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An assessment of supercritical water oxidation (SCWO) Existing problems, possible solutions and new reactor concepts

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Abstract

The process of supercritical water oxidation (SCWO) is a promising alternative to the incineration of aqueous organic waste streams and has received an enormous interest during the last decade. However, SCWO as an end-of-pipe technology has some disadvantages that have hindered an industrial application of the process. Beside technical problems due to reactor corrosion and salt precipitation, problems result from the fact that SCWO often is claimed as a "general" technology for all possible waste streams, a claim that the technology cannot fulfill. In this article, the existing problems of SCWO as an end-of-pipe technology are described and possible solutions are discussed, different reactor concepts are elucidated, and a suggestion for future research and technical procedure in the SCWO field is given. Additionally, an assessment of possible energetic applications of the SCWO process is given, in which SCWO is more than a waste treatment technology.

Keywords: Supercritical water oxidation; Corrosion; Reactor; Salt plugging

1. Introduction

In the last two decades, supercritical water ($T_c = 374°C$; $p_c = 22.1\,MPa$) has become an interesting medium for chemistry [1–6]. One of its most investigated applications is the oxidative treatment of aqueous wastes containing organic compounds in the so-called "supercritical water oxidation" (SCWO) process [7–11]. This process can be seen as a further development of the well-established process of wet air oxidation (WAO), running at temperatures up to 320°C and pressures up to 20 MPa [12–14]. Reaction times in the WAO process are normally up to several hours, and a complete destruction of the organic material is seldom achieved, so a further waste treatment is necessary.

The SCWO process is based on the special physical properties of supercritical water. When exceeding its critical point, the values of density, dielectric constant, and ionic product of water drop down, so supercritical water acts as a non-polar solvent of high diffusivity and excellent transport properties (see Fig. 1) [15–17]. Consequently, even non-polar organic compounds and gases like oxygen become completely miscible with the supercritical fluid [18–20]. During the SCWO process, the organic compounds react completely with the oxidant — mostly oxygen — in a single-phase reaction forming CO_2 and H_2O. The hetero-atoms chlorine, sulfur, or phosphorus present in the organic wastes are transformed into the mineral acids HCl, H_2SO_4, or H_3PO_4, respectively. Organic bounded nitrogen predominately forms N_2 and small amounts of N_2O. Thereby, N(-III) nitrogen is oxidized by the oxidant, while N(+V) — e.g. in nitrates — is a powerful oxidant itself and is reduced. Undesired by-products known from incineration (dioxines, NO_x) are normally not formed. Typical process parameters of SCWO are reaction temperatures of 500–700°C and pressures of 24–50 MPa. Reaction times, at which a complete conversion is observed, seldom exceed some minutes. A simplified flow sheet of the process is shown in Fig. 2.

The variety of employed wastes include warfare agents, rocket propellants, radioactive wastes, contaminated soils, and wastes from the paper and chemical industries [7,8,10,21–24]. The Swedish company "Chematur" has started experiments with an industrial scaled plant ("Aqua Critox") licensed from Eco Waste Technologies, USA, in 1997. The plant consists of a tubular nickel-base alloy 625

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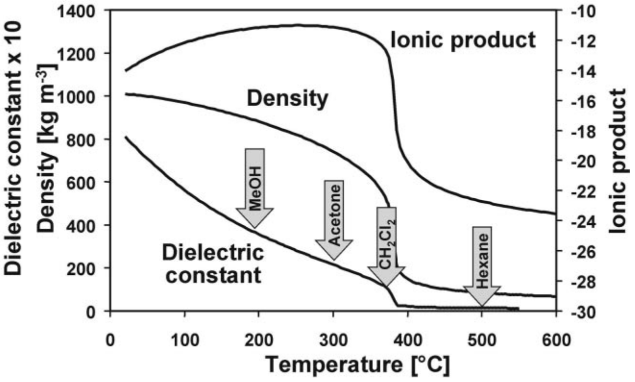


Fig. 1. Physical properties of water at a pressure of 24 MPa versus temperature. Dielectric constants of typical organic solvents at room temperature are indicated. Data calculated after [15].

reactor and has a capacity of 250 kg aqueous organic waste per hour [24]. A variety of waste-streams have been successfully treated. Among these were wastes from the amine production, de-inking sludge from paper recycling, and cutting liquid. However, none of these waste streams contains the acid-forming hetero-atoms mentioned above, and corrosion has not been a critical item for that plant so far.

The research SCWO activities in the USA, Europe and Japan are reviewed in detail elsewhere [25].

2. Problems of SCWO

The fact that SCWO has not become a current waste treatment technology so far, can be seen in three reasons:

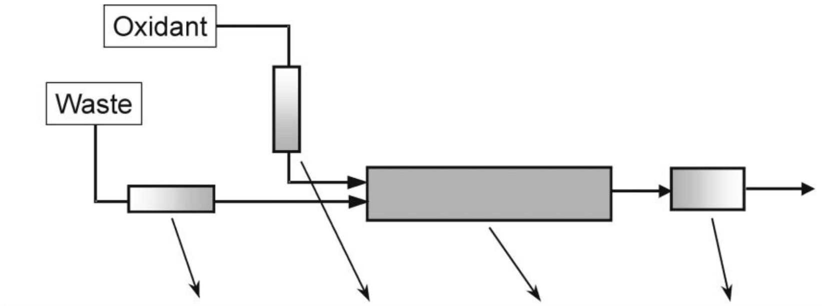
- Severe reactor corrosion caused by acids, which are formed during the treatment of e.g. halogen-, sulfur-, or phosphorus-containing organics.
- Serious plugging of the reactors caused by precipitating salts at supercritical temperatures and low densities. It must be mentioned that most waste streams contain salts in higher concentrations.
- Due to the lack of experimental data, cost evaluations, especially for the scale-up of SCWO plants to an industrial scale, are hard to perform.

All three disadvantages are linked with each other and should be discussed in more detail in the following sections.

2.1. The corrosion problem

Before SCWO was introduced, almost no experiments were performed in which materials were corroded under that harsh conditions which occur during the SCWO process (see e.g. [26]). Especially, the presence of acids in the highly oxidizing high-temperature medium leads to severe corrosion problems. As mentioned previously, it is extremely unlikely that a single reactor material can withstand every conceivable acidic solution [27–30]. On the other hand, it was shown that some materials possess a satisfactory corrosion resistance against some acids. Unfortunately, these materials fail in the presence of others [28,29]. For example, titanium is almost not attacked by oxidizing HCl solutions at any temperature, but shows poor resistance against H_2SO_4 or H_3PO_4 at temperatures above some 400°C [31,32].

The stability of most reactor materials depends strongly on the solubilities of the protecting oxides. Due to their amphoteric character, the solubilities of the oxides are high



	Waste Preheater	Oxidant Preheater	Reactor	Heat exchanger
T (°C)	25 → 380		600	600 → 25
Reactions	Pyrolysis may occur		Oxidation	Formed acids dissociate
Agressive species	Salts, (HCl) no O_2	O_2	HCl; O_2	H^+; Cl^-; O_2
Main Problem	Slight corrosion	No problem	Salt precipitation	Severe corrosion

Fig. 2. Conventional SCWO process and reactions leading to problems in the particular parts of the plant (oxidant must not be nitric acid).

at either strong acidic or strong alkaline pH values and in high-temperature solutions of high density. This explains the observations made by several authors for stainless steels and nickel-base alloys: Their corrosion is extremely high at subcritical temperatures and thus high densities, where acids and bases are dissociated leading to extreme values of pH [33–42]. On the other hand, corrosion is low at highest — supercritical — process temperatures, where the density of the solution is low and acids/bases are not dissociated and thus the solution is “neutral” [33–41].

The interconnections between physical properties of water, dissociation of attacking species, solubility of gases, and solubility of protecting oxides and thus corrosion are described in detail elsewhere [29,40] and shall only be discussed briefly in the present article:

- An increase of the solution density increases the dissociation of attacking species (acids, bases), resulting in higher concentrations of H^+, or OH^-, respectively. Since strongly acidic or alkaline solutions favor oxide dissolution, corrosion is accelerated by high densities.
- Beside this “indirect effect”, the solubility of oxides and thus corrosion is directly influenced by the density of the solution. The greater number of hydrogen bonds and thus more polar character makes high-density water a powerful solvent for salts. It must be pointed out that also supercritical water — namely supercritical water of high pressure and thus high density — may cause high corrosion [37,38,43]. This phenomenon is often overlooked in the literature when supercritical water is automatically regarded as a solvent of low density.
- Anions play an important role in corrosion processes. Special anions may possess a detrimental effect on corrosion resistance. An example is the oxide-film destructive character of chloride and bromide. On the other hand, some anions are incorporated in the oxide film and lead to its enhanced protective character. The anion effect depends on both — metal and anion. For instance, chloride is extremely aggressive against stainless steels, while titanium is immune.
- Aqueous solutions of NaOH or KOH are highly corrosive to nickel-base alloys at supercritical temperatures under oxidizing conditions [28]. The reason is the occurrence of a liquid hydroxide melt, in which salts like the protecting oxides are soluble [44]. On the other hand, NaOH solutions are almost not corrosive nickel-base alloys at subcritical temperatures [37,40].
- Other materials (e.g. titanium, niobium, tantalum) may follow a different behavior [31,32,45,46].

Conclusion: For every acidic solution, which is the reaction product of many SCWO processes, there exists at least one material with an acceptable corrosion resistance, but this material may fail in the presence of other acids. For this reason, corrosion can be avoided by either a selection and separation of feed-streams and/or by an application of different feed-specific materials for the different parts of the reactor. As shown in Table 1, for each part of a reactor, an “ideal” material with low corrosion susceptibility is available. Titanium — e.g. in the form of liners — is the material of choice for subcritical conditions in the absence of fluoride. At supercritical temperatures and low densities, the corrosion resistance of nickel-base alloys is at least as good as that of titanium. Thus, nickel-base alloys should be favored as material for the reactor itself.

2.2. The salt-plugging problem

Room-temperature water is an excellent solvent for most salts — typically several 100 g/l. On the other hand, the solubility of most salts is low in low-density supercritical water (typically 1–100 ppm) [47–52]. This results in the formation of a fine-crystalline, slimy “shock precipitate” when a subcritical salt-containing solution is rapidly heated to supercritical temperatures [48,49]. The precipitating salts lead to a plugging of the reactors, even at high flow velocities. To overcome this plugging problem, different arrangements are conceivable:

- *Increasing the pressure and thus density of the supercritical solution*. This indeed leads to an enhanced solubility of most salts [16,51,52]. However, the solubilities of all salts are increased by this procedure, and so unfortunately those of the metal-protecting oxides. Thus, increasing the pressure leads to severe corrosion also in the reactor of a SCWO plant, which normally is not attacked (see above).
- *Introduction of a “mobile surface” on which the precipitating salts can settle down* [53]. This attempt might work successfully in test runs lasting only several hours, but over a long time of operation — typical for an

Table 1
Corrosion resistance of nickel-base alloys and titanium against different media at sub- and supercritical temperatures taken from literature[a]

	$T < T_c$; high density		$T > T_c$; low density	
	Good resistance	Poor resistance	Good resistance	Poor resistance
Nickel-base	H_3PO_4, HF	HCl, HBr	All acids	$[H_3PO_4] > 0.1\,\mathrm{mol/kg}$
Alloys	Alkaline solutions	H_2SO_4, HNO_3		NaOH
Titanium	All acids	F^-	HCl	H_2SO_4, H_3PO_4

[a] Data for titanium after [31,32]; data for nickel-base alloys after [35–40,42,70,77].

industrial application — it should be not possible to remove all the precipitating salts. As a result, sooner or later, reactor plugging should occur.
- *Special reactor concepts, in which a settling-down at the wall surface is prevented*. Such concepts include simple tank reactors, in which the salts sink down to zones of lower subcritical temperature where they are dissolved again [54,55]. Problems arise from the low settling speed of the fine particles in combination with the high vertical turbulence inside the reactors, leading to their agglomeration on the walls.

Alternatively, salts precipitating in the reaction zone have to be dissolved before they deposit at the wall. This can be realized by an enclosure of the reaction zone by a stream of colder subcritical water, which was the idea of the hydrothermal burner concept developed at the ETH Zürich, Switzerland (LaRoche et al., 1997 [56]). Another promising concept is the transpiring wall reactor equipped by an outer pressure-resistant tube and an inner porous tube [57–59]. Through the porous wall, clean supercritical or subcritical water is pumped, forming a thin, protecting water film on the surface. This film prevents deposition of salts and reduces corrosion. However, the need of an additional water stream, which has to be heated, increases the running costs. Long-time tests to prove the suitability of these reactor concepts for an industrial application have not yet been performed with any of these new reactor concepts.

Conclusion: Salt precipitation can be seen as the major problem of SCWO. A plugging of the reactors cannot be avoided by variation of the process parameters without a simultaneous triggering or rising of new problems. On the other hand, the new reactor concepts seem to be too susceptible to fail in a long-time application. Consequently, the best possibility to overcome the plugging problem is the minimization of the salt content in the waste streams.

2.3. The cost problem

Several cost estimations were performed to evaluate if SCWO is a “profitable” technology [10,60–63]. Since no industrial-scale SCWO plant exists so far, those rough estimations are inaccurate and deviations between them are high. Certainly, all cost estimations amount for the total costs of the destruction of one wet ton of organic waste with an organic content of 10 wt.% to below 300 US$. Most cost-intensive are the investment costs for the plant itself, the staff costs, and the costs for the oxidant (regularly oxygen). Though the oxygen costs are considered for one of the major costs, some pilot studies run with 200% or more of the stoichiometric oxygen demand, though other studies have proven that even 5% excess may be sufficient for total oxidation [22,64]. Thus, high oxygen excess is not necessary and thus not realistic for a prospective industrial application.

Running costs vary with the size of the plant and with the country where the plant is in use (e.g. in Europe, staff costs are by means higher than in the US). It must be critically remarked that an assumed useful time of 10 years for the whole plant given in some studies may be too optimistic, since no data exist for the long-time stability of the material.

Especially, more complicate reactor designs will for sure increase costs (by higher investment costs, more control is necessary during operation, resulting in higher staff costs). It can also be contested that delicate and thus susceptible reactor designs may be suitable for high useful times and that operation times of 300 or more days per year are realistic for such reactors. It must be held in mind that in a SCWO reactor, a waste treatment process occurs and not a clean chemical synthesis of a well-defined pure product starting from pure educts.

Summarizing the reasons mentioned above, a reactor should

- be as easy (and thus as cheap) as possible;
- solve or avoid the corrosion problem;
- solve or evade the plugging problem.

3. Attempts to overcome the problems — new reactor concepts

3.1. The history of the problems

In the early 1980s, the birth of SCWO, the process was claimed to be a technology, which is able to solve every waste problem. The boundless optimism of the inventors covering up the serious problems, which might never be solved for all kinds of wastes, hindered (and still hinders) an industrial application and thus a broader distribution of the technology. It must be pointed out that SCWO can only become an alternative to incineration in special — limited cases.

3.2. Salt-free waste streams

Salt-free waste streams can easily be oxidized in tube reactors. Beyond, organics containing only C, H, O, and N cause no severe corrosion problem also at longer service times [24,65]. No special reactor design is necessary for these wastes.

Due to the possible corrosion problems in the cool-down section caused by acids released during the oxidation of organics containing other hetero-atoms, the reactor has to be modified. A simple addition of bases to the feed solutions in order to neutralize these acids “in situ” is described by several authors [27,54,66,67]. This kind of treatment cannot be recommended due to precipitation of carbonates and corrosion problems at supercritical temperatures (see above). Alternatively, the alkaline solution has to be introduced downstream of the reaction zone. A simplified flow chart of, and the actual temperatures and pH values in such a tube reactor are shown in Fig. 3 (after [68]). The feed-stream and

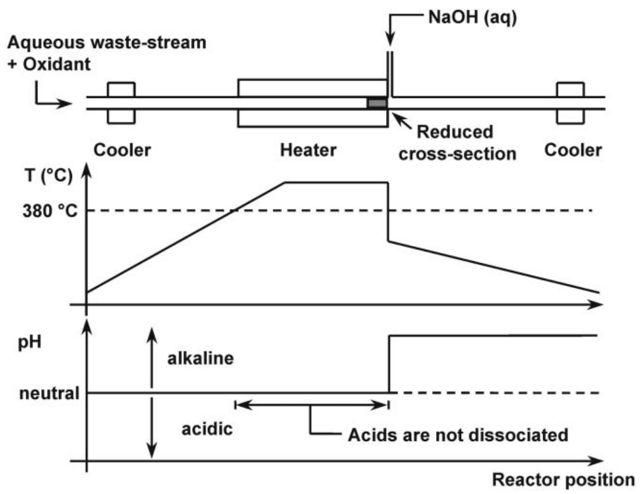


Fig. 3. Modified SCWO process with quenching the supercritical reaction mixture with colder NaOH solution resulting in an alkaline, subcritical solution (after [68]). It must be mentioned that a pH value definition for supercritical temperatures is hard to make. For the present figure, "neutral" means $[H^+] = [OH^-]$.

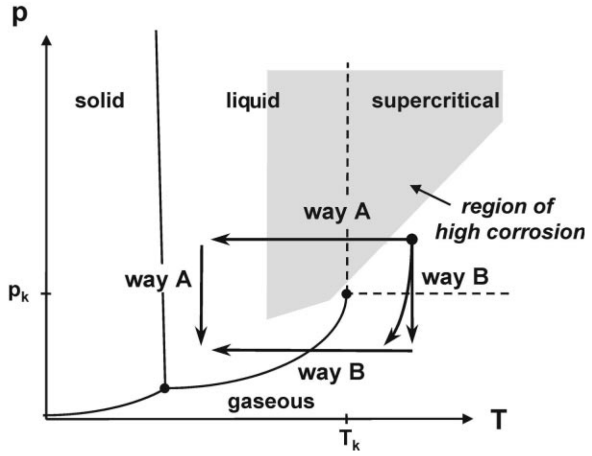


Fig. 4. Modified cooling down strategy of the supercritical reaction mixture. Conventional processes follow way A (cooling down the supercritical solution first followed by expansion) and have to cross a p–T-area where severe corrosion occurs. The modified process expands the supercritical solution in a first step (isobaric or isenthalpic) leading to a hot, less corrosive steam of low density. The second step is the cooling down of the steam to ambient temperatures.

oxidant may also be introduced in separately. If only one preheater is planned, it should be made of titanium, since acids may be released by fast pyrolysis/oxidation of some organics even in the preheater, leading to high corrosion rates of common materials in the oxidizing environment. The reactor itself running at temperatures of 500–700°C should be constructed from high-temperature nickel-base alloys. Due to possible corrosion, it must be guaranteed that everywhere in the reactor, the solution's density is clearly below 200 kg/m^3. After the reaction zone, the solution is quenched by an aqueous stream of colder NaOH or KOH, leading to a weakly alkaline subcritical solution. It has been shown previously that the temperature gradient between supercritical and subcritical temperatures has no influence on the seriousness of corrosion [39,69]. Since alkaline solutions are highly corrosive at supercritical temperatures (see above), a longitudinal back-mixing of the base must be excluded. This can be achieved by a reduced cross-section of the tube at the end of the reactor. Further, it must be assured that the resulting solution is indeed alkaline, since neutral high-density solutions lead to severe corrosion in the presence of chloride or bromide [37,67,70].

Another strategy to reduce corrosion in the cool-down section is shown in Fig. 4. In this case, the presence of an effluent of both high temperature and high density at the same time is avoided. In opposite to conventional SCWO plants, where the supercritical solution is cooled down first, followed by expansion (way A in Fig. 4), an adiabatic expansion of the subcritical solution is applied in the first step (way B in Fig. 4). For instance, an adiabatic expansion from 600°C and 25 MPa to 1 MPa reduces the temperature to values of 510°C. The resulting hot gas of low density is by far less corrosive and its corrosivity is well known from flue gas scrubbers. Additionally, the low mechanical load in this part of the reactor allows a less expensive design and the application of other less pressure-resistant materials (e.g. glass-lined steels). The gas then is cooled down to room temperature.

A disadvantage of both concepts is the somewhat worse energy balance of both process designs compared to those of conventional SCWO plants equipped with a suitable heat exchanger. On the other hand, they completely solve the corrosion problem.

It must be mentioned that the cost-saving catalytic SCWO, where organics are oxidized over a heterogeneous catalyst [71–73], may also be performed in both kinds of reactors.

3.3. Salt-containing waste streams

Waste streams that contain salts in too high concentrations will sooner or later lead to plugging of every kind of reactor. Such waste streams should better be treated by other techniques. Waste streams with only low salt concentrations may be successfully treated by the special reactors mentioned above, but long-time studies are necessary to prove their suitability. Certainly, these reactors will increase the costs. It should be evaluated, if a salt separation in a first step (e.g. by filtration) followed by SCWO in a tube reactor may be a cheaper way of treatment. A fundamental problem of this kind of treatment might be a simultaneous separation of the organics leading to another contaminated waste.

4. Outlook and suggestions

4.1. SCWO as a waste-treatment technology

To make SCWO a "current" end-of-pipe technology, the following rules should be fulfilled:

1. *Further research — filling up the gaps*. Though a lot of research on reactions and thermodynamic data in supercritical water has been done in the last two decades, many questions are still open. For instance, measurements of the solubilities of most oxides are rare and only rudimentary research has been performed on phase diagrams containing more than two components. For this reason, SCWO in some cases is still an unpredictable process and thus may be "dangerous" for technical applications, especially when evaluating the lifetimes of reactors. As an example, the presence of a new, unexpected phase in the system H_2O–O_2–H_3PO_4 leads to severe corrosion and thus failure of the reactors at too high acid concentrations, while slightly lower acid concentrations are not corrosive at all [23,39].
2. *Searching for SCWO-optimized waste streams*. SCWO is not and most probably will never become a "general" technology for all kinds of waste-streams. Consequently, the wastes suitable for SCWO have to be found and selected carefully. For each of these wastes, an "ideal" reactor made of an "ideal" reactor material can be built, which may be resistant over long useful lifetimes.
3. *Performing long-time tests with these waste streams*. For an industrial application, it is of minor interest if a destruction rate of a certain organic compound is 99.99 or 99.999% (which is the object of most studies). On the other hand, it is absolutely necessary to prove the long-time applicability of an industrial process. These missing tests must neither be performed with "harmless" model compounds nor over reaction times of only several hours. Additionally, they have to be performed with exactly these wastes selected before.

When all these requirements are fulfilled successfully, SCWO will surely become a waste treatment process of industrial interest.

4.2. SCWO for energetic use

Much less investigations deal with SCWO treatment for energetic use, although supercritical water is already used in power stations [74–76]. In contrast to conventional coal- or oil-fired power stations, where the water is heated "externally" by the fuel, oil as energy source be oxidized in the water itself in an SCWO power generating process. Due to the single-phase character of the solution and the high heat capacity of the supercritical solvent compared to those of steam, high heat transfer efficiency is achieved. Thus, less complicated reactor designs may be realized.

Additionally, the energy source in the energetic SCWO process is not limited to liquid organic fuels like oil, since all organics present in aqueous streams can be oxidized exothermically. Thus, also energetic less attractive substances like aqueous biomass wastes could be used economically.

Unfortunately, also little work has been done in this field to find (a) the optimum reactor concept and (b) the optimum process parameters. For a better understanding and evaluation of the "energetic" SCWO, the results obtained from different reactor concepts of the "waste-treatment" SCWO may contribute to the required information. Fortunately, salt precipitation and corrosion problems are by far less critical in the energetic application, so cost estimations can be more exact and are less risky. Thus, the primary aim for SCWO as an energetic source is finding the optimum process parameters, and the optimum reactor concepts, respectively, for highest efficiency and thus lowest costs.

5. Conclusion

SCWO for waste treatment is a technology with many problems — corrosion, reactor plugging, and the high costs — that have hindered an industrial scale-up of the process so far. Salt plugging seems to be the most severe problem, and all attempts to solve it in a satisfactory way, lead either to new problems, make a long-time operation doubtful, or increase the costs. Consequently, waste streams containing salts in elevated concentrations should not be treated with SCWO with any of the current reactor technologies. Corrosion can be reduced or even avoided by the right material choice and/or a slightly modified reactor concept.

Further, "ideal" waste streams have to be selected and with the help of these waste streams, long-time runs have to be performed. These long-time runs are indispensable for accurate cost evaluation and to awaken the interest of industry. Then (and only then), SCWO (and other supercritical water applications) has the opportunity to become a "common" waste treatment technology.

The evaluation of SCWO as an energetic source is also just at the beginning and much research has to be done in this field. Certainly, the basic investigations done for the waste treatment SCWO are valid for this application, and e.g. research on reactor concepts can easily be transferred.

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