EFFICIENCY OF A STIRRED REACTOR TO TREAT ORGANIC EFFLUENT CONTAINING MINERAL SALT IN SCWO

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1. INTRODUCTION

Mixings of radioelements and organic solvents are commonly produced in the nuclear industry. However, usual processes cannot treat these kinds of waste. Thanks to its former experience in nuclear and high-pressure fields, the CEA-Pierrelatte carried out research on the promising process of Supercritical Water Oxidation (SCWO) in order to treat such high-level contaminated organic 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.

Corrosion is caused by the presence of acids in this highly oxidant medium [1]. As Ni-based alloys, usually used to make high pressure autoclaves, show poor resistance to most acids, corrosion is a real problem for this process.

The well-known reactor plugging is caused by the precipitation of dissolved salts in the supercritical region. Indeed the weak dielectric constant in supercritical water induces a strong weakening of the screening effect of water molecules and thus the precipitation of dissolved inorganic salts. Combined with corrosion this phenomenon leads to plugging of the reactor during the processing of mixtures containing salts, even at high flow velocities

In order to overcome these drawbacks, especially salt sedimentation, various technological innovations are studied like cooled-wall [2], transpiring wall [3], or double-shelled reactors [4].

We will present here our last results concerning a new reactor, which is adapted to the oxidation of salt containing organic compounds. This reactor has both a double shell preventing the autoclave from corrosion and a stirrer enabling a better mass and heat transfer and preventing sedimentation of particles.

Our interest was focused on two model compounds related to the two main problems of SCWO. We chose a mixing of dodecane and tributylphosphate for the corrosion and a mixing of dodecane and an inorganic salt, sodium sulfate, for the salt plugging.

2. MATERIALS AND METHODS

The reactor, shown on figure 1, 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 [5]. 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 400 to 1000°C because of the combustion reaction, while exiting flow temperature, i.e. in the end of the cold section, stays around 40°C.

A 0-1000 bar TESCOM backpressure regulator placed downstream from the reactor regulates pressure. Just in upstream of it two filters of 60 and 7 micron respectively are placed in order to protect the backpressure regulator from solid particles

The main innovative point of the reactor, compared to existing double shelled SCWO processes [6] [7], 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.

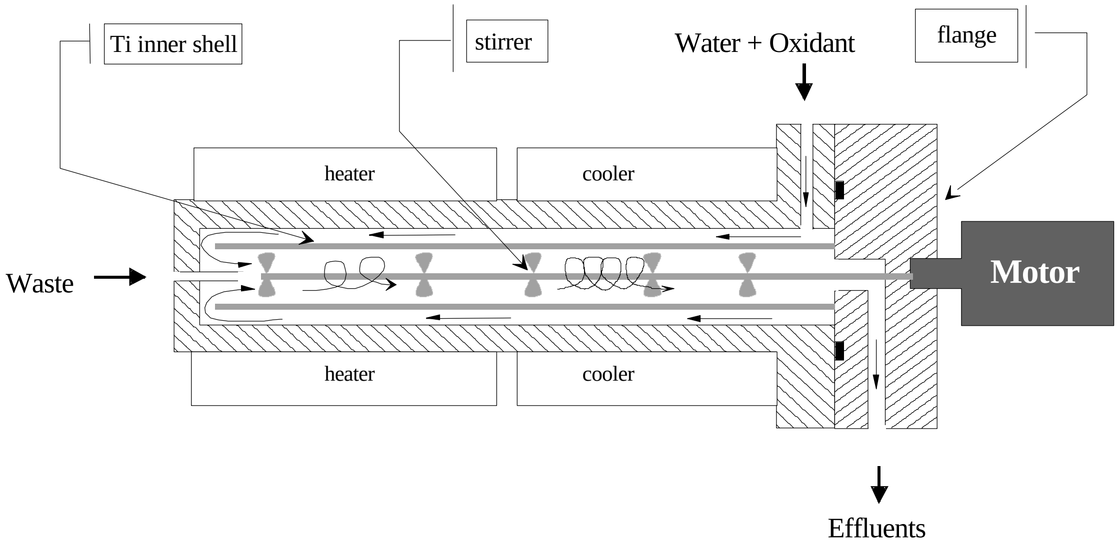

Figure 1: *Detailed scheme of the stirred reactor*

The gaseous stream is analyzed by online gas chromatography thanks to VARIAN 3600 apparatus. We can thus measure formed CO2 concentrations, O2 and N2 amounts in excess and even CO and CH4 concentrations. The liquid phase is analyzed by SHIMADZU Total Organic Carbon Analyzer (TOC) to determine the organic compounds concentration in solution. TOC is given in mg/L.

Results from both phases are gathered and compared to the calculated TOC of the initial organic waste in order to calculate a conversion yield (?), which is therefore similar to a total oxidation efficiency of the process. This yield has been estimated by classical ways, as follows.

$$c = 1 - \frac{\left(\%_{CO} + \%_{CH4}\right) * D_{Exiting\ \ gas\ phase} + \dfrac{TOC}{M_C} * D_{Exiting\ \ liquid\ phase}}{D_{TC\,\mathrm{int}\,roduced}}$$

where TOC is the amount of Total Organic Carbon in the exiting effluent, MC is the molar weight of carbon, $D_{Exiting\ \ liquid\ phase}$ is the molar flow rate of the liquid exiting phase, and $D_{Exiting\ \ gas\ phase}$ the molar flow rate of the gas exiting effluent. Here, we take into account the amount of undesired gases like CO and CH4. Their amount was usually found to be less than 0.02 % and 0.01 % respectively. A previous work [8] clearly showed that in our system no NOX molecules are formed.

3. RESULTS

3.1 Phosphorus containing waste

We focused our attention on a waste containing tributylphosphate (TBP), which is an organic compound commonly found in the nuclear industries and known to corrode, and plug, supercritical water oxidation installations. The waste composition was 70 vol % of dodecane and 30 vol % of TBP which is a classical mixing in nuclear industry. We assume that most of the phosphorus is transformed into mineral phosphoric acid H_3PO_4.

We carried out experiments with a constant pressure of 300 bar, a PM1 flow rate varying between 0.8 and 3.3 kg.h-1, PM2 flow rate fixed to 0.4 kg.h-1, an oxidant stoechiometric between 1.5 and 2.7, and a chosen concentration varying between 1.3 and 5.6 %. The stirring rate was fixed to 400 rpm.

The most relevant step for this study is the probe of the effect of sample concentration on the conversion yield with fixed water flow rates. This is usually one of the most sensible parameters for SCWO. Figure 2 shows the evolution of both total organic carbon (full circles), i.e. the amount of organic carbon still in the effluent, and the conversion yield (hollow squares).

The process is more efficient for concentrations above 4.0 %. Up to this value, the conversion yields is under 99 % but increases with concentration. Above it the conversion yield reaches a plateau where it stays above 99.5 %, even reaching 99.9 % at 5 %. The TOC, which gives information on the real amount of undesired organic carbon in the exiting flow, has a similar behavior and stays under 100 mg/L at concentrations around 4.5.

Moreover, for most experiments, some white powder has been found on the stirrer and on the filters after each run. This powder has been identified as mainly composed of TiP2O7 by X-ray diffraction. This means that some phosphorus atoms are not transformed into phosphoric acid but precipitate in solid form. Combined with corrosion, Ti compounds are thus formed. However neither carbon, chromium, iron nor nickel have been found in significant amount in the white powder, which means that corrosion only occurred in the inner part of the Ti shell and therefore that the stainless steel autoclave is not corroded at all. Moreover no plugging ever occurred for any run. We can notice that the stirrer is really efficient for preventing salt sedimentation and dissolve it in the subcritical zone.

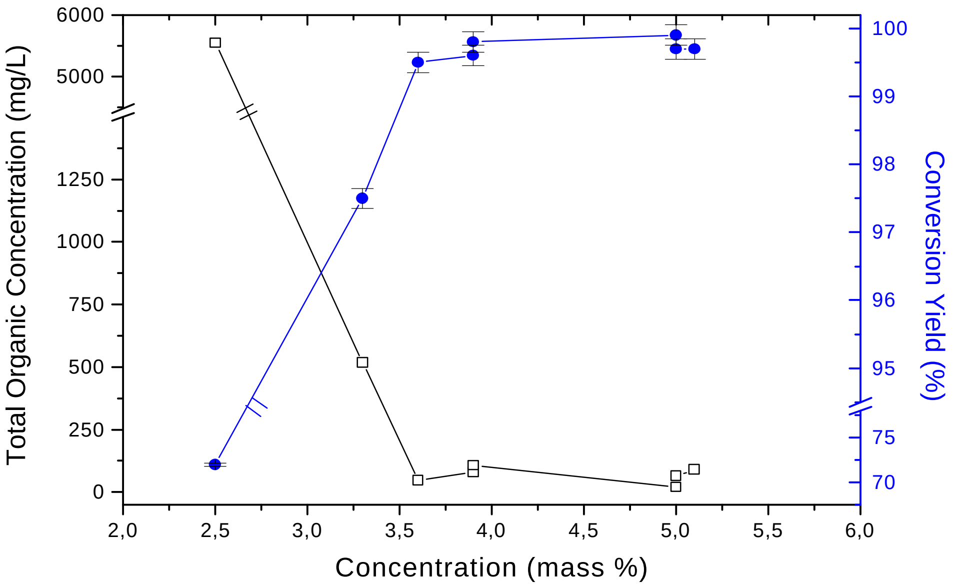

Figure 2: *Influence of sample concentration on conversion yield (full circles) and TOC (hollow squares).*

3.2. Sodium sulfate containing system

We were interested on the effect of inorganic salts in significant concentration (>1 % in the reactor instead of the usual maximum value of 0.1 %). The addition of an organic compound to the salt, n-dodecane, in the reactor aimed to study salt behavior when oxidation reaction occurs, that is in real temperature, pressure and mass transfer conditions. In this way we should be able to check the influence of the salt effect on plugging and corrosion.

The experimental conditions were a pressure of 300 bar, a temperature of 400 °C, an organic waste concentration of 5 % with a stoechiometric coefficient of 2.15 and a total water flow rate of 1.6 kg/h.

The detection of salt amounts in exiting effluents was made thanks to ionic chromatography. SO_4^{2-} ions detection was chosen.

We carried out experiments at various salt concentrations, up to 4 wt % of salts in the reactor, i.e. up to 40 g/L in waste for typical functioning conditions.

No occurrences of plugging neither in the reactor nor around the injection have been noticed. Experiments duration was fixed at 3 hours and never ended because of reactor plugging. After each run, water flow rates were rapidly stopped and the reactor's inside was probed in order to get information on the sedimentation effect without diluting the precipitated salts. Such salts were not found in significant amount on the stirrer, even in the hot reaction zone of the reactor.

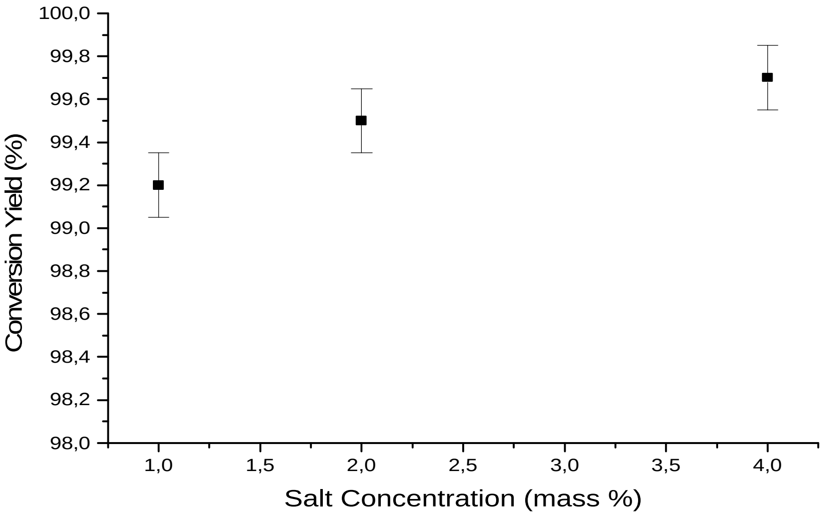

Figure 3: *Conversion yield changes with the concentration of salts in the waste.*

Our typical results are shown on figure 3. The conversion yield stays constantly above 99 % whatever is the salt concentration. Thus, the oxidation efficiency is not changed by the presence of salts in the reactor, within probed concentration range. Ionic chromatography showed that the amount of salts in exiting effluents was found in large amounts, until roughly 100 % of recovery at 4 % of salt. This complete sulfate mass balance proves the efficiency of the reactor.

CONCLUSION

We proved the efficiency of our new reactor for the destruction of organic wastes containing hetero-atoms and salt containing wastes. We performed conversion yields greater than 99,8 % for all treated systems.

For organic molecules concentrations lower than 6 % and inorganic salt concentration (if any) lower than 4 %, 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, even if Ti compounds can be found on the stirrer after taking down. Indeed after lots of running time, no macroscopic trace of corrosion can be observed on the double shell.

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