Oxidation of Hazardous Wastes by Supercritical Water Oxidation(SCWO)

Super**C**ritical **W**ater **O**xidation (SCWO) is an end of pipe technology applicable to industrial waste effluents or sludges breaking down the hazardous toxic compounds into carbon dioxide and water.

Due to the typical operation conditions of 26 MPa and 650°C, SCWO process takes place in a homogeneous fluid phase with high space-time yield. Hetero-atoms are mineralized to the corresponding acids or salts. The production of nitrous oxides is suppressed due to the low oxidation temperatures.

Some physico-chemical properties of water at 25 MPa as function of temperature are shown in Figure 1

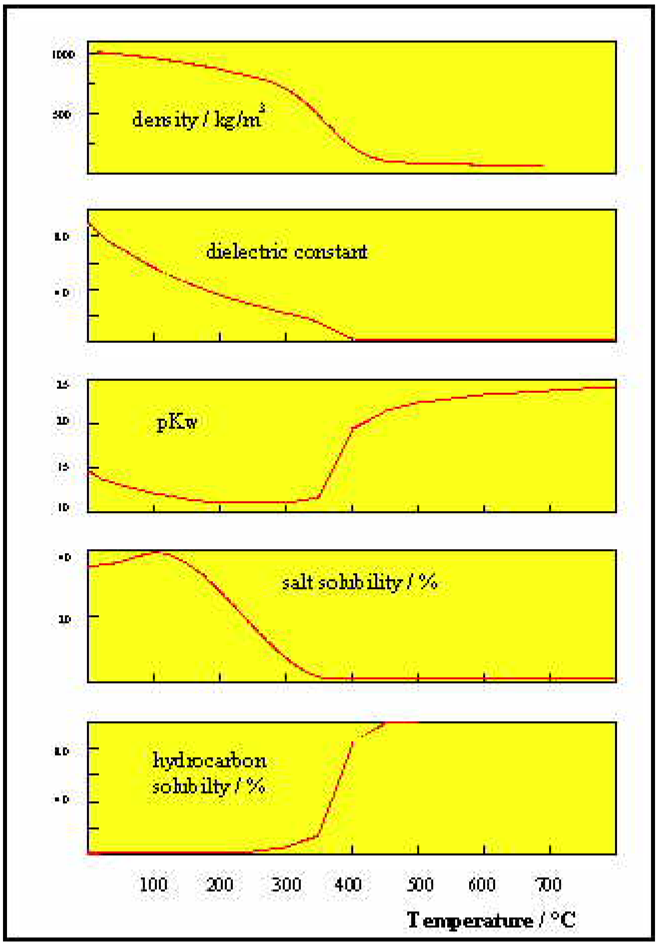


Figure 1

As density and dielectric constant decrease, solubility of organic chemicals increases and solubility of salts decreases. At SCW conditions water behaves like an organic solvent. These properties make it ideally suited for the SCWO process.

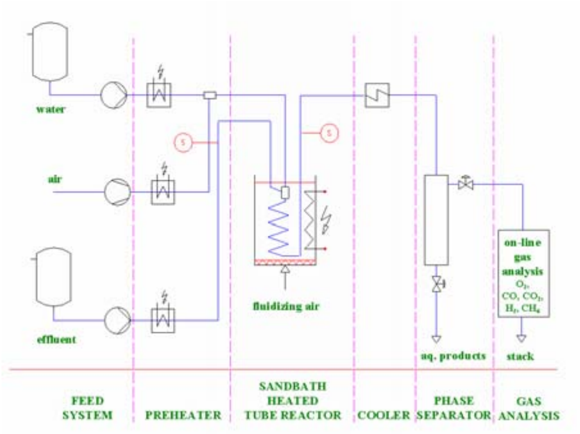
Pilot Plant

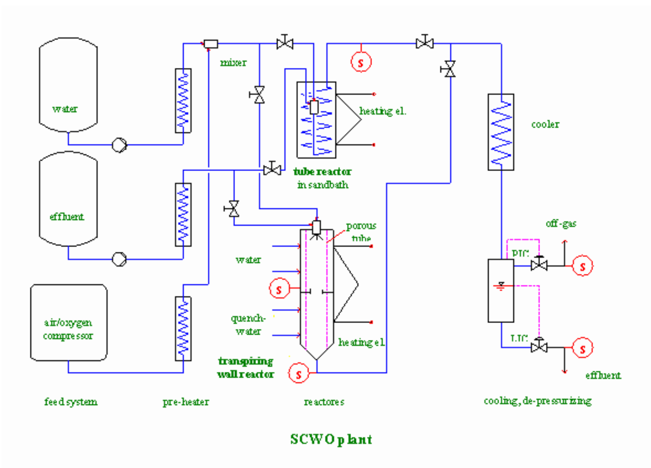
We operates a SCWO plant using two types of continuous reactors:

- SCWO pipe reactor (PR)
- SCWO transpiring wall reactor (TWR)
- Complete SCWO plant

Design parameter for the SCWO plant:

Pipe reactor (PR)	
Pressure	32 MPa
Temperature	630 C
Feed flow rate (max. 2 % TOC)	20 kg/h
Air flow rate	20 kg/h
Length	15 m
i.d./o.d.	8 mm
Transpiring wall reactor (TWR)	
Pressure	32 MPa
Temperature (at outer wall)	630 °C
Feed flow rate (max. 20 % TOC)	20 kg/h
Air flow rate	50 kg/h
Transpiring water flow rate	40 kg/h
Quench water flow rate	60 kg/h
Length	0.95 m
I.d., outer pipe	80 mm
I.d., inner pipe	60 mm
Porosity of inner pipe	30 µm





Typical operation conditions for the PR and TWR:

Parameter	PR	Unit	TWR
Pressure	26	MPa	26
Temperature	600	°C	>700
Waste or organic feed conc.	1	wt%	30
Waste or organic feed rate	5	kg/h	10
Air feed	10	kg/h	40
Stoichiometric excess	200	%	200
Residence time	30	s	120
Flow velocity	1	m/s	0.02

Experimental work

SCWO of model substances using the PR

The oxidation of the model substances ethanol, toluene, and phenol was investigated at 26 MPa (organic feed 0.25 kg/h, water feed 10kg/h, flow velocity 0.4-1.5 m/s, residence time 10-35 s, Reynolds number 17000-33000). Experiments were performed between 400 °C and 550 °C with three different air feed rates.

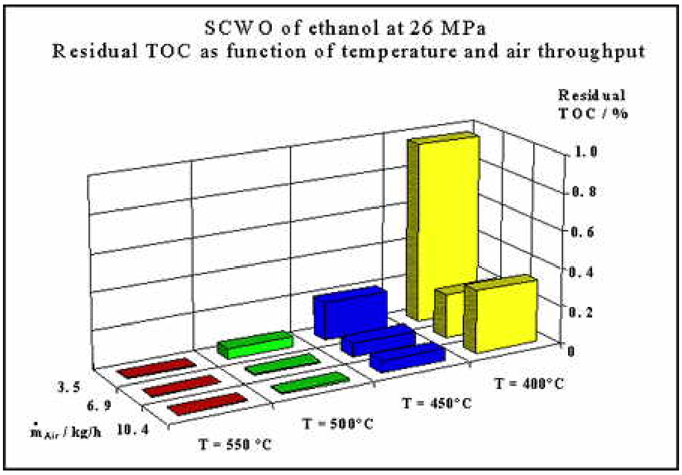


Figure 2

The residual TOC decreases from 1 % to 0.01 % with increasing temperature and air (oxygen) supply (A). Similar results were obtained for toluene..

SCWO with salt loading (PR)

Experiments with a 0.8 %wt aqueous solution of Na_2SO_4 at 26 MPa and temperatures above 400 °C with the tube reactor. Conductivity measures showed at supercritical conditions all of the salt precipitated in the reactor - around 150 g of Na_2SO_4.

SCWO of real waste waters (PR and TWR)

The results and conditions of SCWO of real wastewaters from different industrial branches are summarized in the table. Both, PR and TWR was used.

Origin	Feed-TOC/ppm	Conversion/% (TOC)	Temperature/°C	Salts/ +/-	Solids/ +/-
Pharmaceutical industry	1000 7000 20000	86.00 83.00 97.00	450 410 550	++ ++ +++	- - -
Chemical industry	23000 4500	99.99 99.98	550 550	- -	- -
Paper mill (sludges)	2000 2000 11000	98.00 99.00 97.00	450 500 500	+ + +	+ + +
Sewage plant	1000 630 5400	85.00 98.00 99.80	500 550 550	+ + +	+ + ++
Polymer producer	128000 193000 235000	99.99 99.99 99.98	710 860 760	++ ++ ++	+++ +++ +++

Conversion is almost complete at suited reaction parameters, e.g. above 550 °C. At high salt concentrations plugging of the PR might occur. This blockage can be washed out. A better solution is making use of the TWR concept, which can avoid plugging and corrosion.

This TWR concept is seen as the most promising waste treatment solution for industrial effluents containing salts and solids.

The following photographs show effluent samples before and after SCWO treatment from paper mill and polymer effluents. Almost complete conversion of the hazardous organic compounds has been achieved.

Only salts and solids, insoluble in water, remained.

SCWO of paper mill effluents

SCWO of polymer effluents

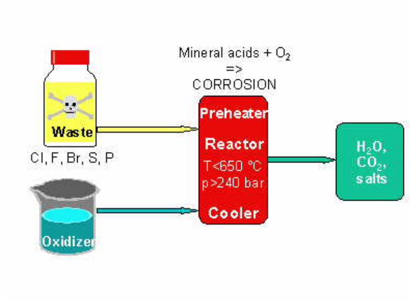
Corrosion in Supercritical Water

Together with plugging caused by solids or salts, corrosion is the obstacle for an industrial application in broad, particularly when using the PR. To overcome this obstacle, TWR is under investigation and results so far are very promising.

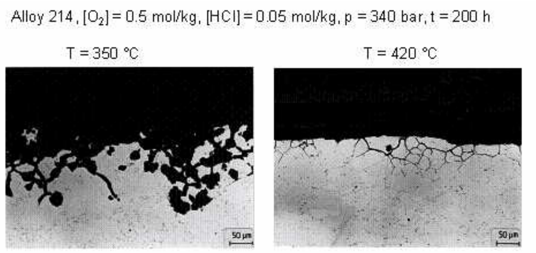
- Corrosion prevention for SCWO-reactors
- Quantification of corrosion
- Clarification of corrosion mechanisms

SCWO Process

Corrosion in hot high-pressure water in the presence of mineral acids is one of the challenges for the SCWO-process. Because of the high oxygen excess the chemical surrounding is strongly oxidizing.



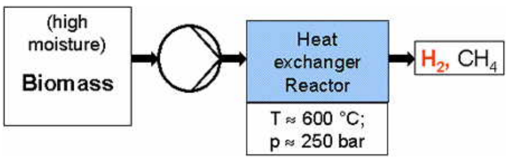
SCWO-process.



Under supercritical conditions (right) corrosion occurs less distinctive than under undercritical conditions (left).

SCWG Process

The gasification of organic matter in supercritical water oxidizes carbon to CO_2 and besides methane mainly hydrogen is formed (Figure 3). Thus, the chemical surrounding is considerably more complex compared to the SCWO-process. Phenomena like loss of ductility of the reactor materials play an important role.



Advantages of SCWO technology

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