Supercritical water oxidation: from reactors concept to hydrothermal oxidation of nuclear wastes

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Abstract
Within the framework of nuclear industry some organic wastes, mixing of radio elements and organic solvents, are produced and cannot be treated by usual processes especially due to high concentration of chlorinated compounds. Thanks to its former experience in nuclear and high-pressure fields, the CEA-Valrho carried out research on the promising process of supercritical water oxidation (SCWO) in order to treat chlorinated high level contaminated wastes.
The SCWO process has two well-known limitations, which hinder large industrial development in the case of the destruction of a waste, which is not purely organic: corrosion and salt plugging. Several generation of possible reactors have been designed in order to manage these significant drawbacks. This presentation is an overview of the strategy and the methodology that we carried out to obtain a final industrial process, applied to nuclear wastes management. It also enhances the Hydrothermal Oxidation of hazardous wastes containing chlorines and high concentrated mineral salts.

INTRODUCTION

Wastes management is nowadays a topic of most interest. Hazardous wastes, such as toxic compounds or radioactive organic compounds produced by nuclear industries, cannot be destroyed by classical biological or thermal treatments. Thus, new concepts, which are harmless for human being and its environment, must be developed. Supercritical water oxidation process (SCWO), which involves the destruction of organic compounds in supercritical water ($P>22.1$ MPa and $T>647$ K), seems to be a good alternative technique to dispose of those dangerous wastes. The SCWO advantages are linked to the special physical properties of water under supercritical conditions. The low values of density, dielectric constant and ionic product actually induce a non-polar solvent behavior of water. As a consequence, organics [1] and oxygen [2,3] are completely miscible with water and form a single phase. Thanks to this monophase system and the high diffusivity of supercritical water, it is possible to carry out rapid reactions and achieve high destruction rates. Moreover, oxidation is confined which allows effluent control. Hydrocarbons are completely oxidized with formation of CO_2 and H_2O. Nitrogen present in the organic compound forms molecular nitrogen N_2 and small amounts of N_2O [4], so that no pollutants such as NOx are encountered in the gaseous effluent. The heteroatoms such as chlorine, phosphorus or sulfur yield mineral acids, HCl, H_3PO_4 and H_2SO_4, respectively. These acids with the oxidant create such aggressive environments that any material suffers from corrosion attack [5]. This phenomenon is enhanced in the presence of halogenated compounds. In order to prevent the reactor from corrosion, alkalis are usually added as neutralization reagent. This leads to the formation of inorganic salts. On the one hand, inorganic salts are highly soluble in water under ambient pressure and temperature, on the other hand, they are insoluble [6] under

supercritical conditions because of the low density and the small dielectric constant of water. As a result, salts present in the waste or formed during the reaction, precipitate and can cause the reactor fouling. Corrosion and salt precipitation are the two main limitations of SCWO process. They have to be overcome in order to extend the SCWO applications. So, for new reactors, they have to be well suited to treat very hazardous wastes from nuclear activities for instance. That is the reason why the Nuclear Energy Division of the CEA has been studying for years several kinds of possible reactor.

The research conducted in the nuclear facilities of the French atomic commission (CEA) tends to produce small amounts of contaminated solvents, which have to be eliminated. They are mainly made of extractant molecules such as tributyl phosphate (TBP), diluents such as kerosene, which result from the liquid-liquid extraction of spent nuclear fuel reprocessing, but are also technological organic effluents such as halogenated solvents... These organic effluents make a minor volume of the global amount of the contaminated waste, but their efficient management is compelled by the risk they produce : the risk of fire due to the organic matrix of these effluents enhances the risk of dissemination of the radioactivity which has to be managed for all the nuclear materials, and particularly for the effluents.

This paper describes the design of three reactors, which was developed at the CEA.

The first one was a very simple reactor developed in the early 1990's and dedicated to the first validation experiments carried out on model solutions [7-11].
The second reactor belongs to the transpiring wall technology in which the common metallic porous inner shell was replaced by an α–alumina one. Two main aspects were considered, the methanol treatment and the water flow modelling [12-13].
Then, we will present here our last results concerning a new reactor, which is adapted to the oxidation of salt containing organic compounds or halogenated species. This reactor has both a double shell preventing the autoclave from corrosion and a stirrer enabling a better mass and heat transfer and preventing particles from sedimentation [14].

I THE INITIAL CONCEPT
The contaminated waste management is an increasing sensitive topic. One of the disposal strategies studied by the Atomic Energy Commission (CEA) is the vitrification of ultimate waste (after sorting and reduction of volumes) and the storage of the vitrified packages. In the case of contaminated organic wastes, a preliminary mineralization step is necessary.
Referring to high-level radioactive wastes, several mineralization techniques were currently studied. Among them, hydrothermal oxidation (HTO), also called supercritical water oxidation (SCWO), uses water at high temperature and high pressure as a reactional medium to carry out complete and fast conversion of organic compounds into water and carbon dioxide.
A test bench was built in 1993 [7] in the CEA Pierrelatte research centre and was validated for the destruction of a model molecule, the dodecane (cf. figure 1). The test bench designed on the base of a tubular coiled reactor, enabled us to treat 4 kg.h^{-1} of water containing 5 to 15 % of organic compounds, in a range of temperatures and pressures from 673 to 873 K and 20 to 60 MPa. Those preliminary studies demenstrated that one could reach dodecane conversion rates up to 99.9% for residence times shorter than one minute. The challenge of this work was to adapt the composition of model wastes in order to approach as much as possible the real wastes exhausted from the fuel cycle. In this case, we pointed out that it was possible to achieve the destruction of dodecane solutions containing 30% in volume of tributylphosphate (TBP) and up to 250 mg.l^{-1} of natural uranium. A particular attention was given on

phosphorous and uranium balance, due to the poor solubility of mineral compounds in supercritical water.
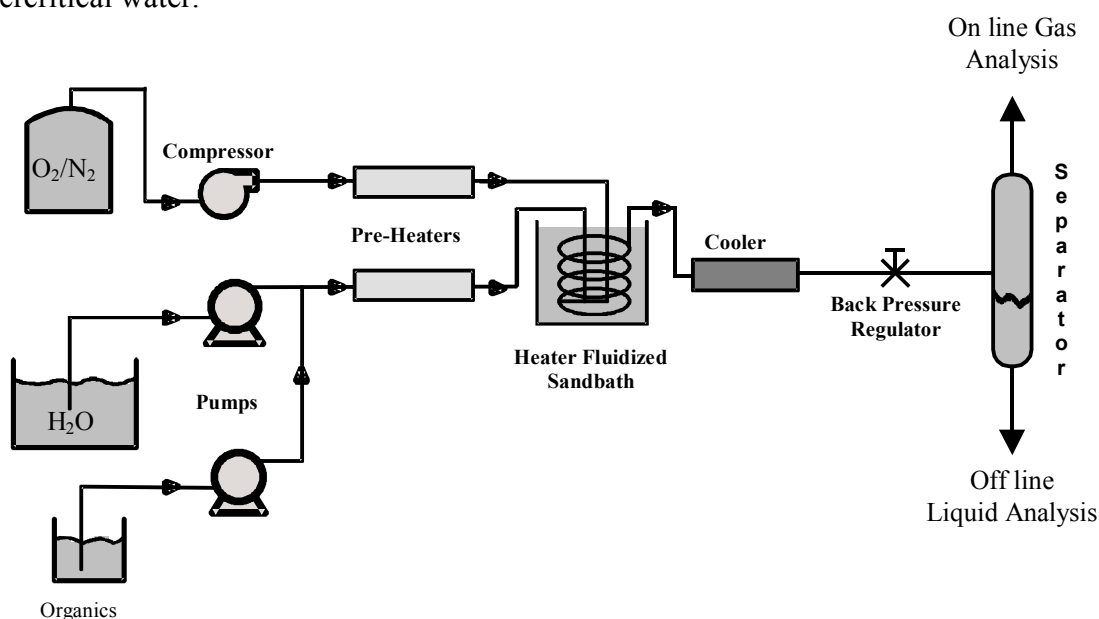

Figure 1: Scheme of the initial SCWO plant (1993).

A test was carried out with a dodecane/TBP mixture containing 250 mg.l^{-1} of natural uranium enable us to process 103,4 mg of uranium in the bench during a three hours experiment. Then the pipes were cleaned separately during 3 hours with nitric acid 5N at 323 K. Previous tests have shown that beyond 3 hours the rate of recovery does not increase significantly. Table 1 shows the results obtained for the uranium balance of this handling, for different bench localization: water output, reactor tube, intermediates tube between reactor and cooler, cooler and filter.

	Water output	Reactor	Intermediates	Cooler	Filter	Overall
U (mg)	***21,90***	28,72	22,15	1,62	0,04	**74,42**

Table 1: Uranium balance.

It appears that only 20 % of uranium are found in the aqueous effluents at output of process. This decrease of direct uranium recovery (before cleaning) when the initial uranium concentration increase may be related to the salt precipitation in the reactor. The missing U mainly precipitated in the zone ranging between the entrance tube reactor and the cooler. The sum of recovered uranium is 75 %. Concerning the fraction that precipitates in the reactor, our tubular geometry was not enable us to avoid the precipitation in this zone.

Some analyzes realized by TRLIF, indicated that uranium was only present on its uranyl UO_2^{2+} form. These very improving results were also limited by the geometry of the simple tubular coiled reactor. So, in 2000, we decided to move to and other more convenient design.

II A TRANSPIRING WALL REACTOR WITH AN INNER ALUMINA POROUS TUBE FOR SCWO

This chapter describes the design of a new reactor, which was developed at the CEA. It belongs to the transpiring wall technology in which the common metallic porous inner shell was replaced by an α-alumina one.

The general set up of the system including the SCWO reactor is shown in Figure 2.
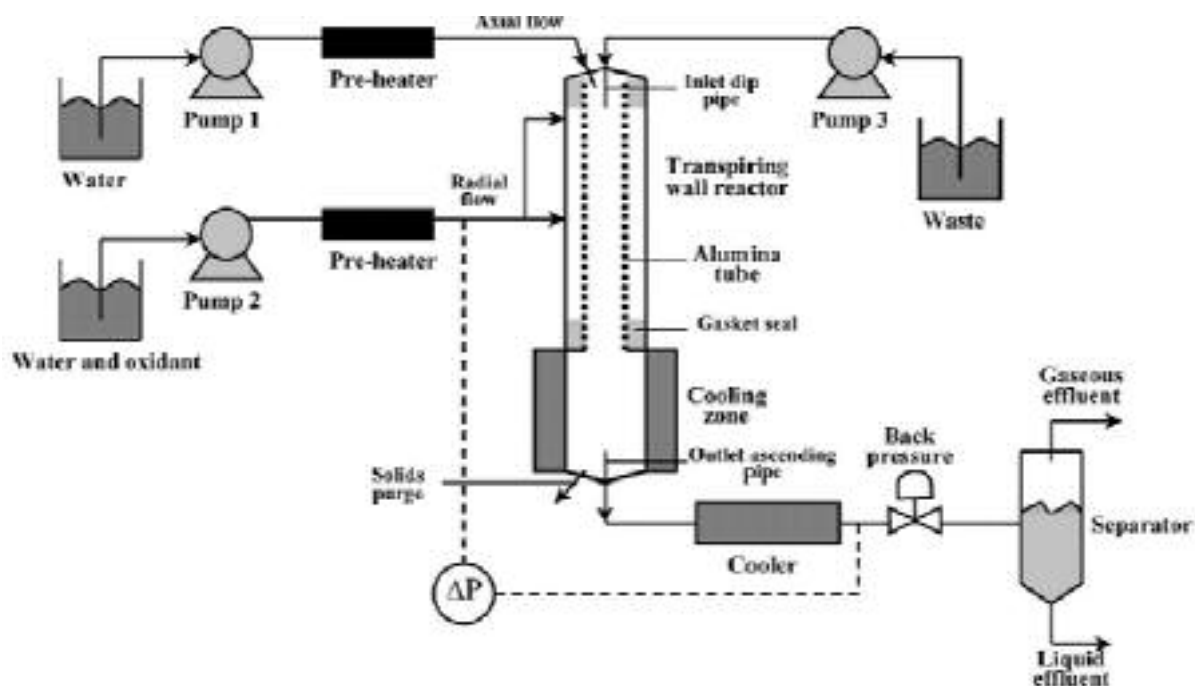
Figure 2: Experimental set up.

The vertical reactor is divided into two main parts. The upper one is the reacting zone where is located the double concentric shell. In this part, water is under supercritical conditions, generally around 25 MPa and 723 K. The external vessel with an inner diameter of 24 mm is made of stainless steel 316. The inner porous barrier is composed of pure α alumina. This material has been chosen because of its corrosion resistance in presence of chloride in SCWO process.

Anyway, this double-wall reactor with an inner porous tube was designed to minimizing salt deposition and corrosion. At 723 K and 25 MPa, the oxidation of methanol, used as a model compound, was achieved with high destruction rates (>99.5%). As the inner ceramic tube is sensitive to thermal gradients, the use of pressure drop measurement as a control method of its integrity was investigated. Liquid and supercritical water flows were then modeled. They both follow the Darcy's law. Thus, the permeability of the porous tube was determined and equal to 7.4×10^{-15} m². This characteristic property remained constant whatever the nature of fluid (liquid or supercritical). The pressure drop measurement was proved to be an *in-situ* control method of the tube integrity even if this control was not possible during an oxidation. The pressure drop measurement caused by liquid (or supercritical) water flow in the porous tube allows to check if the tube is still intact. It avoids the disassembly of the reactor.

However, this attractive concept was limited by the set-up and the thermal gradients applied on the ceramic tube. The risks of a possible breakdown of such reactor lead us to move up to a new design in 2002.

III A STIRRED REACTOR TO TREAT ORGANIC EFFLUENT IN SCWO
In this part, we present there our last results concerning a new reactor, which is adapted to the oxidation of salt containing organic compounds or halogenated species. This reactor has both

a double shell preventing the autoclave from corrosion and a stirrer enabling a better mass and heat transfer and preventing particles from sedimentation.
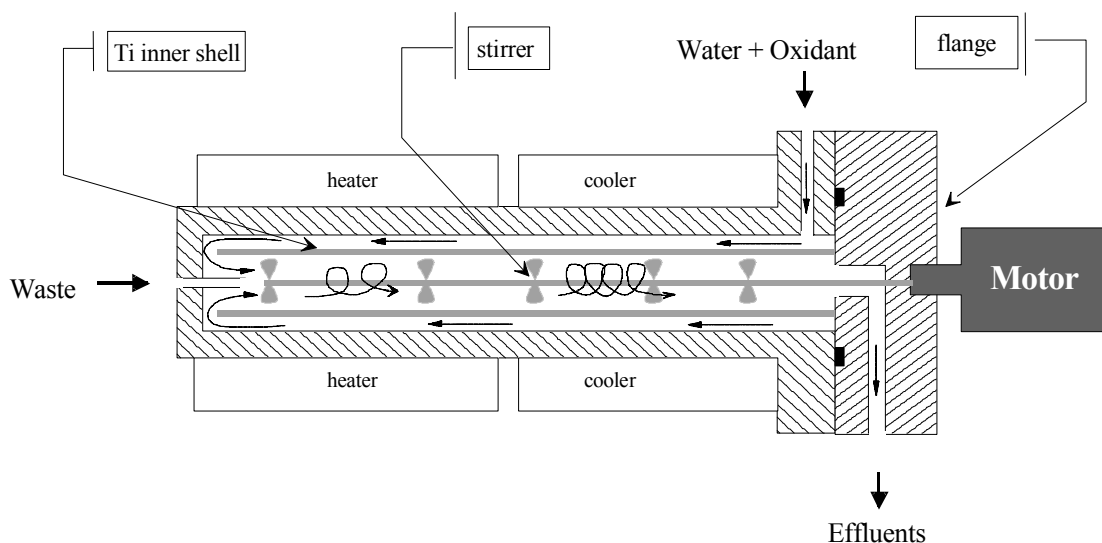

Figure 3 : Detailed scheme of the stirred reactor

The reactor, shown on figure 3, is made of a horizontal high pressure autoclave of 316 stainless steel and of a stirrer and a double shell, both in titanium. It has been developed in order to overcome corrosion and salt-plugging problems when oxidizing complex compounds containing halogens or mineral. Along a half of it, 3 ceramic heaters are disposed. Along the rest of it a cooling shell is placed. On the temperature point of view, two main parts can thus be distinguished, the hot one around the heaters and the cold one around the coolers. The hot section reaches temperatures ranging from 673 to 1273 K because of the combustion reaction, while exiting flow temperature, i.e. in the end of the cold section, stays around 313 K.

The main innovative point of the reactor, compared to the previous double shelled SCWO processes, is the high turbulent flow generated by the stirrer in the core of the reactor. Indeed in the inner part of the tube is placed the titanium stirrer, which is made of a central axis and of blades maintaining a turbulent flow along the whole reactor. Thus the stirrer enhances the heat and mass transfers where the reaction occurs. It also prevents the precipitated salts from decanting in the high temperature supercritical zone and brings them in the cold subcritical zone of the reactor, where they are dissolved again.

We proved the efficiency of this reactor for the destruction of organic wastes containing hetero-atoms, salt or chlorinated species. So, Our interest was focused on model compounds related to the two main problems of SCWO. We chose a tributylphosphate diluted in dodecane and a mixing of chlorinated compounds for the corrosion and the salt plugging. We always performed conversion yields greater than 99,8 % for all treated systems. We resolved the salt-plugging problem thanks to a stirrer, which enable a turbulent flow limiting sedimentation.

Finally, the titanium double shell appears very useful to prevent corrosion of the stainless steel autoclave. Indeed after more than 60 hours running time, no microscopic trace of corrosion can be observed neither on the titanium double shell nor on the autoclave. The minor degradation of the injector in titanium could be easily modified in order to guaranty long runs with chlorinated waste.

CONCLUSION

Several operations of the nuclear fuel cycle (mainly liquid-liquid extraction) involve organic solvents, which are then contaminated and partly degraded by radiation from the fission

products during fuel reprocessing. These solvents must either be partially recycled or eliminated. Research and development studies on nuclear fuel reprocessing also generate various contaminated organic liquids (hydraulic fluids, lubricants, scintillation liquids…), that must be discarded.

Because of its former experience in nuclear and high-pressure fields, the CEA-Valrho has been carried out research on SCWO since 1993, in order to treat chlorinated high level contaminated wastes.

The SCWO process has two well-known limitations (corrosion and salt plugging). Several generations of possible reactors have been designed during more than 10 years in order to manage these significant drawbacks. The strategy and the methodology that we carried out to obtain a final industrial process, applied to nuclear wastes management had to step three different kinds of reactors. The last one presents both a double shell preventing the autoclave from corrosion and a stirrer enabling a better mass and heat transfer and preventing particles from sedimentation. It enhances the Hydrothermal Oxidation of hazardous wastes containing chlorines and high concentrated mineral salts. The development of a nuclear lab-scale facility (Mini-DELOS) and its acceptance by the French safety authorities has led to the definition of the industrially-scaled DELOS process, which operation should start in early 2006, to treat the old remaining organic waste of the CEA.

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