

A TRANSPIRING WALL REACTOR WITH AN INNER ALUMINA POROUS TUBE FOR SUPERCRITICAL WATER OXIDATION : EXPERIMENTAL RESULTS ON CORROSIVE SOLVENTS DESTRUCTION

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Supercritical water oxidation ($P > 22.1$ MPa and $T > 374^\circ\text{C}$) proves to be very effective to treat hazardous organic wastes : high destruction rates, rapidity and confining of reaction, no NO_x in gaseous effluent. But its development is limited by two major problems, corrosion and salt precipitation.

Transpiring wall reactors are emerging to cope with these limitations. They consist of a concentric double wall reactor in which the corrosive reactants are maintained inside a porous inner shell which can withstand to aggressive media, whereas pressure resistance is ensured by a stainless steel external vessel. A water flow through this porous inner shell prevents sticky solid particles from depositing on the wall. Although the geometry of this kind of reactors is rather complex, they may be well suited to handle organic effluents generated by nuclear activities. That is the reason why the CEA develops a transpiring wall reactor in which the inner porous shell is made of pure α -alumina. This material is reported to be among the most resistant ones against highly corrosive media generated by supercritical water oxidation.

The reactor proved not to be efficient to oxidise salty effluents. But experimental results concerning the oxidation of the mixture dodecane/tributylphosphate, used as a model effluent, confirmed the ability of the reactor to treat corrosive wastes. High destruction rates were actually encountered. Phosphorus was totally recovered in the aqueous effluent as phosphoric acid. No corrosion was noticed in the reactor except upstream in the waste injector. The inner alumina tube shielded the pressure vessel from corrosion as it was expected. The assumed sensibility of alumina to thermal gradients was not a limiting factor of the reactor operation.

INTRODUCTION

Supercritical water ($P > 22.1$ MPa and $T > 374^\circ\text{C}$) supplies a good medium to destroy organic compounds. Under such conditions, organics and oxygen are actually completely miscible in water and the exothermic reaction yields CO_2 , H_2O , N_2 and mineral acids. The SCWO process presents several advantages : oxidation is confined allowing effluent control, reaction is rapid with high destruction rates. The outlet effluents are said to be clean, no NO_x is detected in the gas. However, the process presents two main drawbacks, salt precipitation [1] and corrosion [2,3]. Salts are actually not soluble in supercritical water and the reacting medium is very aggressive with a large excess of oxidant and the presence of acids as by-products. New technologies of reactors aim at overcoming these drawbacks. Double-wall reactors are emerging to cope with corrosion [4-6] and transpiring wall reactors [7,8] combine this design with a porous inner wall to minimise both salt precipitation and corrosion. Among these promising reactors, we find the reactor developed at the CEA. Its main characteristic is

the nature of the inner wall made of pure α -alumina. This material has been chosen because of its corrosion resistance in presence of chloride in SCWO process [9,10].

This article deals with the performances of this reactor while treating salty or corrosive compounds. Sodium sulphate and the mixture dodecane/tributylphosphate were chosen as models respectively of salts and aggressive species.

I – MATERIALS AND METHODS

The reactor design

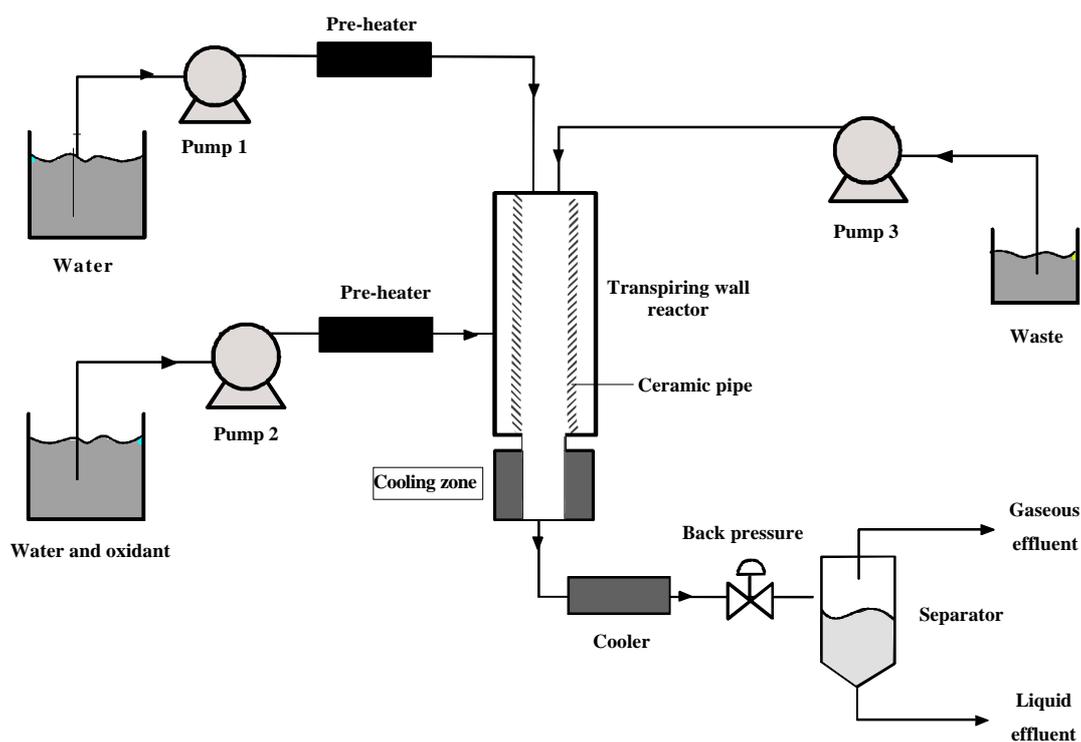


Figure 1 : Experimental set-up of the SCWO reactor

This reactor (Figure 1) segregates corrosion stress from pressure stress. On one hand, a stainless steel shell, with an internal diameter of 24 mm and a volume of 0.39 dm³, provides pressure resistance. On the other hand, an inner ceramic tube, with an internal diameter of 15 mm and an external diameter of 19 mm, confines corrosive compounds. As a consequence, the stainless steel vessel has no contact with the aggressive solutions generally treated by hydrothermal oxidation. Supercritical water transpires through the porous wall supplying pressure balance between both sides of the wall and plays three important roles. First it dilutes corrosive species at the vicinity of the wall and reduces their effect. Secondly it cools the reacting medium where a highly exothermic reaction takes place. Finally it also prevents sticky solids from depositing on the wall. Solid species are driven downstream to a subcritical cooling zone where they are soluble ; cooling is supplied by an external jacket.

A 25 MPa pressure, kept constant with a back pressure valve, is achieved by means of chromatographic pumps 1 and 2, which can each one deliver 50 g.mn⁻¹. Pump 2 aims at feeding water and oxygen peroxide as oxidant, and provides a radial flow through the porous tube. Pump 1 supplies pure water to induce a downward stream in the vertical reactor. The lack of oxidant in this flow allows to avoid a local exothermic reaction at the top of the reactor. Both aqueous flows are heated at 380 °C by two preheaters so as to be in a supercritical state before entering the reacting zone. Reactor is heated at 450 °C with three

cast heaters located at the outer side. Typical conditions downstream the lower cooling zone is 25 MPa and 15°C. An isochratic pump (pump 3) supplies organic waste at the top of the reactor and imposes the inlet weight fraction. Waste is injected by the inlet dip pipe which supplied the feed into the tubular reacting zone defined by the presence of the inner tube.

The liquid effluent is analysed with a Total Organic Carbon analyser from Shimadzu (TOC 5000A). The concentration of sulphate is determined by ionic chromatography from Waters. The composition of the gaseous effluent is analysed online by gas chromatography (VARIAN star 3600 CX).

In the following section, the treatment of sodium sulphate and dodecane/tributylphosphate is considered.

II – Experimental results

1. Sodium sulphate

Sodium sulphate was chosen to simulate the behaviour of salts in the reactor because it was well studied in literature [4,11-12] and it is not the root of corrosion.

Every test (450°C 25 MPa) lead to a rather poor removal of salts. The recovery did not exceed 10 mol% of the introduced salt. As a consequence, salts settled in the reactor and could cause a plug. The pressure sensors allowed to locate this solid deposit at the top of the tubular space defined by the inner porous tube. But the water flow, during the cooling period following an injection, enabled to remove entirely the salt.

These experimental results show that it is difficult to treat salty effluents in the transpiring wall reactor in our configuration. As a matter of fact, we chosen to keep a laminar flow with no added water diluting the output stream. The presence of salts in a reactor can result from, either the composition of the effluent or the neutralisation step of mineral acids, produced during the oxidation. Thus, the treatment of salty effluents in the double wall reactor would require to consider a semi continuous process involving an oxidation period and a removal period. For the concern of compounds which are supposed to yield to mineral acids, it seemed not to be appropriate to neutralise the acids. But it was of most important, at that moment, to verify that corrosion was limited in the reactor.

2. Mixture dodecane/tributylphosphate

Dodecane/tributylphosphate is used in the nuclear reprocessing with a composition of 70/30 vol%. Its oxidation in a SCWO reactor yields to phosphoric acid which is corrosive for the construction material.

The oxidation of dodecane was first investigated because it accounts for 70 vol% of the mixture and it does not produce aggressive compounds. This should allow to verify if the alumina tube could withstand to the exothermic oxidation (1) [13].



Pure dodecane was introduced into the reactor (T=450°C and P=25 MPa) with a mass flow rate noted q_w . The amount of hydrogen peroxide was twice as much as the amount required by the stoichiometry of reaction (1). The axial flow rate of water, q_{axial} , was fixed at 10 g mn^{-1} . The experimental results concerning various inlet weight fractions of dodecane and residence times are gathered in Table 1. The performances of destruction are expressed in

term of destruction ratios, $D = 1 - \frac{\text{TOC}}{\text{TOC}_0}$ (TOC is the total organic carbon measured in liquid effluent and TOC_0 is the value that should be measured if reaction had not occur).

Case	q_{radial} (g mn^{-1})	q_w (g mn^{-1})	$[\text{C}_{12}\text{H}_{26}]_0$ (wt%)	D (%)	$[\text{CO}]_{\text{gas}}$ (mol%)	$[\text{CH}_4]_{\text{gas}}$ (mol%)
1	20	0.38	1.2	96.3	0.75	0.61
2	15	0.3	1.2	98.9	0.56	0.50
3	10	0.24	1.2	99.9	0.15	0.37
4	20	0.58	1.9	99.7	0.43	0.47
5	15	0.53	2.1	99.8	0.01	0.04

Table 1 : Destruction ratios determined during the oxidation of dodecane (P=25 MPa, T=450°C and $q_{\text{axial}}=10 \text{ g mn}^{-1}$)

This table highlights an efficient oxidation of dodecane. The destruction of the waste exceeds 96% with a good quality of gaseous effluent. Moreover the destruction ratio increases with the inlet weight fraction of hydrocarbon and the residence time (reduction of radial flow rate).

These various cases also proved that the inner tube was quite resistant to the exothermicity of reaction. In fact, no damage was noticed after each run. As a consequence, it was possible to oxidise dodecane with an inlet weight fraction up to 2% and this value was not limited by the resistance of the tube, but by the pilot configuration (preheaters efficiency and the concentration of commercial H_2O_2 solutions used).

It was then interesting to study the mixture dodecane/tributylphosphate which causes both thermal problems and corrosive effects. The overall formula of the mixture is $\text{C}_{12}\text{H}_{26.26}\text{O}_{1.04}\text{P}_{0.26}$ and the oxidation by hydrogen peroxide follows equation (2).



Operating conditions remained at 25 MPa, 450°C and an axial flow rate of 10 g mn^{-1} . The excess of hydrogen peroxide was twice as much as the stoichiometry of reaction (2) and, thus, it limited the inlet weight fraction of waste at 2.1%. The experimental results are presented in Table 2.

Case	q_{radial} (g mn^{-1})	q_w (g mn^{-1})	$[\text{waste}]_0$ (%)	D (%)	$[\text{CO}]_{\text{gas}}$ (mol%)	$[\text{CH}_4]_{\text{gas}}$ (mol%)	R_P (%)
6	20	0.36	1.2	98.6	0.09	0.34	105
7	15	0.31	1.2	98	0.48	0.24	106
8	10	0.24	1.2	98.1	0.79	0.39	98
9	15	0.54	2.1	99.8	0.02	0.07	95
10	10	0.43	2.1	99.4	0.12	0.16	106

Table 2 : Analysis of aqueous and liquid effluents for various experimental conditions (P=25 MPa, T=450°C and $q_{\text{axial}}=10 \text{ g mn}^{-1}$)

Table 2 clearly shows that the oxidation of dodecane/tributylphosphate was achieved with high destruction ratios ($D > 98\%$) and a very good quality of the gaseous effluent. The destruction ratio reaches a higher value with an inlet weight fraction of waste of 2.1% than with one of 1.2%. The variation of radial flow rate, which means a variation of the residence time, does not seem to have much influence on the oxidation.

According to equation (2), phosphorus from tributylphosphate should be removed in the liquid effluent as phosphoric acid. This acid was measured out by sodium hydroxide and enabled to calculate a removal criterion of phosphorus, $R_p = \frac{[P](q_{axial} + q_{radial} + q_w)}{[P]_w q_w}$

([P]: concentration of phosphorus element measured out in the liquid effluent, $[P]_w$: concentration of phosphorus element in the waste). This criterion was determined with an accuracy of 7%. Table 1 highlights that the phosphorus from the waste is totally removed in the liquid effluent as phosphoric acid. As a consequence, the behaviour of this acid which is produced during oxidation is quite different from the behaviour of salts.

Moreover, the porous tube did not present any damage and yet, its inner surface was slightly covered by a green layer which was composed of phosphorus, oxygen, iron, chrome and nickel (SEM analysis). It was certainly due to the corrosion of the inlet dip pipe from which the waste is introduced into the reactor. A weight loss of the injector was actually noticed. The green layer proves that the porous tube confines very well the reacting medium inside the tubular space. In fact, no corrosion was detected on the pressure vessel made of stainless steel. The deposit was not at the root of phosphorus accumulation because this element was totally removed as phosphoric acid. It could only disturb the good working of the reactor.

The treatment of corrosive effluents involves an improvement of the waste introduction so as to reduce the corrosion of the inlet dip pipe. Titanium should compose the pipe instead of stainless steel. Titanium [14-16] actually withstands to corrosion while heating. The introduction of water thanks to a fourth pump could also allow to avoid corrosion. This is both supposed to increase the residence time of the waste through the inlet dip pipe and dilute the aggressiveness of corrosive species.

CONCLUSION

The transpiring wall reactor with an inner alumina tube proved not to much efficient to treat salty effluents such as sodium sulphate. Salts actually settled in the reactor and could plug it. It may be also due to a very laminar flow because of small amount of added water. As a consequence, the neutralisation of mineral acids which are produced during oxidation seems to be useless, all the more so since acids do not cause much corrosion. The oxidation of dodecane/tributylphosphate revealed that the inner alumina tube protected the reactor from corrosion. The porous barrier did not undergo any damage. Its assumed sensibility to thermal gradients was not a limiting factor of the reactor operation. The inlet dip pipe remains the only part of the reactor that needs to be improved in order to handle very aggressive compounds.

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