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REVIEW PAPER

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## SUPERCRITICAL WATER OXIDATION: FUNDAMENTALS AND REACTOR MODELING

*Supercritical water oxidation (SCWO) is a technology that takes advantage of the special solvation properties of the water above its critical point (374°C, 22.1 MPa), to achieve a complete destruction of organic wastes. The oxidation of the organics dissolved in supercritical water (SCW) can be carried out in an homogeneous phase due to the complete miscibility of oxygen with SCW. If the temperature is high enough (above 650°C) a complete destruction of a large variety of organics can be achieved with residence times lower than one minute. Although the energy consumption of the SCWO is very high, with an appropriate heat integration system, the process can be energetically self-sufficient or even produce an excess of energy. The two main challenges of the SCWO are corrosion problems and salt deposition. These problems can be overcome by the use of special construction materials and adequate reactor designs. Due to the high cost of the construction and operation of these reactors, the development of simulations is of great interest.*

*This work gives a brief description of the process and its present challenges, focussing on the calculation of the physical properties of the water and its mixtures, and on the description of the kinetics from an engineering point of view, to finish with a short general description of the state of art in SCWO reactor modelling.*

*Key words: Supercritical water oxidation, water physical properties, reactor modelling, CFD.*

In general, taking a mixture of a liquid and a gas in equilibrium conditions, when the pressure and the temperature increase, a 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 supercritical fluid (SCF) (Figure 1).

Technically, a SCF is a gas but not a vapor. The term "gas" refers to any phase which "will conform 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 depends on its density, making SCF tunable solvents. Some processes such as an extraction, a crystallization or even a reaction have taken advantage of the special properties of the supercritical fluids. The most frequently used SCFs are carbon dioxide and water.

Supercritical water possesses unique physical properties that make it an excellent medium for the oxidation of organics. The polarity of water changes with

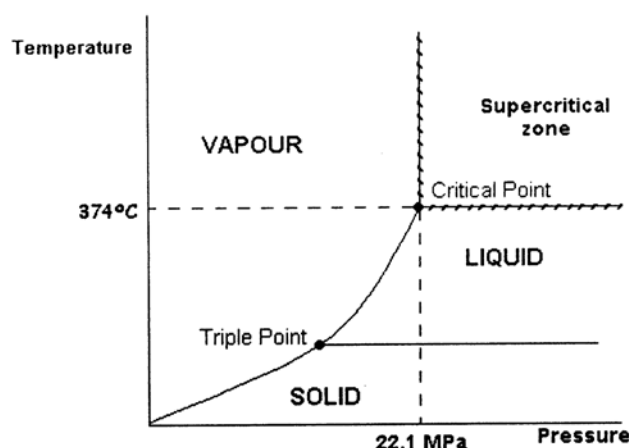


Figure 1. Phase diagram of water

the pressure and the temperature. At supercritical conditions, water is a non-polar solvent being completely miscible with organics. Supercritical water (SCW) also is completely miscible with oxygen and other gases creating homogeneous reaction media for the oxidation of organics. The process known as supercritical water oxidation (SCWO) consists of the homogeneous oxidation of chemical compounds in an aqueous medium using oxygen or hydrogen peroxide as oxidizing agent, at temperatures and pressures above the critical point of water (647.3 K and 22.12 MPa). The main application of the SCWO is the destruction of wastewaters and sludges, especially those containing recalcitrant, xenobiotic and non-biodegradable pollutants. At the appropriate reaction temperatures, pressures and residence times,

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almost any pollutant can be completely destroyed by SCWO with residence times less than 1 minute.

The SCWO process uses a great quantity of energy in pressurizing and preheating the reactants, but the integration of the process allows the recovery of the energy from the hot pressurized product stream for preheating or even to the production of the electricity [1]. In this way, the companies involved in the development of the SCWO process achieve favorable economical balances of the SCWO [2,3].

In this work we wish to present an introduction to the modeling of reactors in SCWO. For doing so, some practicalities as the physical properties calculations and reaction kinetics, are considered. Special attention has been paid to the EoS, correlations and kinetics models that have been useful for the authors in their modeling work. A brief description of the SCWO process and its present situation is provided in order to make the limitations and necessities of the SCWO process uses. Selected models found in the literature are briefly described. At the end, the application of different models for modeling of particular reactors is presented.

## PROPERTIES OF WATER AND ITS MIXTURES

In the region near to the critical point, water properties vary sharply, being quite different from those of normal liquid water or steam. For instance, at the critical point the density of water ( $300 \text{ kg/m}^3$ ) is intermediate, between that of liquid water ( $1000 \text{ kg/m}^3$ ) and that of steam ( $1 \text{ kg/m}^3$ ) [4]. The calculation of thermodynamic 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, though the Peng and Robinson's EoS with the translated volume correction [5] is able to estimate densities of the system water-air quite accurately, and to describe the behavior of real SCWO reactors [6,7]. If salts are present in the system, more complicated EoS are necessary. For modeling a high temperature and supercritical aqueous systems, Anderko & Pitzer [8] developed a comprehensive EoS able to represent LV and SL equilibria, as well as volumetric properties of the water-NaCl system at temperatures higher than 573 K and pressures up to 500 MPa within the experimental uncertainty. In 2001, Kosinski & Anderko extended the EoS to multicomponent water-salt-non electrolyte systems and developed a corresponding-states methodology for systems for which very little experimental information is available [9].

Solvation properties of supercritical water differ considerably from that of liquid and gaseous water. The static dielectric constant of water drops from 78.5 at 25 °C to 5 in the near critical region and, finally, to 1-2 at 450 °C [10-12]. As a result, SCW acts as a non-polar dense gas, and its solvation properties resemble those of a low polarity organic compound. This is the reason why typically non-polar compounds are completely

soluble in water under supercritical conditions. SCW also is completely miscible with "permanent" gases, such as nitrogen, oxygen, and carbon dioxide [4,13-15]. In contrast, inorganic salts are practically insoluble in SCW [16].

The viscosity of supercritical water is low. Diffusivities in supercritical water are usually high. In the region above the critical point these properties are only slightly affected by temperature, and can be predicted [17]:

- For the calculation of the viscosity, the International Association for Properties of Water and Steam (IAPWS) [18] recommends the Sengers & Kamgar-Parsi equation [19]. In 1999, Marcus [20] developed a correlation taking into account the relative void volume, the enthalpy of vaporization, and the hydrogen bonding.

- Sengers et al. [21] developed an equation for the calculation of the thermal conductivity of a supercritical steam as a function of the temperature and the density that is able to predict thermal conductivity with a deviation lower than 3% with respect to the experimental values. The correlations proposed by Chung [22,23] can be used for calculating both viscosity and thermal conductivity [6].

- For calculating the diffusivity of other species in water Lieball [6] suggests the correlation of He [24]. For the self-diffusion coefficient of water, the correlation by Liu and Macedo [25] or Marcus [20] can be used.

More information about the calculation of the physical properties and its mixtures can be found elsewhere [26].

## KINETICS

The combination of the solvation and physical properties makes supercritical water an ideal medium for the reaction of organics. In the last years a growing interest in the reaction of organics in supercritical or near critical water has been developing. A number of works that study the organic reactions in SCW in depth focusing on the influence of the properties of water and the kinetics modeling have been developed [32-30]. Thus, in this work, only a few remarks about the SCWO reactions and their kinetics modeling from an engineering point of view are presented.

Frequently, the kinetics of the SCWO of organic is considered as a first order or pseudo first-order kinetics with respect to the concentration of the organic compounds [31-34], considering that the oxidation rate is independent of or weakly dependent on the oxidant concentration. In 1991, Li et al. [31] proposed a generalized kinetic 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 organic compounds are directly destroyed into the final oxidation products, while others are transformed into stable intermediates with slower oxidation rates. In



concentration, and especially the reaction temperature, which is the most influencing factor affecting the conversions in the SCWO process. When the reaction temperature 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, the required residence times are lower than 50 s, independently of the contaminant treated [39]. Total removals are obtained working with the stoichiometric quantity of the oxidant [40]. When pressure is above the critical pressure of water (22.1 MPa), the conversion is not improved by increasing the pressure. At lower pressures [41], the conversions decrease, but if the reaction temperature is high enough, the detrimental effect of the pressure can be compensated [42].

SCWO has a number of characteristics that make it especially favorable for the corrosion process [43,44]. The main ones are the 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. Due to the corrosion and to the necessity for working at high pressures and temperatures, both reactors and heat exchangers of the SCWO process should be constructed in materials resistant to corrosion and high temperature. The most widely used construction materials for the SCWO facilities are [45]: stainless steel (AISI 316) (300°C < T < 500°C, low concentration of Cl<sup>-</sup>), Titanium alloys (Ti-Gr2, Ti-Gr9 and Ti-Gr12) (at "low temperature" areas or as a coating of another material), Al or Si based ceramics like alumina, silicium carbide or nitride (pH < 12) and Ni alloys 625 and C-276, being the most promising materials used in the SCWO.

### Salt separation

Due to reduced salt solubility, the eventually stable solid particles are present in SCWO processes. These particles can cause equipment fouling, plugging and erosion. In fact, the plugging of reactors produced by the salt precipitation is the main reason of commercialization delaying of the SCWO process for some applications [46,47].

In order to solve the plugging problem different solutions have been proposed Marrone et al. [48], have summarized some of them, such as: solubilize the salts, by elevating the operation pressure to increase the solution density; increase the velocity of the fluid, in order to keep the particles suspended and avoid the deposition (solution adopted by Chematur in their commercial applications [3,49]); the use of additives dissolved in the feed; the introduction of mobile surfaces where the salts can precipitate; and new reactor designs, such as the transpiring wall reactor and the MODAR reverse flow reactor, where the precipitation of salts in the wall is avoided.

In conclusion, Kritzer and Dinjus [46] pointed out that the best solution to avoid salt precipitation inside the reactor is to reduce the quantity of the salt present in the feed. This can be achieved by using solid-fluid separation devices such as hydrocyclons [50] or filtration systems [51]. These devices can be also used for the recovery of valuable products.

### Depressurization and heat recovery

The gaseous products of the reaction (CO<sub>2</sub> and N<sub>2</sub> if air is used as oxidant), along with the supercritical water, leave the reactor at a temperature around 650°C and the pressure higher than 23 MPa. This stream must be cooled and depressurized down to room conditions, and then separated into a liquid aqueous phase and a gas phase.

For diluted aqueous wastes (i.e. with low heat of reaction) it is possible to use the residual heat of the products to preheat the waste up to the operation temperature using a heat exchanger. The minimum concentration of organic matter depends on the heat exchanged. Feeds with a heating value of 900 kJ/kg (equivalent to a 2 wt % hexane) can generate an effluent, with enough energy content to preheat the feed from room temperature to 400°C and to generate the electric power equivalent to that consumed by the high pressure pump and the air compressor [1]. Lavric et al. [52] obtained similar results working with a 5 wt % of hexane, and using different ways of producing electricity. An excess of thermal energy contained in the effluent can be used to generate steam for external consumption, to produce electricity or for heating in the industrial processes at high temperature [1,53]. The plant for the SCWO of sludges, situated in Harlingen (Texas, USA) and developed by Hydroprocessing LLC, is presented as more profitable than other processes for sludge treatment, due to the sale of the excess of thermal energy as hot water and the use of the produced CO<sub>2</sub> for the neutralization of industrial effluents [2].

For a larger scale, the energy recovery system may potentially take the form of the power generation by direct expansion of the reactor products through a supercritical steam turbine. Such a system would be capable of generating a significant power in the excess of that required for air compression, or oxygen and feed pumping. In a theoretical study of the power generation from oxidation of coal by SCWO, an energetic efficiency of 37% with the steam at 650 °C and 30 MPa is achieved [55]. Fujie et al. factor studied the combustion behavior of brown coal in SCW obtaining a complete destruction at 600°C and 30 MPa in a residence time lower than one minute and without the production of NO<sub>x</sub> or SO<sub>x</sub>, suggesting that the exhaust gas processing would be unnecessary, thus making the possibility of a power station working with the SCWO of coal more attractive.

More detailed studies of the SCWO process and its problems can be found elsewhere [26,46–48].

### MODELLING SCWO REACTORS

In the last years, the interest in the SCWO process modeling is increasing. To obtain reliable simulations, the accurate values of densities, enthalpies and heat capacities are needed, for both water and aqueous mixtures. In some cases the values of the transport properties such as viscosity, heat conductivity and diffusivity are also needed.

With the scaling of the processes and the interest in the heat integration [1,52–55], the models based on mass and energy balances were developed. For modeling the heat integration of the process, it is common to assume that the conversion is 100% (so the kinetic is not modeled), and to calculate the heat released in that case [1,55]. For these calculations the accurate values of enthalpies and heat capacities are needed. Also a good description of the phase equilibrium of the system is required to perform accurate flash calculations. So only mass and energy balances are usually performed. This kind of modeling is sometimes performed with a commercial program such as ASPEN PLUS [1,52,54]. These balances can be combined with heat integration techniques, like the Pinch Analysis or/and the chemical reactors energy integration (CREI) concept, in order to determine the ideal configuration for the heat integration [54].

It is interesting sometimes to model the performance of a concrete reactor. A model of the reactor considering mass and energy balances and simple flow patterns (plug flow or perfect mixing) can be very appropriate for describing tubular reactors or CSTRs [35,36,56,57]. This kind of models should include a kinetic model and the energy balance inside the reactor, so that precise values of densities, enthalpies and heat capacities are needed. At low concentrations of reactants and with the use of oxygen or water peroxide as an oxidant, the properties of the mixture can be replaced by the properties of pure water [59]. When working with high fuel concentrations, especially if air is used as an oxidant, the content of water in the reaction mixture can be decreased down to 65% or even less. The properties of the mixture differ considerably from those of pure water and it is convenient to use an EoS to calculate the properties of the mixture. As an example of this kind of modeling, Anikeev and Ermakova [56] modeled their facility considering the tubular reactor and several heat exchangers combining methods of non-ideal thermodynamics with the Redlich–Kwong–Soave EoS.

It is sometimes necessary to predict the evolution of the operation variables during the start up of the facility, or when one of the operational parameters is changed. For these purposes, non-stationary models are developed [58]. In 2001, Muske et al. [58] developed

a model of a plug flow reactor and use it in a predictive control of the effluent composition. When the models are integrated in a more complex system, (i.e. a predictive control system), it is highly valuable that the calculations can be performed rapidly. In this case, the use of simple flow patterns to model the reactor is highly recommended.

Due to the problems of corrosion and salt deposition in the SCWO process, several complicated reactor designs been developed [26]. These new reactors usually have hot and "cold" areas, and sometimes even several phases are involved. It is expected that the flow patterns inside these reactor is quite different from the plug flow or to perfect mixing. In addition, it becomes essential to model properly the heat transfer inside the reactor.

The development of these new reactor designs and the awareness of the importance of the reactants mixing [38] have led to more complicated models using CFD tools [6,59–63], in order to describe the flow pattern inside the reactor accurately. For doing so, the momentum balance should be solved, and the accurate values of the transport properties such as viscosity, heat conductivity and diffusivity are needed.

Zhou et al. [61] used a CFD model to evaluate the behaviour of a tubular reactor, a 3D CSTR and a coaxial reactor. The CFD analysis of the last one at different feed flows, and the direction of flow (upwards and downwards) allowed them to improve the performance of the reactor. Avoiding short-circuiting by adding a deflector. Marias et al. [63] simulated the expansion of the products mixing in a capillary tube and considering a momentum and energy balance in order to get a careful expansion of the mixing when salts are present.

Three examples of these reactors and the ways in which they have been modeled are presented.

### Modeling of the cooled wall reactor

The *cooled wall reactor* separates temperature and pressure effects by using a cooled wall vessel, which is maintained near to 400°C, and a reaction chamber, where reactants are mixed and reaction takes place. Cocero and Martinez [36] performed a steady state simulation of a fixed-fed reactor, based on the mass and energy balances. The heat transfer was modeled using global coefficients and the flow pattern was assumed to be a plug flow. The chemical reaction was described using the Li et al. [31] kinetic model. The physical properties of the mixture are calculated as shown in equation (1).

$$\text{Prop}(T, P) = \sum x_i \cdot \text{Prop}(T, P)_i \quad (1)$$

where  $x_i$  is the molar fraction of each component, and the physical properties are those tabulated for each pure substance. Even considering the simplicity of this model, it is possible to solve the temperature and concentration profile inside the reactor in a few minutes. The agreement of the predictions of the model with the ex-

perimental results was very good, so it is possible to give a simple explanation of the behavior of the reactor.

### Modeling of the reverse flow tank reactor with brine pool

The *reverse flow tank reactor* with a brine pool comprises a reaction chamber with a supercritical temperature zone in the upper region and a subcritical temperature zone in the lower region [48]. The oxidation takes place in the supercritical temperature zone. Dense materials (including the precipitated inorganic salts) fall into the liquid phase provided 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 salts deposit on the walls of the reactor vessel.

Oh et al. [60] developed a steady state CFD model for describing this kind of reactor. The tri-dimensional reactor was approximated to an axisymmetric 2D reactor, and mass, momentum and energy balances were solved. Turbulence flow was simulated using the RNG  $k-\epsilon$  turbulence model. The physical properties of the entire component were determined by the Redlich-Kwong EoS form, as proposed by Schartsentruber & Renon [64]. Two kinetics models considering kinetics and diffusion rate as controlling mechanisms were considered. This model was able to describe the temperature and conversions. It also shows a recirculation area in the reactor and gives a useful insight in the salt deposition inside the reactor.

### Modeling of the transpiring wall reactor

The *transpiring wall reactor* (TWR) consists of a reaction chamber surrounded by a shell through which clean water circulates, forming a cool, protective film against corrosive agents, salt deposition, and high

temperatures. In the last years a number of TWRs have been developed [65–69], and several authors have developed computational models to explain the behavior of the reactor. Bermejo et al. [35] developed a model describing a TWR based on the mass and energy balances and a combination of simple flow patterns. This model was validated by comparing the calculated temperature profile to the experimental one. Fauvel et al. [70] modeled their reactor considering it as a cascade of ideally mixed tanks with a stage radial feed, after carrying out a residence time distribution study to investigate the flow pattern. The proposed hydrodynamic model was validated in the case of the ethanol oxidation in supercritical water. Other researchers developed computational fluid dynamics models (CFD) [6,67,68,71] to get an insight into local flow conditions and species concentrations inside the reactor and around the transpiring wall, because this information was hardly accessible to measurements. In these cases, local temperatures and destruction efficiency are used to validate the computational results.

As an example of the applicability of different types of models we will show the utility of two different kinds of model in the scaling of a transpiring wall reactor. The reactor used is described by Bermejo et al. [66] as a reactor design 3. The simple flow pattern model described by Bermejo et al. [35] was applied to the performance of the reactor working with a feed flow 200 kg/h and using oxygen as an oxidant. This model explains the behavior of the reactor and predicts the temperature and concentration profiles along the reactor. Using it we were able to determine in what conditions the reactor was going to perform successfully, as shown in Figure 4.

A CFD model, still in development by the High Pressure Process Group of the University of Valladolid, has been applied to the same reactor in the same operational conditions. This model describes the reactor

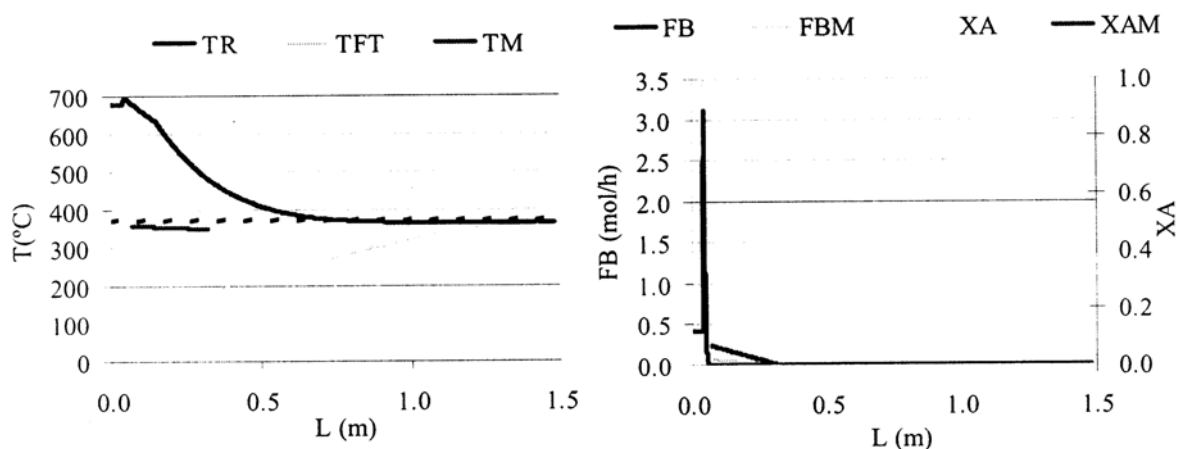


Figure 4. Predictions of the simple flow patterns model for the behavior of the UVA transpiring flow reactor with a Feed=200 kg/h, Transpiring flow=120 kg/h, Fuel=7% IPA. TR: temperature in the reaction chamber, TFT: temperature of the transpiring flow, TM: temperature in the mixer, FB: acetic acid flow in the reaction chamber (mol/h), FBM: acetic acid flow in the mixer, XA: IPA conversion in the reaction chamber, XAM: IPA conversion in the mixture.

using a 2D axial symmetry. Mass, energy and momentum balances are solved assuming laminar flow. To describe the kinetics and to calculate physical properties, this model is based on the same assumptions as the previous one. This very simple CFD modeling gives new information about the reactor. Now not only the temperature variation along the reactor but also the radial variation and the flow pattern, among other parameters, are known, providing information about whether the transpiring wall is protected against the salt deposition and the high temperatures ( $T_{\text{wall}} < 650 \text{ K}$ ). The temperature profile predicted by the CFD simulation is shown in Figure 5.

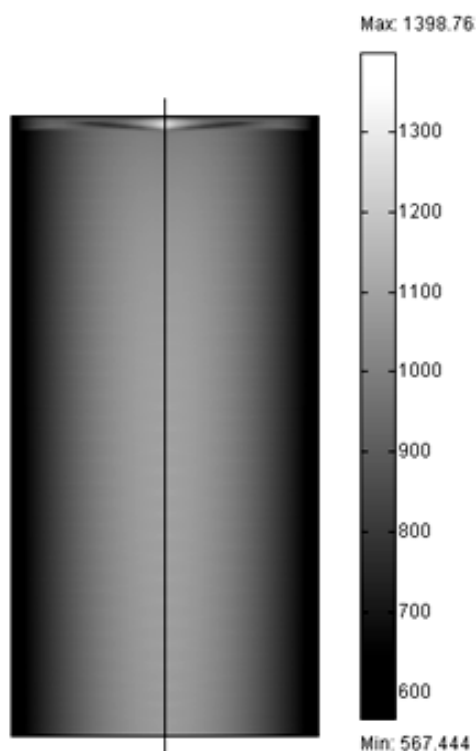


Figure 5. Surface temperature plot predicted by the CFD model of the TWR of the UVa Feed flow=200 kg/h, oxidant: oxygen, ( $T$  in K)

## CONCLUSIONS

As shown in this work, SCWO is a very powerful technology able to achieve the complete destruction of a great variety of wastes with residence times of a few seconds. In the present the development of this technology is limited by high operational costs and the corrosion and salt deposition problem.

Theoretical studies show that SCWO can be performed in a energetically-profitable way, what would make this technology very attractive for industrial applications. But for accomplishing this objective new construction materials and especially more efficient salt separation devices have to be developed.

Corrosion and salt depositions problems are being solved through the design of new reactors. But due to

high costs of the SCWO research, modeling becomes an essential step in the development of these new reactors. CFD models are able to give an insight in to the reactor behavior which is difficult to obtain experimentally, and specifically a better understanding of the mixing of reactants.

For getting correct simulations of the reactors, it is essential to use accurate values of thermodynamical and transport properties of the aqueous mixtures. A lot of research is necessary in this field: transport properties of pure water can be easily predicted, but this is not the case for mixtures with supercritical water. The prediction of thermodynamic properties and phase equilibrium of the aqueous systems are still a handicap, especially when inorganic salts are present in the mixture.

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