate exposed to SCW containing HCl or NaOH [40]. The oxygen affinity of chromium is higher than those of iron and nickel, and thus Cr generally may be selectively oxidized to Cr(OH)₃ and Cr₂O₃. The Cr(III) of Cr₂O₃ can be transformed into Cr(VI) by further oxidation in the oxidizing high temperature water, and unfortunately the Cr(VI) possibly loss by the dissolution. A more continuous and stable Cr₂O₃ layer was formed at higher temperatures (450 and 500°C) than at 400°C in oxidizing SCW [41]. A series of results indicate that alloys generally suffer the more serious corrosion in high temperature subcritical water rather than in SCW at low density. Mo improves the resistance to pitting corrosion in subcritical salt solution obviously [42]. In nickel-based alloys, the synergistic effect of Mo and Cr on improving the corrosion resistance is remarkable [43]. The nickel-based alloys often show a severe depletion of nickel in high-density aqueous systems [32, 37], while NiO, which is an effectively protective oxide, covers the alloy substrate in SCW environments at low density [44].

For a specific reactor material, the corrosion behavior is commonly influenced by the dissociations of acids, salts, and bases, the solubility of corrosion products and gases, and the stability of protective oxide scales. All these characteristics are

affected by density and ionic product of the solution [11, 20]. In order to decrease corrosion rate, it is better to adjust the solution density to be below 200 kg/m^3 [31], which may result from the variation in corrosion mechanisms at high- or low density aqueous systems. Lots of studies have been carried out on the mechanism of corrosion scales grown on metal materials in SCW [29, 45, 46]. Two typical mechanisms, such as solid-state growth mechanism and mixed model (formation of the inner layer by solid-state growth process and formation of the outer layer by a metal dissolution-oxide precipitation mechanism) depending on the water density below or above $100\text{--}200 \text{ kg/m}^3$, have been proposed [24, 29, 45, 47, 48]. Solid-state growth mechanism has been used successfully in corrosion problems of various materials such as alloys and ceramics in high temperature gaseous environments such as single gas (O_2 , N_2 , and CO_2), air, high temperature steam, and a series of mixture gases. According to the diffusion rate of metals involved in the substrate, some alloying elements with relative slow rate are retained and enriched in the inner layer, while the outer layer grows outwards resulting from that the metal ions, especially irons, transport along oxide grain boundaries outwards and then react with gas species at scales/environment interface [29, 38, 45]. However, the mixed model, obtaining satisfying application in condensed aqueous systems, emphasizes that the outer layer is formed by a metal dissolution-oxide precipitation mechanism, and the precipitated metal ions are released from the corroding metal itself or originate elsewhere in the system [27]. The dissolved metal cations combine with anions such as OH^- in aqueous environments to form oxides or hydroxides; they then precipitate on specimens surface to form and/or thicken the outer layer [49]. Li et al. [30] reported that the corrosion of Inconel 600 and Incoloy 825 in low density SCW containing sulfides also follows the solid-growth mechanism.

2.2 Salt precipitation

Salt management was identified as a critical issue for the success of SCWO technology. Except for the inorganic salts initially present in the feedstocks, a majority of inorganic salts derive from the SCWO treatment of high-concentration, stubborn organic matters including hetero-atoms such as chlorine, sulfur, and phosphorus [50]. Solubility of salts is reduced evidently in SCW, which is usually lower than 100 mg/L , and thus they are prone to deposition. In addition to corrosion issues, plugging triggered by salts precipitation is another main obstacle to hinder SCWO commercialization, which is induced by sticky salt agglomeration and deposition on the internal surface of reactor.

When plugging takes place, the SCWO plant has to be shut down, washed, and restarted, which will directly decrease the reliability of the plant and increase its running cost. Inorganic salts, whether soluble or not, may come from feedstock or reaction byproducts, and their viscosities decide the tendency of depositing on the reactor wall. In general, different salts own different deposition characteristics [51]. Salt deposition principles and the corresponding solutions have been systemically presented in the previous literatures [50, 52, 53]. In a commercialized SCWO plant, reactor plugging can be avoided by particular reactor designs, special instruments, and operation means [18]. Possible solutions are to adopt reverse flow tank reactor, reverse flow tubular reactor, transpiring wall reactor, centrifuge reactor, mechanical brushing, rotating scraper, reactor flushing, crossflow filtration, density separation, additives, high flow velocity, homogeneous precipitation, and extreme pressure [17]. In fact, precipitated salts are relatively difficult to be removed out of SCWO plant during the operation process; thus, most SCWO plants do not have salt removal function. Salts in SCWO are classified into Type 1 or Type 2, according to their solubility [54], Type 1 salt has a high solubility in the

range of water's critical temperature, while Type 2 salt has a low solubility in this region. Type 2 salt can be separated by properties of SCW [50], and the suitable supercritical conditions should be controlled at approximately 400°C and 25 MPa according to the solubility of salts mentioned in the previous studies [52, 55]. Hydro cyclone or centrifugal reactor helps to remove soluble salts under the above-mentioned supercritical conditions, but severe wearing problem is inevitable. Of course, low salt concentration in feedstock is helpful for avoiding reactor plugging. Appropriate reactor configuration and pre-desalination before reactor may solve reactor plugging problem effectively and economically.

In addition, when the preheating temperature of feedstock is in the range of 200–450°C [56], some undesired intermediate products like tar and char will be generated, which may also plug preheating pipeline. To overcome this problem, the following options are taken into consideration, which include enlarging the inner diameter of the preheating pipeline, adding a small amount of oxidant into the preheating pipeline to inhibit the formations of tar and char, increasing the heating rate of feedstock, and preheating feedstock up to a lower temperature even not preheating [57]. However, the improvement of the heating rate is limited by setting space of heating part, heating methods, and withstanding temperature of preheater wall. The above fourth approach means that a large amount of heat will not be recovered into the SCWO system, which will undoubtedly reduce the energy efficiency and increase the running cost.

Salt deposition also accelerates catalyst inactivation rate and reactor corrosion rate, and reduces heat transfer coefficient [22, 58]. The potential catalysts for SCWO reactions may be poisoned and/or polluted quickly by precipitated salts in SCW [59]. It is also difficult to replace catalyst in traditional reactor configuration. That may be the reason why Savage has reported that no catalyst is implemented commercially for catalytic SCWO for organic waste treatment [60]. Thereby, it is important to separate these precipitated salts before they contact heterogeneous catalyst. Comparing with salt of ion form in subcritical water, salt in the form of molecule in SCW is relatively less corrosive [19, 21–23, 61]. Salt precipitated out from SCW mainly results in chemical corrosion through oxidation reaction. Salt in subcritical water or high density SCW mostly promotes electrochemical corrosion [58, 62], and may result in inter-granular corrosion starting from the edge of metal grain [49]. Nowadays, two contradictions of preventing salt deposition and minimizing reactor corrosion rate are displayed as follows: first, preventing salt deposition needs high SCW density because it will exhibit a relatively improved solvent property for precipitated salts. However, minimizing corrosion rate requires low SCW density to decrease the content of ionic salts [31]. Kritzer et al. [63] controlled SCW density at less than 250 kg/m³ in order to reduce reactor corrosion rate. Second, adding alkali compounds independently or in feedstock before reactor is helpful for inhibiting reactor corrosion, but the possibility of reactor plugging increases because of salt deposition [19]. That is why some alkali compounds are delivered into reaction system from reactor outlet.

Salt deposition control achieves significant improvement through the innovation of research methods, the studies of salt deposition and separation performance, the evolution of salt control techniques, and new reactor configuration designs. However, several challenges such as the transport properties, deposition mechanisms, and practical salt control techniques, still restrict the technology application. Operation parameters play important roles in salt deposition processes, and various ions in the mixture may exhibit mutual influence or common effect. Thus, the prediction of salt deposition is quite difficult and needs extensive information on salts phase behavior in SCW. Moreover, the mechanisms of salt deposition in the multi-component system have not been recognized deeply, and the entire evolution

process of salts from microscopic nucleation to macroscopic deposition in SCW requires to be further revealed. Hence, it is necessary to gain more phase behavior data for analysis in depth. The combination of the experiment and numerical simulation is a desired method for the investigation of salt deposition.

In future, salt deposition control in a SCWO system requires global considerations and designs instead of previous single or local protection. Certainly, reactor configuration design has the priority to the whole SCWO system due to its crucial roles in salt control. Wise reactor concept combines with appropriate operation techniques before the reactor, in the reactor and/or after the reactor, forming multiple control and security units. Notably, the determination of salt control schemes should also consider the characteristics of wastewater and each technique, as well as the economic costs. With the solution of salt deposition problems and the development of reactor corrosion resistant materials, SCWO will be able to achieve large-scale commercial applications.

3. Advanced technologies and equipment

Since the occurrence of SCWO technology firstly proposed by Modell at the Massachusetts institute of technology in the early 1980s, a number of researcher and industrial engineers have been devoted to related research on prevention and control of corrosion and salt precipitation, enhancement of SCWO economy, safety, automation control, etc. A series of effective solutions, technologies, and equipment were proposed, and some have been applied to the actual industrial SCWO plants, which are not focused in this chapter. Here, several latest or typical advanced technologies and equipment are introduced in detail.

3.1 Development of novel reactor

Beyond all doubt, reactor is the most important core equipment of SCWO plants. The produced salts due to SCWO reaction together with those initially contained in feedstock may result in reactor plugging and increase corrosion rate of equipment. In terms of whether or not the precipitated solid-state salt is promised to accumulate on reactor's internal surface, the precipitated salt and the internal surface of reactor have two kinds of relations in reactor [53]. For the former case, salt removal can be accomplished by special instruments such as mechanical brushing, rotating scraper, reactor flushing, etc. For the latter case, it can be achieved by particular reactor designs and operation means. They include reverse flow tank reactor with brine pool, reversible flow tubular reactor, transpiring wall reactor, centrifuge reactor, crossflow filtration, density separation, additive, high velocity flow, and homogeneous precipitation. Moreover, extreme pressure is provided to avoid salt precipitation in SCW. Philip et al. [53] have objectively reviewed the properties of the above specific reactor configurations and operational approaches in commercial applications. Furthermore, there are some other special reactor configurations such as cool wall reactor reported by Cocero and Martinez [64] and two pipes reactor introduced by Baur et al. [65]. Calzavara et al. [66] set a stirrer in their reactors. Příkopský [67] installed a protective metal sleeve replaced easily to prevent salt from depositing on the internal surface of their axial reactor in SCWO. There is no doubt that no one reactor design or operation mean has been proven to be clearly superior to the others in all aspects.

Next, three kinds of typical reactor configurations are given to introduce the development of the novel reactors. MODAR reactor or its variation belongs to a reverse flow tank reactor with brine pool, which separates/removes salt by SCW

properties, as shown in **Figure 2**. Precipitated salts under supercritical condition fall down into the subcritical zone at the bottom of reactor by gravity, inertia, and forced convection. MODAR reactor has overcome the three disadvantages of tubular reactor, which are too long structure size, not suitable for dealing with salt-containing feedstock and easy to be plugged. However, due to the low falling velocity of small particle salt and the disturbance at the vertical direction, salt deposition is easy to take place on the internal surface of MODAR reactor in supercritical zone. Moreover, MODAR reactor may be eroded severely because its internal surface directly contacts corrosive reaction fluid.

Cool wall reactor [64] and transpiring wall reactor [68, 69] can help to solve salt deposition problems existing in MODAR reactor. These two kinds of reactors are divided into pressure-bearing wall and non-load-bearing wall. For cool wall reactor, precipitated salts are re-dissolved in a subcritical water film on the internal surface of no-load-bearing wall. The film is formed by low temperature feedstock cooling the no-load-bearing wall. However, severe corrosion still takes place because of the contact between corrosive reaction fluid and internal surface of no-load-bearing wall. When scale on the internal and external surfaces of no-load-bearing wall is left uncontrolled, the cool wall reactor will not continue to work normally since heat transfer efficiency reduces drastically. Transpiring wall reactor can not only prevent salt deposition but also decrease reactor corrosion rate through a porous transpiring wall element. Clean water flows across the porous wall to form a protective film to continuously dilute corrosive species, re-dissolve precipitated salt particles, and/or sweep them away from the internal surface of reactor. The transpiring wall (no-load-bearing wall) can be made of porous ceramic, sintered metal, or many thin and porous metal layers/platelets bonded together. The operational characteristics of transpiring wall reactor have been tested for a long time by some researchers. It is found that the concentrations of iron, nickel, chromium ions in reactor effluent were very low, so proving that the

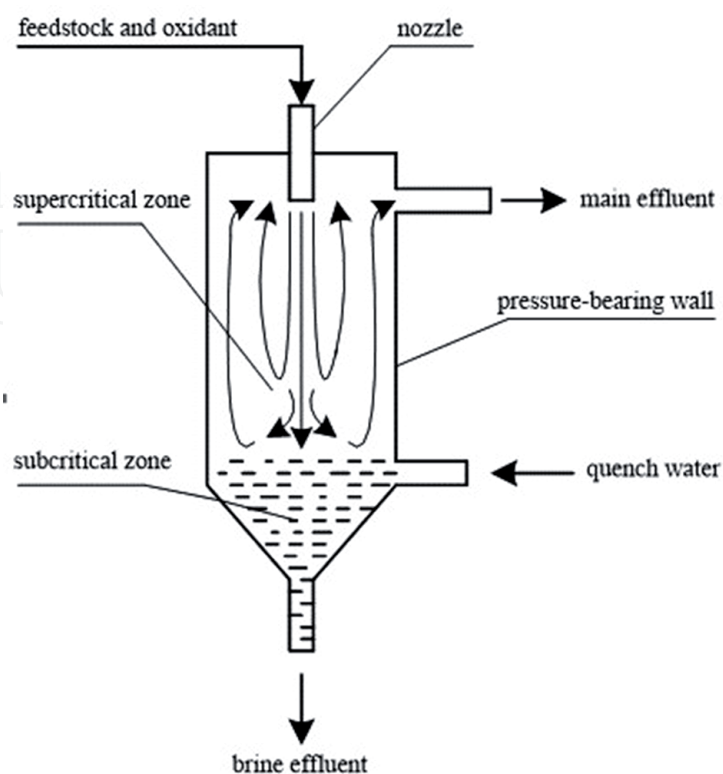


Figure 2.
A schematic diagram of reverse flow tank reactor [53].

corrosion rate of transpiring wall reactor was low. Fauvel et al. [70] also verified that the transpiring wall reactor had a good corrosion resistance property. Thus it can be claimed that the transpiring wall reactor is the best reactor configuration for minimizing reactor corrosion rate at present. Nonetheless, plenty of energy is required to preheat the transpiration water entering into the reactor. The pressure difference of two sides of transpiring wall should be adjusted at a suitable range since it has a bad mechanical property.

On the basis of summarizing characteristics of previously main reactor configurations, a novel concept reactor is designed and manufactured by the authors, as shown in **Figure 3**, which is the reactor installed into the first pilot-scale SCWO plant constructed in China finished by the authors [71]. The novel reactor owns characteristics of transpiring wall reactor and MODAR reactor for the first time, which is simply nominated as “TWM reactor.” Similar to MODAR reactor, TWM reactor is also divided into supercritical zone above and subcritical zone below. Precipitated salts under supercritical condition fall down into the subcritical zone (formed by pumping into quench water) and are re-dissolved. After removing salts, clean fluid flows toward the top outlet of the reactor by the differences of density and flow resistance. The valves equipped on pipe lines of top and bottom outlets of reactor are used to regulate the flow rate of fluid at top outlet. Dirty fluid flows out TWM reactor from its bottom outlet, which contains a large amount of salts and solids. The flow pattern of TWM reactor is helpful for eliminating natural convection effects which were mentioned by Welling’s group for transpiring wall reactor [55]. The MODAR reactor wall which is replaced by a porous transpiring wall and a pressure-bearing wall is set to surround it to form fundamental configuration of TWM reactor. Clean and cool transpiration water is pumped into TWM reactor and forms a protective film on the internal surface of transpiring wall. TWM reactor configuration is expected to prevent salt deposition and decrease corrosion rate.

Center pipe of MODAR reactor is comparatively thin and long, while transpiring wall reactor has no center pipe. For TWM reactor, the mixing of oxygen and sewage sludge preheating is accomplished by a specially simplified mixer equipped on the pipe line of reactor inlet. Center pipe is inserted into the reactor deeply and its diameter is big enough to avoid plugging. Reactants in center pipe are further preheated by high temperature fluid around or by reaction heat yielded through partial oxidation. Ideally, the mixture of oxygen and sewage sludge just reaches supercritical temperature at the outlet of center pipe. It is better to maintain subcritical temperature in center pipe because salt will not deposit on the internal surface of center pipe. The center pipe is set on a fixed platform by screw thread, which is easy to be replaced when plugged or eroded severely. Generally, the traditional transpiring wall reactor is a tubular reactor with a hydrothermal burner [69, 73, 74]. However, no hydrothermal burner is set in TWM reactor in order to decrease design temperature of reactor and operation cost of sewage sludge SCWO treatment.

3.2 Corrosion prevention and control

Marrone and Hong [75] have reported in detail some corrosion control approaches, which includes utilization of high corrosion resistance materials, liners, coatings, transpiring wall/film-cooled wall reactors, adsorption/reaction on fluidized solid phase, avoidance of corrosive feeds, pretreatment to remove corrosive species, vortex/circulating flow reactors, pre-neutralization, cold feed injection, feed dilution with noncorrosive wastes, effluent dilution/cooling, and optimization of operation conditions. The following text will exhibit several latest solutions of corrosion issues, which also have been verified by industrial applications.

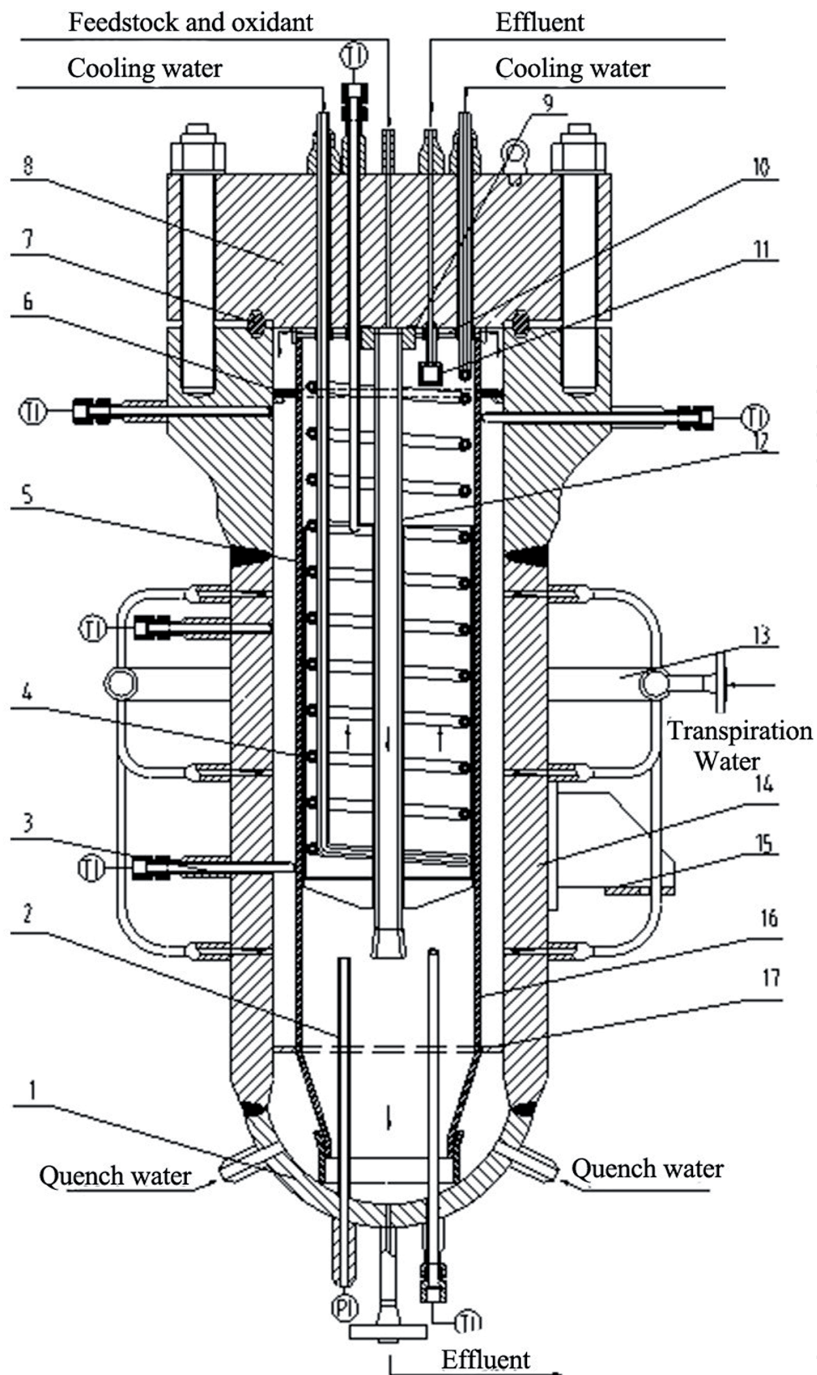


Figure 3.

A schematic diagram of TWM reactor for treating sewage sludge by SCWO [72]. 1—spherical head; 2—pressure measurement tube; 3—temperature measurement tube; 4—cooling spiral coil; 5—catalyst box; 6—support ring; 7—eight-square cushion; 8—top cover; 9—fixed platform; 10—cooling cover; 11—filter; 12—center pipe; 13—annular water box; 14—pressure-bearing wall; 15—ear base; 16—transpiring wall; 17—locating ring; TI—temperature indication; PI—pressure indicate.

3.2.1 On-line desalination in SCW

The existence of aggressive anions in SCWO environment is one of the key factors that causes severe corrosion problem in the SCWO system. Therefore, some methods should be used to remove the inorganic salts in the feed for SCWO treatment. Unfortunately, the conventional desalination methods (such as electrical dialysis, reverse osmosis, ion exchange, electrical adsorption) are difficult to be applied in the SCWO system for an organic wastewater with a high salinity.

An on-line desalination process in SCW, which is able to effectively separate the inorganic salts from the feeds, was firstly proposed by the authors, as

exhibited in **Figure 4**. It is noteworthy that this diagram is just a part of a whole SCWO system, and the on-line desalination units can be added into any SCWO systems, which has no effects on the other parts of the system. The mixed wastewater is pressurized by a high-pressure metering pump and then sent to the heating furnace for preheating. A heat exchanging coil tube of the heating furnace in the system is arranged in two sections (including a high temperature section and a low temperature section). Fluid at an outlet of the low temperature section (namely the middle outlet of the heating furnace) reaches a supercritical temperature. After entering the hydrocyclone separator, most solid salts with a particle size more than 10 μm in reaction fluid are separated by centrifuging. After salts removal, the fluid enters the high temperature section of the heating furnace through the top outlet of the hydrocyclone, so as to ensure a heat exchanging coefficient of the heat exchange coil at the high temperature section, and effectively prevent pipes and reactors following the hydrocyclone from plugging. At the same time, solid inorganic salts separated at the bottom of the hydrocyclone are spirally sent to the buffer oxidizer by a motor installed on the hydrocyclone. When the buffer oxidizer is full of the solid inorganic salts, a cut-off valve at the top inlet of the buffer oxidizer is closed, the motor installed on a top portion of the hydrocyclone is closed, a bottom cut-off valve of the buffer oxidizer is slowly opened, and a spirally transporting motor installed on the buffer oxidizer is started, for transporting the solid inorganic salts in the buffer oxidizer to the expansion device. A fluid containing the solid inorganic salts expands in the expansion device. Steam generated enters the storage tank. Heat generated is recycled. The separated solid inorganic salts enter the salt storage and are taken out for further landfill at a certain period. In addition, after being spirally sent into the buffer oxidizer, the fluid with a high salinity separated by the hydrocyclone reacts with oxygen previously injected through an oxygen pipe, which harmlessly removes organic pollutants. After the supersaturated fluid with a high salinity enters the buffer oxidizer, supercritical fluid at the top of the buffer oxidizer, which hardly contains solid inorganic salts, enters the top outlet of the hydrocyclone. Meanwhile, the solid inorganic salt will deposit at the bottom of the buffer oxidizer.

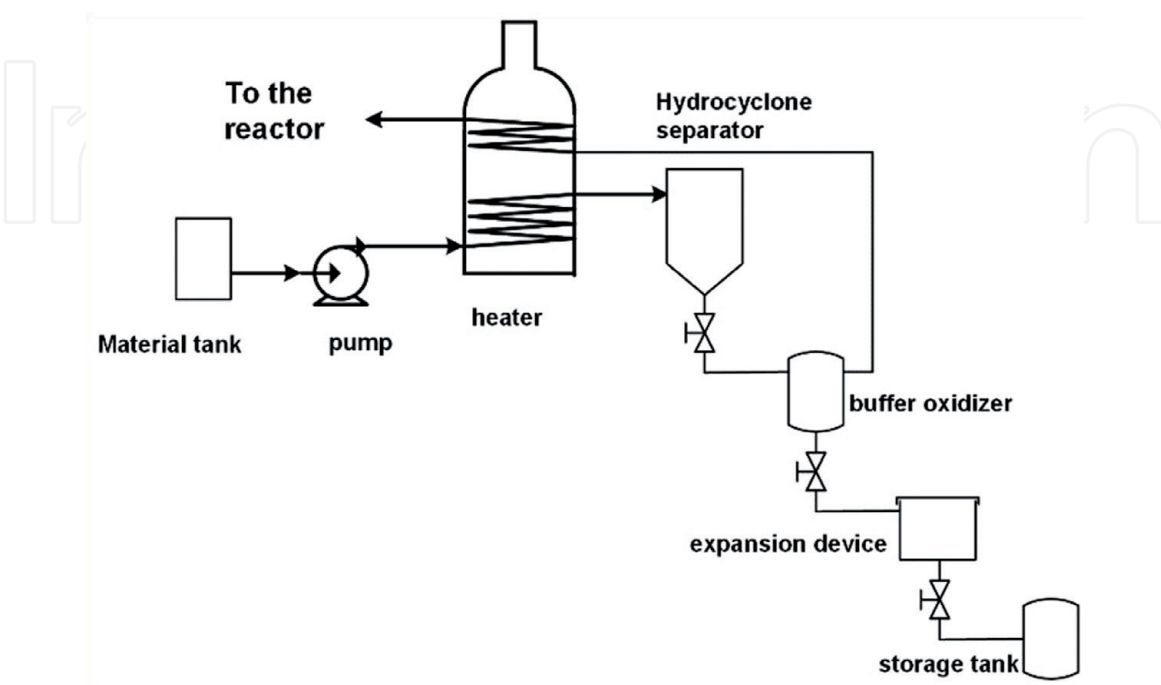


Figure 4.
 A schematic diagram of the on-line desalination units.

3.2.2 A new scheme for mild SCWO condition and high removal

A high temperature and a high oxygen concentration are needed in order to achieve a satisfied removal efficiency of organic matters in a SCWO system. However, the corrosion of structural materials is also apparently promoted by the increasing temperature and oxygen concentration. Therefore, a new operation scheme should be used to achieve a high organic matters removal efficiency, but not at the expense of the facilities materials corrosion. The core concept of the new operation scheme is to reduce the operation temperature and oxygen concentration in a reactor. As a result, the chemical oxygen demand (COD) removal efficiency cannot reach the standard value, and the concentration of ammonia nitrogen in the effluence was also unsatisfied. To work around this problem, some secondary treating methods were used for thorough removal of ammonia nitrogen and COD, including an ammonia stilling process, a phosphorous removal process, and a biochemistry process, which are all conventional water treatment techniques and can be operated easily with a relatively low operation cost.

3.2.3 Multipoint injection mixer

In a reactor, the heated feed and oxygen first meet in a mixer, where the local oxygen concentration is much higher than that in other areas in the reactor. There exist two technical drawbacks. First, drastic oxidation reaction occurs once the sludge and oxygen are mixed, producing a dangerous increase in temperature in the reactor. Second, the local high oxygen concentration and local high temperature in the mixer and the forepart of the reactor cause severe corrosion of structural materials, leading to unpredictable corrosion effects, such as pitting corrosion and stress corrosion cracking. A new multipoint mixer is developed to optimize the oxygen injection process in the reactor. As seen in **Figure 5**, this mixer consists of six oxidant injection holes in the core tube, and helical mixing elements are used to enhance mixing. The size number of the holes are determined by computational fluid dynamics (CFD) simulation to ensure that the input rate and flow distribution of oxygen are appropriate. Through this method, severe corrosion occurrence and hot-spot formation are avoided.

Additionally, it worthy to say that the design of appropriate reactors is also a very effective approach to overcome reactor corrosion and plugging issues. The detail of a novel design of the anti-corrosion reactors is available in Section 3.1.

3.3 Safety and automatic control technology

According to the schematic diagram of a typical SCWO process (see **Figure 6**) proposed by the authors, some safety and automatic control technologies are introduced, as follows.

3.3.1 Pretreatment of feedstock: thermal hydrolysis

Thermal hydrolysis pretreatment (THP) is widely used for sludge pretreatment, which has been proven to be an efficient method to reduce the viscosity of sludge [76]. To some extent, the use of thermal hydrolysis pretreatment is a safety control technology. The power of the diaphragm pump must be increased to transport viscous sludge, which will significantly increase the risk of overload of the pump's motor. Additionally, a large heat exchange area is needed if high viscosity sludge is fed into the heat exchanger, which substantially increases the risk of plugging. As

shown in **Figure 6**, the feed is heated to 85°C in the preparation tank (4), and the thermal hydrolysis of the sludge occurs in the sludge buffer tank (8). The reaction time and reaction temperature of the sludge in the tank (8) are 180 min and 170°C, respectively. Thus, the viscosity is as low as 33 mPa·s and to a certain degree, avoids the overload of the pump and the plugging of the heat exchanger.

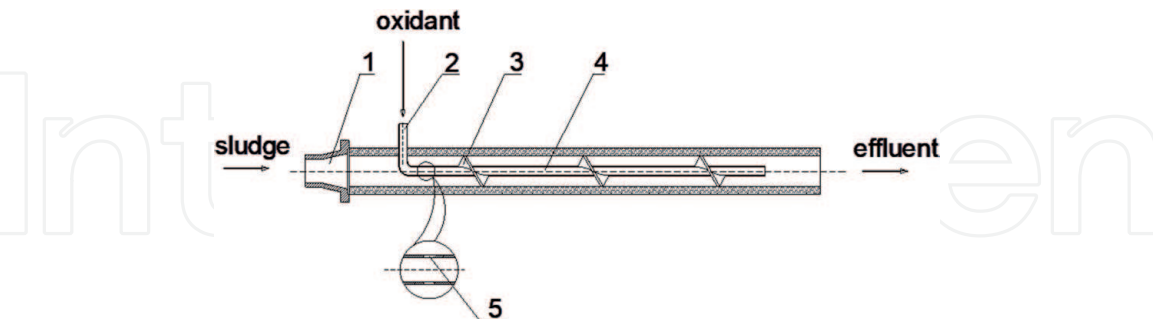


Figure 5.
A schematic diagram of the novel mixer: 1—adapter flange; 2—core tube; 3—helical mixing element; 4 and 5—injection holes.

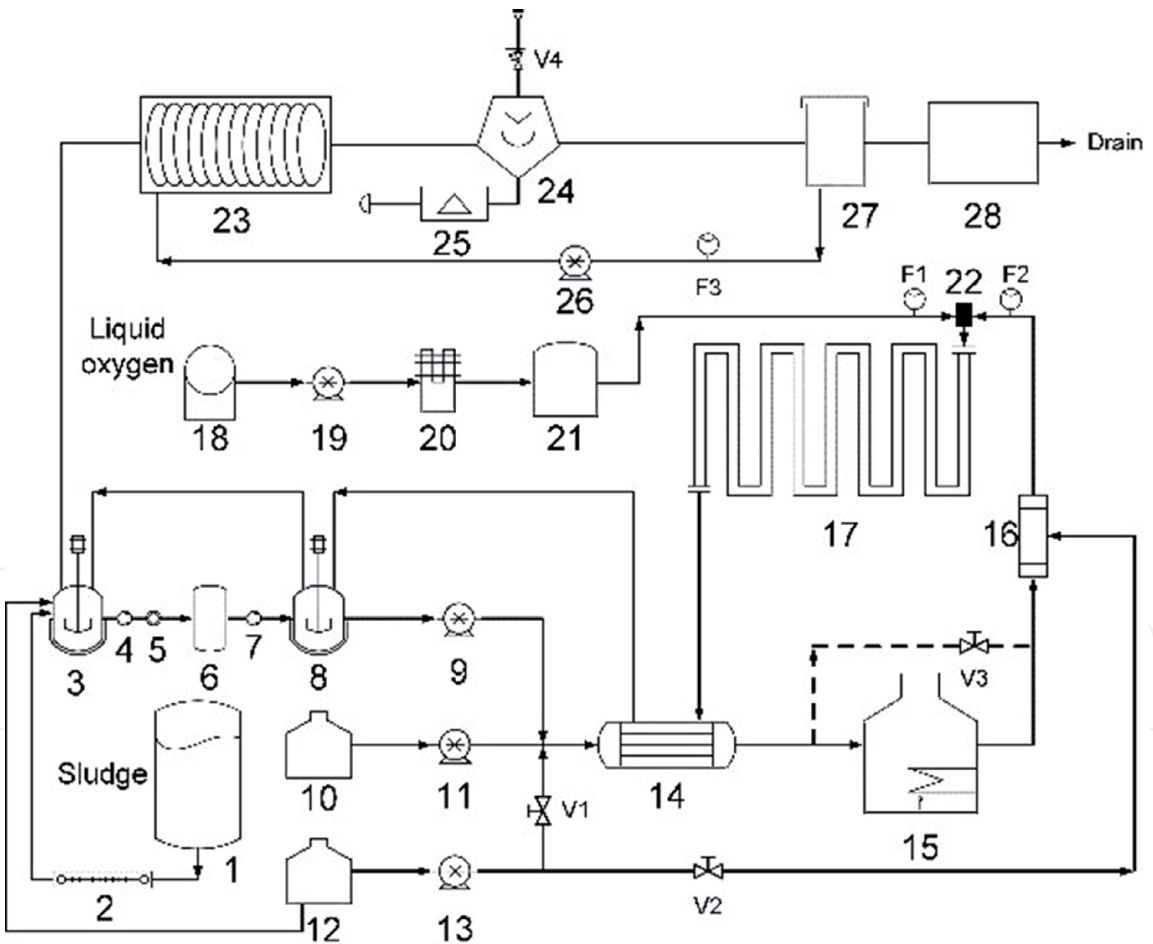


Figure 6.
A schematic diagram of the commercial plant for mixed sludge SCWO treatment: 1—sludge tank; 2—screw conveyor; 3—preparation tank; 4—screw pump; 5—homogeneous emulsification pump; 6—sludge tank for sampling; 7—screw pump; 8—sludge buffer tank; 9—diaphragm pump; 10—methanol tank; 11—plunger pump; 12—water tank; 13—plunger pump; 14—heat exchanger; 15—heating furnace; 16—multiple nozzle desuperheater; 17—tube reactor; 18—liquid oxygen pump; 19—liquid oxygen tank; 20—vaporizer; 21—oxygen buffer; 22—mixer; 23—pressure relief device; 24—three phase separator; 25—centrifugal dehydrator; 26—plunger pump; 27—effluent buffer tank; 28—secondary treatment unit; (F1-F3)—flowmeter; (V1-V5)—electric valve.

3.3.2 System start-up with auxiliary methanol

In traditional SCWO plants, during start-up process, water is heated in a heating module to reach supercritical temperature (generally 400°C) and then the feed is switched to organic wastes. Once the process has started, the effluent is used to preheat the cold sludge in the heat exchanger, and the heat released by the oxidation reaction is enough to preheat the cold feed, which makes the process self-sufficient and permits the heating module to be switched off. Generally, the organic waste to be treated often contains some soluble salts that have low solubility in SCW. In the pipes of the heating module, the pipe walls are heated directly and are the first to reach supercritical temperature, forming a high-temperature microenvironment. Many studies have shown that inorganic salts tend to crystalize in the overheated microenvironment and stick to the inner walls of pipes, leading to clogging and interruption of the continuous process.

Here, the proposed start-up strategy can effectively avoid or relieve the risk of plugging and overheat in the heater. As shown in **Figure 6**, not the sludge but the methanol solution in the methanol tank (10) is fed into the system and is heated by the heating furnace (15). When the final preheating temperature achieves to approximately 400°C, the first step of start-up is finished. Then, the heating furnace is shut down, and oxidant is injected into the tube reactor (17) to react with methanol. A large amount of heat is released during the oxidation reaction, which maintains the energy balance of the whole system. After a few minutes, the electric valve (V3) is opened, and the heating furnace (15) is bypassed. Then, the feed is switched to sludge in the sludge buffer tank (8), which has already been heated to 170°C. Through this method, no sludge passes the heating furnace, so effectively avoiding plugging in the heating facility. Additionally, only pure water, whose corrosivity is obviously lower than that of sludge at supercritical temperature and pressure, passes through the heating furnace. As a result, the risk of corrosion is also reduced.

3.3.3 Thermal control of the SCWO reactor

The temperature of the SCWO reactor is one of the key parameters which affects the COD removal efficiency of organic matter. Thus, various methods were designed to realize precise thermal control of the SCWO reactor in this commercial plant. There are several temperature measurement points in the reactor. If the temperature of the reactor increases, as shown in **Figure 6**, the electric valve (V5) is slightly opened to allow some of the high-temperature effluents to bypass the heat exchanger (14), decreasing the temperature of the outlet of the heat exchanger (14). However, the opening of the electric valve (V5) should be limited to prevent a large amount of high-temperature effluent from directly passing through the coil heat exchanger in the sludge buffer tank (8) and causing unpredictable damage. If the temperature of the reactor increases sharply in a short time, the electric valve (V2) will be opened, and cooling will be injected into the system via the multiple nozzle desuperheater (16). If the temperature of the reactor decreases, however, the electric valve (V5) will be slightly closed to allow more hot effluent to pass through the heat exchanger (14). Furthermore, if the heat released by the SCWO reaction is not sufficient, methanol in the tank (10) will be pumped into the reactor (17) and mixed with the feed in order to enhance the SCWO reaction.

3.3.4 Depressurization of fluids containing solids

SCWO plants are high temperature and high pressure systems, meaning that the reaction effluent is still required to be cooled and depressed. As mentioned, cooling

the high temperature effluent can be achieved by the indirect heat transfer system. However, the conventional method normally used to maintain and decrease the pressure of SCWO system by adapting a pressure regulating valve. It means that the pressure drop of the whole system is achieved on one point, which will lead to extremely high velocities of feedstock and noise issues here, make the valve occur failure easily, and eventually affect the operation reliability of the SCWO system. In addition, if the feedstock contains solid particles, the existence of inert inorganic salt will result in severe abrasion or clogging around the regulating valve during the depressurization process of the SCWO system. Therefore, it is not advisable to achieve a complete depressurization in a single step by a regulating valve during the SCWO process, especially for the particles-containing feedstocks. Capillary pressure reduction is achieved by the frictional drag generating from the fluid flowing through the small diameter and high length capillary, realizing the step-down of the system step by step and effectively avoiding the problems about high velocities in tubes and corrosion damage of valves compared with depressurization by a single valve. What is more, adjusting the addition of choke water flowing into the capillary could accurately control the pressure of system, which ensures the reliability of the system operation.

3.4 Economic improvements

3.4.1 Catalytic SCWO

High reaction temperature and pressure result in a relatively expensive running cost, which also further affects the development of SCWO. The effective means may be to load proper catalyst to moderate the harsh reaction conditions, to minimize oxidant consumption, and to recover heat of reactor effluent as well as increase byproduct income. First, catalyst can improve reaction conditions, but it is also easy to be inactive due to the critical reaction conditions. The employed homogeneous and heterogeneous catalysts are mainly heteropolyacids, alkali carbonates, carbons, transition metal oxides, and bulk MnO_2 [60]. Besides, they also especially pointed out that the bulk MnO_2 has high activity, hydrothermal stability, and ability of maintenance, and resistance to metal leaching under supercritical reaction conditions.

3.4.2 Utilization of liquid oxygen

Liquid oxygen, gaseous oxygen, hydrogen peroxide, and air can be applied as oxidants in SCWO. Unfortunately, hydrogen peroxide is not commercially applicable because it is very expensive. Nitrogen in air does not react with feedstock, and costs a lot to separate them from gaseous products. Liquid oxygen is chosen as the oxidant of this plant due to its relatively cheaper price compared with the same amount of gaseous oxygen. Oxygen is regarded as one of the major costs, whereas high oxygen excess coefficient is not necessary because it is not realistic for a prospective commercial application. In this plant, oxygen excess coefficient is anticipated to control at about 1.1 to ensure complete decomposition of organic matters, and to avoid recovering excessive oxygen as well as decrease the running cost. The system uses liquid oxygen cold energy to realize the centralized liquefying and recycling of carbon dioxide, and greatly improves the system economy. In addition, the system is pre-desalted by the system of liquid oxygen cooling, reducing the subsequent desalting load and corrosivity of the system, reducing the grade of the equipment material, reducing the investment of the equipment, and recovering and selling valuable inorganic salts to improve the system economy.

3.4.3 Gas recovery and oxygen reuse

The SCWO system innovatively adopts the process of combining gas-phase product carbon dioxide recovery with oxygen recovery. By developing regular exhaust and compressor variable flow operation technology, high rate oxidation and low rate oxygen consumption are realized in the reaction process, that is, the reactor operates with high oxidation coefficient, and the gas phase after reaction is produced. The excess oxidants in the material are separated and recycled under variable flow conditions.

3.4.4 Waste heat recovery

Energy recovery is often achieved by preheating feedstock through reactor effluent of high temperature via heat exchangers [77]. Surplus energy is able to be utilized to produce steam for electricity generation or to form hot water for industrial application. For a larger scale SCWO system, energy recovery may potentially employ a supercritical steam turbine to generate electricity through the direct expansion of products [78]. However, it is not possible to design and construct a supercritical steam turbine in a SCWO plant presently due to the critical operation conditions and the very difficult separation of solids under SCWO conditions [79]. It is supposed that SCWO would be developed as a multifunctional technology for generating heat and electricity on the basis of removing organic pollutants in future. There is no doubt that sufficient energy recovery and heat income must be adequately considered in order to decrease the running cost, otherwise an external or internal heat source is required. In this apparatus, heat is recovered enough by preheating feedstock to realize a low running cost. In addition, major byproducts such as hot water and CO₂ can be collected for sale or reuse.

4. Industrial applications

Since the early 2000s, the significant maturation of SCWO technology on the basis of better understanding of the core reaction principles and effective solutions for mitigating the corrosion and salt precipitation problems in the past two decades started a shift in emphasis of SCWO activity from fundamental studies to industrial applications. For several feedstocks such as sewage sludge, industrial wastewaters, explosives, and other hazardous wastes, some full-scale SCWO treatment plants have been built under the guidance or promotion of companies, universities and colleges, and scientific research institutes. A series of associated SCWO vendors, such as MODAR, MODEC, Oxidyne, EcoWaste Technologies, and Foster Wheeler, have left this field, but the associated technologies still survived in some sense through acquisition or licenses by the former. For instance, the company Chematur Engineering located in Sweden acquired the assets of EcoWaste Technologies in 1999, and in 2007, licensed the SCWO patents to SCFI Group Ltd. Nowadays, a number of additional firms such as SCFI Group, InnovEOX, SuperWater Solution, XJTU, etc. are active in SCWO field (**Table 2**).

4.1 HydroProcessing

HydroProcessing constructed the first commercial SCWO sludge processing equipment for the Harlingen wastewater treatment plant, in Texas, USA [14]. In the HydroProcessing system, a hydrocyclone is applied to separate the flow after the reactor and to maintain the solids in the underflow. The overflow and subsequent

Company/University	HydroProcessing	Chematur Engineering AB	SuperWater Solutions	Xi'an Jiaotong University
Country	USA	Sweden	USA	China
Capacity	150 t/d	168 m ³ /d	35 dry ton/d	3 t/d
Solid content (wt.%)	6–9	15	10	8
COD (mg/L)	80,000–120,000	110,000	Not available	5750
Temperature (°C)	592	510–580	600	400
Pressure (MPa)	23.47	25	26	25
Reactor	Tubular	Tubular	Tubular	TWM
Capital cost	3 million USD	5 million GBP	33.7 million USD	0.58 million USD
Operation cost	100 USD/dry ton	105 USD/dry ton	268 USD/dry ton	76.56 USD/dry ton

Table 2.
Operation and economic parameters of typical SCWO systems for municipal sludge treatment.

underflow are used to heat the feed. The heated feed mixes with oxygen and they enter the gas-fired heater together for further heating before entering a tubular reactor. The operation results show that the destruction efficiencies are 99.93–99.96, 49.6–84.1, and 92.89–98.90% for COD, ammonia, and total solid in the overflow, respectively. Meanwhile, the destruction efficiencies of sludge are 99.92–99.93, 49.6–86.4, and 62.72–88.94% for COD, ammonia, and total solid in the underflow, respectively. Due to the high ammonia concentration of the effluent, it can be sent to municipal wastewater plants or to industrial plants as a nutrient. A net operation and maintenance cost of approximately 100 USD/dry ton sludge was obtained [80].

4.2 Chematur AB and SCFI

For demonstration purposes, Chematur AB has built a 6 t/d unit in Karlskoga, Sweden, for the treatment of both undigested and digested sludge, which has been in operation since 1998 [15]. Chematur AB licensed the SCWO process to the Shinko Plantech Co. of Japan, and they have built a pilot SCWO unit with a capacity of approximately 26.4 t/d for the treatment of sludge in Kobe, Japan [17]. The developed SCWO process, named as the AquaCritox process, is presented in **Figure 7**. This system consists of a series of homogeneous sludge equipment including a feed tank with a paddle mixer, a macerator, an ultra turrax, and a grinder. The first three facilities along with a mono pump constitute a re-circulation loop, which provides size reduction and homogenization during a batch operation. After homogenization, sludge enters a hose diaphragm piston pump pressurized to approximately 25 MPa and is pumped to a double-pipe economizer heated by the reactor effluent. Fouling problems in the economizer are avoided due to the high velocity and the reduced feed particle size. After heat exchange, sludge enters a heater for further temperature increase. The removal rate of COD is greater than 99.9% when $T > 520^{\circ}\text{C}$. A temperature higher than 540°C is needed to completely destroy total nitrogen (TN). They also evaluated the economic value of a unit treating 168 m³ of sludge per day, being approximately 105 USD/dry ton sludge [17].

In 2007, the SCFI Group acquired patented SCWO technology (AquaCritox®) from Chematur Engineering AB of Sweden. Further work directed by the SCFI group has emphasized the reduction of costs. The residual inorganic fraction of

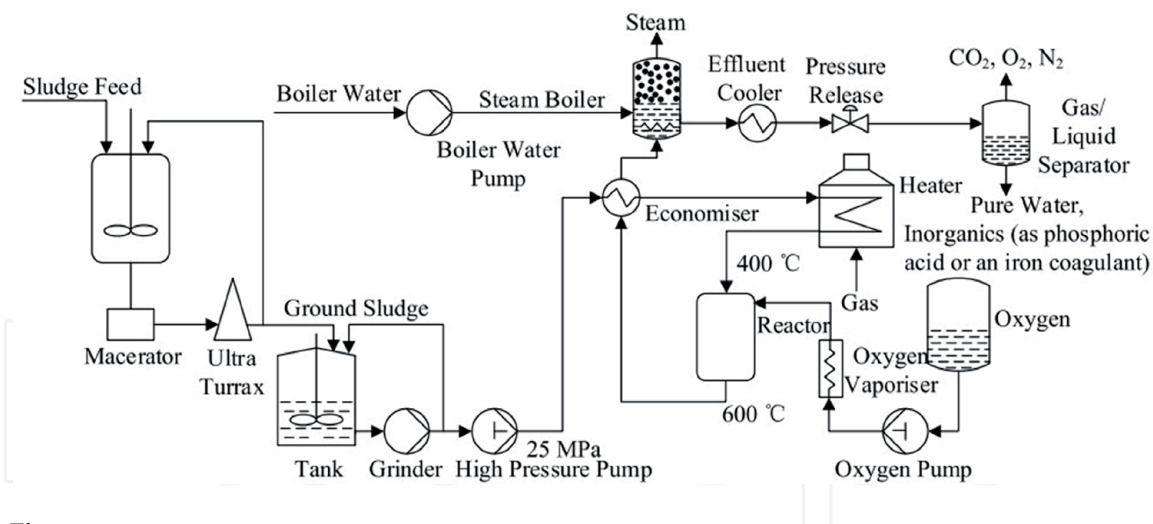


Figure 7.
Flow sheet of the Chematur AB system [15].

the sludge can be recovered as phosphoric acid and iron coagulant if required. The orthophosphates from the supernatant, representing 78% of the total influent phosphorus, can also be recovered by using fluidized bed crystallization technologies [81].

4.3 SuperWater Solution

From 2009 to 2011, SuperWater Solution installed and successfully tested a 5 dry t/d SCWO system for the Iron Bridge Regional Water Reclamation Facility in Orlando, FL, USA [16]. They also assessed the economic value of 268 USD/dry ton for a unit with a capacity of 35 dry tons of sludge per day. For the employed SCWO process. It is interesting that the SuperWater Solution system has an oxygen recycling process based on the difference in liquefaction temperatures between O_2 and CO_2 . Through the oxygen recycling process, the sludge can be oxidized at a high n value with low oxygen consumption, thus increasing the effluent quality and decreasing operation costs.

4.4 Energy and Environment Institute in XJTU of China

Since the early 2000s, Energy and Environment Institute led by one of the authors (Shuzhong Wang) in XJTU, based on the supercritical water technologies, has committed to the related research on harmless disposal and energy-oriented utilization of high concentration organic wastewaters and municipal/industrial sludge, and has accumulated abundant experience in water quality evaluation and products characterization. The research areas are involved in organic molecule reaction mechanisms and kinetics, catalytic characteristics and mechanisms, mechanisms and theories of alloy corrosion, salt crystallization kinetics, fuel and auxiliary heating mechanisms, etc. [6, 11, 21, 22, 28–30, 45, 50, 71, 82–85].

The stepwise engineering amplifications have been performed from initial experimental facility to test equipment (4.5 L/h), to small pilot plant (0.5 t/d). To further verify the industrialization feasibility of SCWO technology in China, in 2009, the authors successfully designed and constructed the first industrial scale plant of China (see **Figure 8**), actually of which the processing capacity of 3 ton/day, filling the China blank in the SCWO field [71]. This SCWO plant installed with the newly developed “TWM reactor” reaches a COD removal rate of more than 99.5% and surplus heat utilization efficiency of >80%. A brine pool is formed in the bottom of the reactor. Fluid in the pool with a high concentration of salts then enters



Figure 8.
 First industrial scale SCWO plant in China [71].

the salt-removing device and is heated to a supercritical state. The salts are precipitated again and finally stored in the salt-collecting tank. The equipment investment is 0.58 million USD, and the operating cost is 76.56 USD/dry ton for sludge, which is much lower than the cost of incineration.

Depending on the accumulated research, design, and construction experiences, for overcoming or improving the potential higher investment, severe corrosion and blockage risk of the heat exchanging units, an indirect heat transfer SCWO process with a capacity of 50 t/d for petrochemical sludge treatment was developed, which is currently in the detailed design phase of the process package. The indirect heat transfer SCWO system is shown in **Figure 9**.

SCWO reactions happen at high temperature and pressure, meaning that the heating and pressuring of feedstock and the opposite process for the reaction effluents are necessary and unavoidable. In a conventional SCWO process, heat exchangers are usually used to cool the reaction effluents by untreated feedstock as cooling medium; meanwhile, the feedstock is preheated to the expected temperature, and then enters the reactor and reacts with the oxidants. But the critical aqueous solutions zones at temperature of 320–410°C corresponding exactly to the heat exchanger, which owns high-density, large dielectric constant and high solubility of inorganic salts, are aggressive to the piping and equipment materials generally inducing serious corrosion issues by improper controls, posing a potential threat to the reliable operation of the SCWO system. In addition, various organic wastes generally contains considerable amounts of heteroatom such as chlorine, sulfur, phosphorus, etc., which are transformed into corresponding inorganic acids after SCWO. Please note that the oxidant supplied into the system is often excessive to ensure the complete degradation of organic matters, causing a high level of residual oxidant in the reaction products. Therefore, reaction effluents are more corrosive than the initial feedstock. For the double-pipe heat exchanger used in conventional SCWO process, the cooling medium in the inner tube is feedstock while the reaction products as thermal fluid exists in the outer tube, causing internal side of the shell tube and both internal and external surfaces of the inner tubes facing serious corrosion problems and requiring expensive corrosion-resistant alloys, which greatly increases the investment of the equipment. Further, when the reaction effluents in the outer tube contains a large amount of inorganic salts or insoluble solids, plugging problems of the shell tube is extremely likely to occur due to its relatively complex multi-turn flow channel. In the indirect heat transfer SCWO system (see **Figure 9**), the feedstock being pre-grinded to 50 μm by a low pressure pump (2) is compressed by a high pressure feedstock

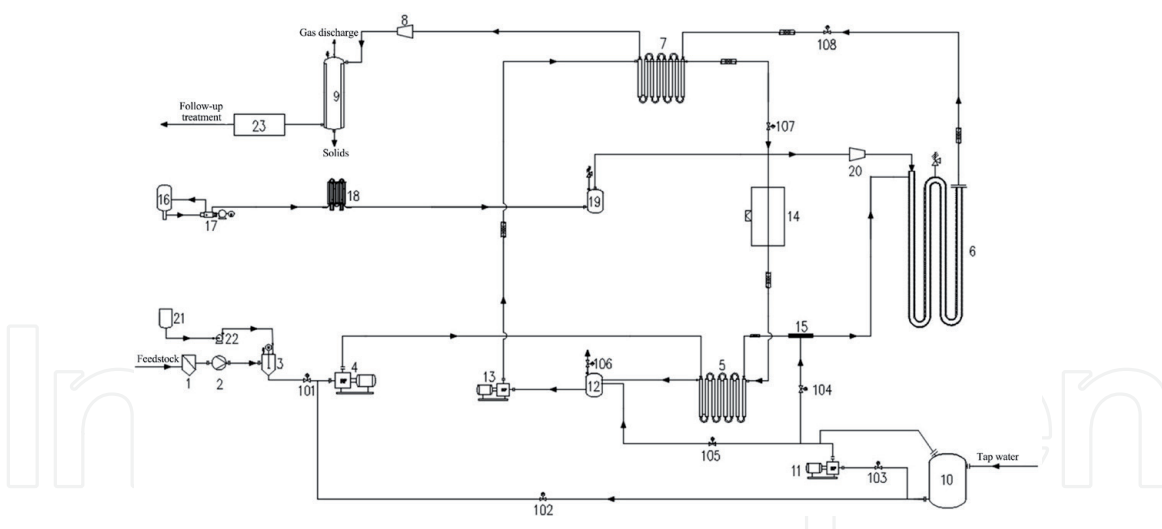


Figure 9.

A Schematic diagram of the indirect heat transfer SCWO comprehensive system: 1—filter; 2—low pressure pump; 3—feedstock tank; 4—high pressure feedstock pump; 5—preheater; 6—reactor; 7—heat exchanger; 8—capillary depressurization device; 9—three phase separator; 10—water storage tank; 11—high pressure water pump; 12—water buffer tank; 13—booster pump; 14—heater; 15—spray desuperheater; 16—liquid oxygen tank; 17—low temperature oxygen pump; 18—vaporizer; 19—oxygen buffer tank; 20—oxygen pressure regulator; 21—caustic tank; 22—low pressure caustic pump; (101—108)—valve; 23—biochemical treatment unit.

pump (4), preheated in the preheater (5) by high temperature intermediate medium, and then made to enter into reactor (6) when reaching the expected temperature. Liquid oxygen is pressured and its flow rate are regulated by the low temperature oxygen pump (17), subsequently gasified in the vaporizer (18), and then gaseous oxygen is stored in the oxygen buffer tank (19), ultimately entering the reactor (6) after being depressurized by the oxygen pressure regulator (20) and reacting with the feedstocks. Meanwhile, the SCWO reaction releases a certain amount of heat and reaction effluent with high-temperature and high-pressure flows into the inner tube of heat exchanger (6) to heat the intermediate medium in the outer tube, and the effluents are also cooled through the intermediate medium at the same time. Then the cooled effluents are reduced to an appropriate pressure by the capillary depressurization device (8). Gaseous products, liquid products, and solid products are similarly separated in the low pressure three-phase separator (9). The intermediate medium from the water buffer tank (12) pressurized by high pressure booster pump (13), firstly absorbs the heat of the reaction effluent through the regenerator (7); flows through the heater (14); and then, if necessary to further increase the temperature, eventually enters the preheater (5) for preheating the feedstock. Therefore, the corrosive fluid only passes through the inner tube of the preheater and the regenerator, and both outer tubes of the heat exchanger are clean water. Therefore, only inner tubes of the preheater and regenerator require the use of high-end corrosion-resistant alloys, and the outer tubes can use cheap carbon steel or low alloy steel, which will greatly reduce the investment cost of heat exchanger for the SCWO process. In addition, the clean water in the outer tube also dramatically avoids the blockage risk compared with dirty fluid containing insoluble solids.

Additionally, in view of specific characteristics of various municipal/industrial sludge and organic wastewaters such as printing and dyeing wastewater, phenol-containing wastewater, pharmaceutical/pesticide-production wastewater, etc., combining with their individual industrial production processes and customer specific requirements, the Energy and Environment Institute in XJTU has carried out the process integration innovation of large-scale supercritical water treatment system to maximize the efficiency, economy, and safety, and has finished a series of mature, reliable SCWO process packages [82].

5. Conclusions

In virtue of the special physicochemical properties of supercritical water, supercritical water oxidation (SCWO) can efficiently and thoroughly degrade a wide variety of organic pollutants into harmless small molecules, such as CO₂, N₂, H₂O, etc., which has been widely regarded as the most promising, environment-friendly treatment technology for organic wastes. Not a specific material can withstand all kinds of SCWO conditions; however, the suitable material can be selected for a certain condition considering corrosion resistance, strength, and economy. Abundant corrosion control approaches can mitigate the equipment corrosion effectively. Salts precipitation, possibly resulting in plugging of pipes and instruments and accelerating corrosion, is another main obstacle to hinder SCWO commercialization. Fortunately, pre-desalination, on-line salt separation, novel reactor configuration such as TWM reactor, etc., all exhibit better performances in preventing and controlling salt deposition and corrosion issues occurred in reactors. The global considerations and designs instead of previous single or local protection will be in focus in the future. On the basis of decades of implementation experience of full-scale SCWO plants, considering the incessant emergence of more advanced technologies and equipment which aims to overcome the abovementioned two key obstacles and to further elevate the system economy, safety, and automatic control level, the industrial SCWO plants will achieve the harmless disposal of various organic wastes in a more economical, safe, credible way.

Acknowledgements

This chapter and involved contents were supported by the Projects from National Natural Science Foundation of China (21576219, 51871179, and 51876174), China Postdoctoral Science Foundation [2019TQ0248], the National High Technology Research and Development Program of China (2006AA06Z313), and the National Key Research and Development Program of China (2016YFC0801904, 2017YFB060360).

Author details

Yanhui Li and Shuzhong Wang*
Key Laboratory of Thermo-Fluid Science and Engineering of MOE, School of Energy and Power Engineering of Xi'an Jiaotong University, Xi'an, Shaanxi, China

*Address all correspondence to: szwang@aliyun.com

IntechOpen

© 2019 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

References

- [1] Brunner G. Near and supercritical water. Part II: Oxidative processes. *The Journal of Supercritical Fluids*. 2009;**47**:382-390
- [2] Gong YM, Guo Y, Wang SZ, Song WH, Xu DH. Supercritical water oxidation of quinazoline: Reaction kinetics and modeling. *Water Research*. 2017;**110**:56-65
- [3] Xu DH, Wang SZ, Zhang J, Tang XY, Guo Y, Huang CB. Supercritical water oxidation of a pesticide wastewater. *Chemical Engineering Research & Design*. 2015;**94**:396-406
- [4] Zhang J, Wang SZ, Guo Y, Xu DH, Li XD, Tang XY. Co-oxidation effects of methanol on acetic acid and phenol in supercritical water. *Industrial & Engineering Chemistry Research*. 2013;**52**:10609-10618
- [5] Veriansyah B, Kim J-D. Supercritical water oxidation for the destruction of toxic organic wastewaters: A review. *Journal of Environmental Sciences*. 2007;**19**:513-522
- [6] Gong YM, Guo Y, Sheehan JD, Chen ZF, Wang SZ. Oxidative degradation of landfill leachate by catalysis of CeMnOx/TiO₂ in supercritical water: Mechanism and kinetic study. *Chemical Engineering Journal*. 2018;**331**:578-586
- [7] Wang SZ, Guo Y, Chen CM, Zhang J, Gong YM, Wang YZ. Supercritical water oxidation of landfill leachate. *Waste Management*. 2011;**31**:2027-2035
- [8] Gong YM, Wang SZ, Li YH. The treatment of concentrated landfill leachate from membrane-based processes by supercritical water oxidation. *Applied Mechanics and Materials*. 2014;**522-524**:560-564
- [9] Gong YM, Wang SZ, Qian LL, Li YH. Supercritical water oxidation of fulvic acid as a model organic compound in landfill leachate. *Applied Mechanics and Materials*. 2014;**522-524**:600-604
- [10] Zhang J, Wang SZ, Guo Y, Xu DH, Gong YM, Tang XY. Supercritical water oxidation of polyvinyl alcohol and desizing wastewater: Influence of NaOH on the organic decomposition. *Journal of Environmental Sciences-China*. 2013;**25**:1583-1591
- [11] Zhang J, Wang S, Li Y, Lu J, Chen S, Luo X. Supercritical water oxidation treatment of textile sludge. *Environmental Technology*. 2016:1-12
- [12] Marulanda V, Bolaños G. Supercritical water oxidation of a heavily PCB-contaminated mineral transformer oil: Laboratory-scale data and economic assessment. *The Journal of Supercritical Fluids*. 2010;**54**:258-265
- [13] SCFI. What Is Super Critical Water Oxidation; 2012
- [14] Griffith JW, Raymond DH. The first commercial supercritical water oxidation sludge processing plant. *Waste Management*. 2002;**22**:453-459
- [15] Patterson DA, Stenmark L, Hogan F. Pilot-scale supercritical water oxidation of sewage sludge. In: *Proceedings of the 6th European Biosolids and Organic Residuals Conference*. 2001
- [16] Sloan DS, Pelletier RA, Modell M. Sludge management in the city of Orlando—It's supercritical! *Florida Water Resources Journal*. 2008:46-54
- [17] Gidner A, Stenmark L. Supercritical water oxidation of sewage sludge—State of the art. In: *Chematur Engineering AB*. 2001

- [18] Marrone PA. Supercritical water oxidation-current status of full-scale commercial activity for waste destruction. *Journal of Supercritical Fluids*. 2013;**79**:283-288
- [19] Kritzer P, Dinjus E. An assessment of supercritical water oxidation (SCWO)—Existing problems, possible solutions and new reactor concepts. *Chemical Engineering Journal*. 2001;**83**:207-214
- [20] Li Y, Xu T, Wang S, Yang J, Li J, Xu T, et al. Characterization of oxide scales formed on heating equipment in supercritical water gasification process for producing hydrogen. *International Journal of Hydrogen Energy*. 2019. In press. DOI: 10.1016/j.ijhydene.2019.01.284
- [21] Xingying T, Shuzhong W, Lili Q, Mengmeng R, Panpan S, Yanhui L, et al. Corrosion properties of candidate materials in supercritical water oxidation process. *Journal of Advanced Oxidation Technologies*. 2016;**19**:141-157
- [22] Tang XY, Wang SZ, Qian LL, Li YH, Lin ZH, Xu DH, et al. Corrosion behavior of nickel base alloys, stainless steel and titanium alloy in supercritical water containing chloride, phosphate and oxygen. *Chemical Engineering Research & Design*. 2015;**100**:530-541
- [23] Tang XY, Wang SZ, Xu DH, Gong YM, Zhang J, Wang YZ. Corrosion behavior of Ni-based alloys in supercritical water containing high concentrations of salt and oxygen. *Industrial & Engineering Chemistry Research*. 2013;**52**:18241-18250
- [24] Li YH, Wang SZ, Yang JQ, Xu DH, Guo Y, Qian LL, et al. Corrosion characteristics of a nickel-base alloy C-276 in harsh environments. *International Journal of Hydrogen Energy*. 2017;**42**:19829-19835
- [25] Li YH, Wang SZ, Li XD, Lu JM. Corrosion of an austenitic heat-resistant steel HR3C in high-temperature steam and supercritical water. *Advanced Materials Research*. 2014;**908**:67-71
- [26] Asselin E, Alfantazi A, Rogak S. Corrosion of nickel–chromium alloys, stainless steel and niobium at supercritical water oxidation conditions. *Corrosion Science*. 2010;**52**:118-124
- [27] Yang J, Li YH, Xu AN, Fekete B, Macdonald DD. The electrochemical properties of alloy 690 in simulated pressurized water reactor primary water: Effect of temperature. *Journal of Nuclear Materials*. 2019;**518**:305-315
- [28] Yang JQ, Wang SZ, Tang XY, Wang YZ, Li YH. Effect of low oxygen concentration on the oxidation behavior of Ni-based alloys 625 and 825 in supercritical water. *The Journal of Supercritical Fluids*. 2018;**131**:1-10
- [29] Li YH, Wang SZ, Sun PP, Xu DH, Ren MM, Guo Y, et al. Early oxidation mechanism of austenitic stainless steel TP347H in supercritical water. *Corrosion Science*. 2017;**128**:241-252
- [30] Li YH, Wang SZ, Tang XY, Xu DH, Guo Y, Zhang J, et al. Effects of sulfides on the corrosion behavior of Inconel 600 and Incoloy 825 in supercritical water. *Oxidation of Metals*. 2015;**84**:509-526
- [31] Kritzer P. Corrosion in high-temperature and supercritical water and aqueous solutions: A review. *Journal of Supercritical Fluids*. 2004;**29**:1-29
- [32] Son M, Kurata Y, Ikushima Y. Corrosion behavior of metals in SCW environments containing salts and oxygen. *Corrosion*. Denver, Colorado: NACE International; 2002. pp. 12
- [33] Was GS, Jiao Z, Teyssseyre SS. Corrosion of austenitic alloys in supercritical water. *Corrosion*. 2005;**62**:989-1005

- [34] Ikushima Y, Kurata Y, Hatakeda K, Kim H, Son M. Corrosion behavior of metals in supercritical water solutions in the presence of salts. *Corrosion*. Houston, Texas: NACE International; 2001. pp. 13
- [35] Daigo Y, Watanabe Y, Sugahara K, Isobe T. Compatibility of nickel-based alloys with supercritical water applications: Aging effects on corrosion resistance and mechanical properties. *Corrosion*. 2006;**62**:174-181
- [36] Sue K, Arai K, Watanabe Y, Tsujinaka N, Adschiri T. Relationship between corrosion rate and metal oxide solubility in supercritical water. *Corrosion*. 2002;**2002**
- [37] Kim H, Mitton DB, Latanision R. Stress corrosion cracking of alloy 625 in pH 2 aqueous solution at high temperature and pressure. *Corrosion*. 2011
- [38] Li YH, Wang SZ, Sun PP, Tong ZX, Xu DH, Guo Y, et al. Early oxidation of Super304H stainless steel and its scales stability in supercritical water environments. *International Journal of Hydrogen Energy*. 2016;**41**:15764-15771
- [39] Schroer C, Konys J, Novotny J, Hausselt J. Aspects of the corrosion kinetics for binary nickel-chromium alloys under conditions found in supercritical water oxidation plants processing chlorinated substances. *Corrosion*. 2006;**62**:444-459
- [40] Fujisawa R, Sakaihara M, Kurata Y, Watanabe Y. Corrosion behaviour of nickel base alloys and 316 stainless steel in supercritical water under alkaline conditions. *Corrosion Engineering, Science and Technology*. 2005;**40**:244-248
- [41] Sun M, Wu X, Zhang Z, Han E-H. Analyses of oxide films grown on alloy 625 in oxidizing supercritical water. *The Journal of Supercritical Fluids*. 2008;**47**:309-317
- [42] Tang XY, Wang SZ, Qian LL, Lu JM. Selection of material with high salt concentration in preheating section of supercritical water oxidation system. In: Zhang H, Jin D, Zhao XJ, editors. *Advanced Research on Material Engineering, Chemistry and Environment*. Stafa-Zurich: Trans Tech Publications Ltd; 2013. pp. 440-443
- [43] Fujisawa R, Nishimura K, Sakaihara M, Watanabe Y, Kurata Y, Nishida T. Corrosion behavior of ni base alloys and 316 stainless steel in less oxidizing or reducing SCW containing HCl. *Corrosion*. 2005
- [44] Kritzer P, Boukis N, Dinjus E. Corrosion of alloy 625 in aqueous solutions containing chloride and oxygen. *Corrosion*. 1998;**54**:824-834
- [45] Li YH, Wang SZ, Sun P, Yang JQ, Tang XY, Xu DH, et al. Investigation on early formation and evolution of oxide scales on ferritic-martensitic steels in supercritical water. *Corrosion Science*. 2018;**135**:136-146
- [46] Li YH, Xu TT, Wang SZ, Fekete B, Yang J, Yang JQ, et al. Modelling and analysis of the corrosion characteristics of ferritic-martensitic steels in supercritical water. *Materials*. 2019;**12**:409
- [47] Viswanathan R, Sarver J, Tanzosh JM. Boiler materials for ultra-supercritical coal power plants-stearnsides oxidation. *Journal of Materials Engineering and Performance*. 2006;**15**:255-274
- [48] Bischoff J, Motta AT. Oxidation behavior of ferritic-martensitic and ODS steels in supercritical water. *Journal of Nuclear Materials*. 2012;**424**:261-276
- [49] Li YH, Wang SZ, Wang LS, Yu PF, Yang JQ. Corrosion behavior of austenitic steel 304 in nearcriticalaqueous solutions.

Advances in Engineering Research.
 2015;**45**:189-192

[50] Xu DH, Huang CB, Wang SZ, Lin GK, Guo Y. Salt deposition problems in supercritical water oxidation. Chemical Engineering Journal. 2015;**279**:1010-1022

[51] Kawasaki S-I, Oe T, Itoh S, Suzuki A, Sue K, Arai K. Flow characteristics of aqueous salt solutions for applications in supercritical water oxidation. The Journal of Supercritical Fluids. 2007;**42**:241-254

[52] Hodes M, Marrone PA, Hong GT, Smith KA, Tester JW. Salt precipitation and scale control in supercritical water oxidation—Part a: Fundamentals and research. Journal of Supercritical Fluids. 2004;**29**:265-288

[53] Marrone PA, Hodes M, Smith KA, Tester JW. Salt precipitation and scale control in supercritical water oxidation—Part B: Commercial/full-scale applications. The Journal of Supercritical Fluids. 2004;**29**:289-312

[54] Schubert M, Regler JW, Vogel F. Continuous salt precipitation and separation from supercritical water. Part 1: Type 1 salts. Journal of Supercritical Fluids. 2010;**52**:99-112

[55] Prikopsky K, Wellig B, von Rohr PR. SCWO of salt containing artificial wastewater using a transpiring-wall reactor: Experimental results. The Journal of Supercritical Fluids. 2007;**40**:246-257

[56] Matsumura Y, Minowa T, Potic B, Kersten SRA, Prins W, van Swaaij WPM, et al. Biomass gasification in near- and super-critical water: Status and prospects. Biomass and Bioenergy. 2005;**29**:269-292

[57] Portela JR, López J, Nebot E, Martínez De La Ossa E. Elimination of cutting oil wastes by promoted

hydrothermal oxidation. Journal of Hazardous Materials. 2001;**88**:95-106

[58] Li YH, Wang SZ, Yang JQ, Zhang Y, Xu DH, Guo Y. Effect of salt deposits on corrosion behavior of Ni-based alloys in supercritical water oxidation of high salinity organic wastewater. Journal of Environmental Engineering. 2019;**145**:04019080

[59] Waldner MH, Krumeich F, Vogel F. Synthetic natural gas by hydrothermal gasification of biomass: Selection procedure towards a stable catalyst and its sodium sulfate tolerance. The Journal of Supercritical Fluids. 2007;**43**:91-105

[60] Savage PE. A perspective on catalysis in sub- and supercritical water. Journal of Supercritical Fluids. 2009;**47**:407-414

[61] Yang JQ, Wang SZ, Xu DH, Guo Y, Yang C, Li YH. Effect of ammonium chloride on corrosion behavior of Ni-based alloys and stainless steel in supercritical water gasification process. International Journal of Hydrogen Energy. 2017;**42**:19788-19797

[62] Wang J, Qian S, Li Y, Macdonald DD, Jiang Y, Li J. Passivity breakdown on 436 ferritic stainless steel in solutions containing chloride. Journal of Materials Science & Technology. 2019;**35**:637-643

[63] Kritzer P, Boukis N, Dinjus E. Factors controlling corrosion in high-temperature aqueous solutions: A contribution to the dissociation and solubility data influencing corrosion processes. The Journal of Supercritical Fluids. 1999;**15**:205-227

[64] Cocero MJ, Martinez JL. Cool wall reactor for supercritical water oxidation—Modelling and operation results. Journal of Supercritical Fluids. 2004;**31**:41-55

[65] Baur S, Schmidt H, Krämer A, Gerber J. The destruction of industrial

- aqueous waste containing biocides in supercritical water—Development of the SUWOX process for the technical application. *The Journal of Supercritical Fluids*. 2005;**33**:149-157
- [66] Calzavara Y, Jousset-Dubien C, Turc HA, Fauvel E, Sarrade S. A new reactor concept for hydrothermal oxidation. *The Journal of Supercritical Fluids*. 2004;**31**:195-206
- [67] Příkopský K. Characterization of Continuous Diffusion Flames in Supercritical Water Oxidation. Zürich: Swiss Federal Institute of Technology; 2007
- [68] Wellig B. Transpiring wall reactor for the supercritical water oxidation. ProQuest Dissertations Publishing; 2003
- [69] Li Y, Wang S, Ren M, Zhang J, Xu D, Qian L, et al. Recent advances on research and application on supercritical hydrothermal combustion technology. *HuagongJinzhuan/Chemical Industry and Engineering Progress*. 2016;**35**:1942-1955
- [70] Fauvel E, Jousset-Dubien C, Tanneur V, Moussiere S, Guichardon P, Charbit G, et al. A porous reactor for supercritical water oxidation: Experimental results on salty compounds and corrosive solvents oxidation. *Industrial & Engineering Chemistry Research*. 2005;**44**:8968-8971
- [71] Xu D, Wang S, Tang X, Gong Y, Guo Y, Wang Y, et al. Design of the first pilot scale plant of China for supercritical water oxidation of sewage sludge. *Chemical Engineering Research & Design*. 2012;**90**:288-297
- [72] Xu DH, Wang SZ, Gong YM, Guo Y, Tang XY, Ma HH. A novel concept reactor design for preventing salt deposition in supercritical water. *Chemical Engineering Research & Design*. 2010;**88**:1515-1522
- [73] Li YH, Wang SZ, Qian LL, Wen S. An assessment of supercritical hydrothermal combustion (SCHC) for organic wastes destruction. *Advanced Materials Research*. 2014;**955-959**:1777-1782
- [74] Qian LL, Wang SZ, Li YH. Review of supercritical water oxidation in hydrothermal flames. *Advanced Materials Research*. 2014;**908**:239-242
- [75] Marrone PA, Hong GT. Corrosion control methods in supercritical water oxidation and gasification processes. *The Journal of Supercritical Fluids*. 2009;**51**:83-103
- [76] Qian LL, Wang SZ, Savage PE. Hydrothermal liquefaction of sewage sludge under isothermal and fast conditions. *Bioresource Technology*. 2017;**232**:27-34
- [77] Dolores Bermejo M, Rincon D, Martin A, Jose Cocero M. Experimental performance and modeling of a newcooled-wall reactor for the supercritical water oxidation. *Industrial & Engineering Chemistry Research*. 2009;**48**:6262-6272
- [78] Bermejo MD, Cocero MJ. Destruction of an industrial wastewater by supercritical water oxidation in a transpiring wall reactor. *Journal of Hazardous Materials*. 2006;**137**:965-971
- [79] Marias F, Mancini F, Cansell F, Mercadier J. Energy recovery in supercritical water oxydation process. *Environmental Engineering Science*. 2008;**25**:123-130
- [80] Svanström M, Fröling M, Modell M, Peters WA, Tester J. Environmental assessment of supercritical water oxidation of sewage sludge. *Resources, Conservation and Recycling*. 2004;**41**:321-338
- [81] O'Callaghan P. Phosphorus recovery from sewage sludge using the

aquacritoxsupercritical water oxidation
process. *O₂ Environmental and SCFI*.
2010;1-8

[82] Yang JQ, Wang SZ, Li YH, Zhang Y,
Xu DH. Novel design concept for a
commercial-scale plant for supercritical
water oxidation of industrial and sewage
sludge. *Journal of Environmental*
Management. 2019;**233**:131-140

[83] Zhang YS, Wang SZ, Song WH,
Yang JQ, Xu TT, Li JN, et al.
Characteristics of sodium sulfate
deposition in hydrogen production
from supercritical water gasification:
A review. *International Journal of*
Hydrogen Energy. 2019. In press. DOI:
10.1016/j.ijhydene.2019.05.125

[84] Zhang J, Wang SZ, Ren MM, Lu JL,
Chen SL, Zhang HM. Effect mechanism
of auxiliary fuel in supercritical water:
A review. *Industrial & Engineering*
Chemistry Research. 2019;**58**:1480-1494

[85] Qian LL, Wang SZ, Ren MM,
Wang S. Co-oxidation effects and
mechanisms between sludge and
alcohols (methanol, ethanol and
isopropanol) in supercritical water.
Chemical Engineering Journal.
2019;**366**:223-234

