

FIRST RESULTS OF A CONTINUOUS SCWO PILOT REACTOR FOR THE ELIMITATION OF ORGANIC LIQUID RADIOACTIVE WASTE

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A continuous supercritical water oxidation pilot has been set up in the Atalante hot laboratory facility of the French atomic commission. This pilot which has recently received its administrative license is the final mineralization step of the Mini-DELOS process, which eliminates the contaminated organic liquids produced by the facility research and exploitation. The adaptation of the hydrothermal oxidation process to the nuclear industry constraints has led to technological options, which have been firstly validated in inactive operation, then in active operation. We here summarize some of these results.

INTRODUCTION

The research conducted in the Atalante nuclear facility 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 vacuum pump oils, scintillation liquids, washing liquids... These organic effluents make a minor volume of the global amount of the contaminated waste produced by the Atalante facility, 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.

The only available outlet for the organic effluents produced in France is a dedicated industrial nuclear incinerator (SOCODEI/CENTRACO), which is limited to very low level waste (α activity lower than 50 Bq/g, $\beta\gamma$ activity lower than 20000 Bq/g). Since Atalante produces highly contaminated liquid organics, it has been decided to set-up a process called Mini-DELOS. The first step of this process is a low-pressure evaporator which enables the decontamination of the main input flow, and produces low level contaminated distillates which can be sent to incineration. Since an organic residue, that concentrates the radioactivity still remains, the second step of the process is a continuous mineralization operation using supercritical water oxidation (SCWO). By this means, the organic matrix is converted into CO₂ which is evacuated through the active general ventilation of Atalante, the radioactive content of the initial effluent being transferred into an aqueous matrix which is fully compatible with the aqueous effluents management of the Atalante facility. Figure 1 illustrates the different flows involved in the Mini-DELOS process. In this figure, the term 'solvent' gathers any kind of organic liquids.

A global 90-95% yield of evaporation can be reached, maintaining a decontamination factor greater than 10³ of the contaminated input. Therefore, the SCWO mineralization step can be minimized, since it is only applied to 5-10% of the initial volume. This strategy has been set up because of the availability of the CENTRACO outlet, on the one hand, and on the other

hand because the chosen mineralization process was to be built at a small pilot scale, in order to make the demonstration of feasibility of SCWO in the French nuclear environment.

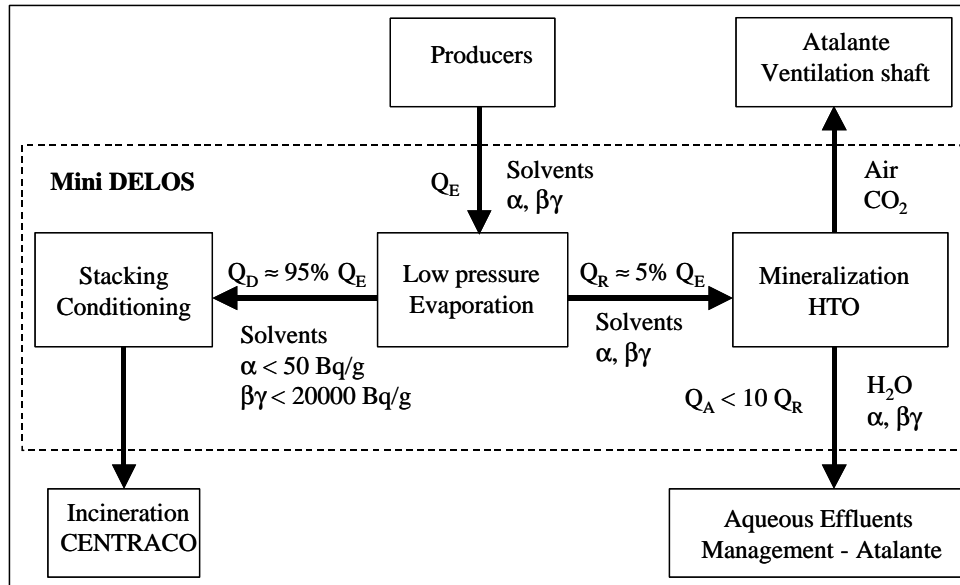


Figure 1: simplified flowsheet of the Mini-DELOS process

In 1998, when the decision was taken to start the development of this SCWO pilot [1], the CEA had gathered most of the needed experience through inactive experiments on the HTO process, applied to solvent models of interest such as dodecane [2] and TBP [3]. Those studies had led to determine the general operating conditions of 30 MPa and 500°C with a residence time greater than 20 s, that lead to a conversion yield of the organic matrix into CO₂ greater than a 99.95% value. The next step to be achieved was to adapt the process to the constraints of the spent nuclear fuel reprocessing industry and research.

The only known analogy is given by Worl et al., who published in 2000 [4] their first active results of a hydrothermal processing of transuranic combustible material which is only a basic set-up in a plutonium glovebox.

I. MATERIAL AND METHODS

A. General principles of radioactive contamination confinement

The contamination management in the nuclear facilities relies on two main principles : the static confinement, and the dynamic confinement. The static confinement is obtained by keeping the nuclear material in an airtight enclosure. A typical air leaking rate of a standard glovebox is 10⁻² h⁻¹. The dynamic confinement is obtained by continuously venting the enclosure and regulating its inner pressure to a value lower than the atmospheric environment one. The relative pressure of a standard glovebox is around -400 Pa. When any kind of leakage occurs the confinement of the nuclear material can be kept by the air entry into the enclosure. The atmospheric renewal rate of the enclosure is typically 10 h⁻¹. The air is extracted through a double very high efficiency filter stage into the facility ventilation, which then releases it at the ventilation shaft after another high efficiency filtration stage.

B. General design of the unit

The SCWO unit is a continuous one. It has been designed to be inserted in an existing standard 1 m³ glovebox of Atalante. A schematic flowsheet of the SCWO process is given on Figure 2.

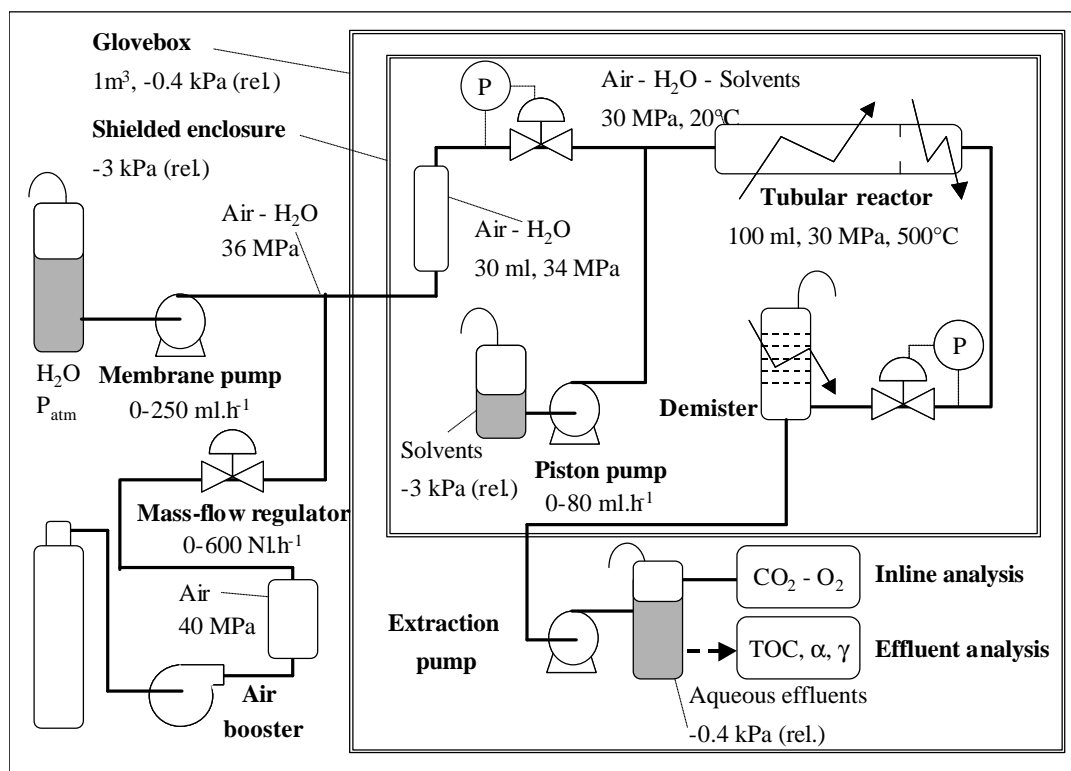


Figure 2 : simplified flowsheet of the SCWO glovebox

Because of the dynamic confinement, the main risk which has to be managed is the explosion one, due to the incidental rupture of the pressurised vessel. All the pressurised parts of the process, which are located in this glovebox are inserted into a shielded enclosure. This enclosure is continuously under-pressurised at a relative pressure of -3000 Pa compared to the glovebox : it protects the alpha enclosure from incidental parts projections and makes it possible that the shielded enclosure and the glovebox remain under-pressurised even when the reactor incidentally explodes. In case of a default detection or an operator decision, the automation can instantaneously purge the reactor in the shielded enclosure by opening a normally opened valve connected to the reactor : the glovebox always remains unaffected.

The unit uses air as oxidant and distilled water as the reaction medium. Both flows are inactive and are produced outside the glovebox. They are injected in the reactor after having been depressed through a backpressure regulator which compels the injection pressure to be at least 3 MPa greater than the reactor operating pressure. The contaminated solvents are directly injected into the reactor by a $0-80$ ml.h⁻¹ piston pump. The reaction tube is a simple horizontal 100 ml tube (17.5 mm i.d.), divided into three zones : a pre-heating zone where the cold organic-water-air mixture is injected, a heating zone, and a down-cooling one. The pre-heating and heating zone are independently regulated. At the down-cooler end, the tube is closed by a simple plug with a viton seal, which makes it possible to easily access the inner of the reactor, and equip this volume with any kind of device, such as baffles or rashig rings, or expose material samples in the reacting flow. The strong temperature transitions, where salt precipitation is generally observed [2] happen in a continuous large section of the tube which prevents (or delays) the clogging. The SCWO effluents are continuously depressurised through a back pressure regulator. Gas and liquids are separated and extracted from the shielded enclosure. Oxygen and carbon dioxide concentrations in the gaseous effluent are respectively monitored by a Servomex 1155 paramagnetic sensor ($0-100$ % full scale) and a

Vaisala GMT 220 NDIR sensor (0-20% full scale). The organic carbon content (TOC) of samples of the contaminated aqueous effluent is measured by means of a Shimadzu TOC-5000 analyser, which has been adapted to a dedicated analytical glovebox. The radioactivity of the organic input and aqueous effluents is measured by conventional radiological means.

II. RESULTS AND DISCUSSION

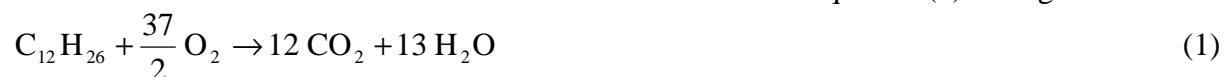
The Mini-DELOS process has been set-up since the end of 1998. Since no available active demonstration of the SCWO process could be found at that moment, the safety demonstration in the french atomic industry constraints took much time and efforts. The complete construction of the pilot and the instruction of the safety analysis by the CEA and then the french atomic nuclear regulatory administration took more than 3 years. The administrative license for this installation was obtained at the beginning of 2002.

The qualification of the process was achieved on two major solvents which have to be treated in Mini-DELOS : dodecane and trilaurylamine (TLA). But, due to the operating procedure of the evaporator of Mini-DELOS, the first contaminated solvent volume that was treated with HTO has been a TBP/TLA residue of the evaporator resulting from the evaporation of U/Pu spent contaminated TBP/TPH .

A. Qualification results

The initial design of the reactor aimed to achieve the total mineralization of 10 g.h^{-1} of pure dodecane, with an excess of oxygen, and a dilution of 10% in the water. Because the design residence time at 30 MPa and 500°C was about 5 min, we tried to observe the limitations of the apparatus in terms of organic flow rate treatment, for the dodecane model solvent. For each air ($200\text{-}550 \text{ Nl.h}^{-1}$), water (120 and 240 g/h) and dodecane ($0\text{-}40 \text{ ml.h}^{-1}$) flowrate, a steady state of the process can be observed by real-time monitoring, through CO_2 and O_2 concentrations in the gaseous effluent and the electrical power calculated by the regulators which is applied to the pre-heater and heater. No meaning difference can be observed between mid (120 g.h^{-1}) and high (240 g.h^{-1}) water flowrates, and even when the remaining O_2 in the effluent is lower than 8 %, meaning that the stoichiometric excess of O_2 is lower than 1, the trend remains unchanged.

The steady-state CO_2 production and O_2 consumption can then be calculated and plotted versus the theoretical values as obtained from the combustion equation (1) on Figure 3.



On the same figure, the energy balance is plotted versus the dodecane flowrate. This energy balance is the difference between the enthalpy variation of the air-water flow during a 30 MPa isobaric heating from 20°C up to 500°C and the steady-state value of the applied electric power to the pre-heater and heater of the reactor.

The calculated O_2 consumption and CO_2 production respectively reach 98% and 83 % of the theoretical ones. The O_2 excess exhibited no influence on these results. The variations around the general tendency are explained by the reproducibility and deviation of the gas sampling system. The steady state heating power is strongly correlated to the dodecane flowrate. Thanks to the efficient thermal insulation of the reactor (around 190 W at 500°C), the fluctuations of heating demand can be observed, and the slope of the correlation line gives a value of 6.16 W.h/ml (i.e. 30 kJ.g^{-1}), which 30% under-estimates the combustion enthalpy of dodecane at 30 MPa and 500°C that can be found in the litterature (i.e. 42 kJ/g , see for example HSC Chemistry 4.0, Outokumpu). This is mainly due to the fact that we consider

that the effluents temperature remains unchanged while entering the down-cooler : this approximation, that was experimentally checked for smaller organic flowrates (0-10 g.h⁻¹), is not precise enough for larger flowrates.

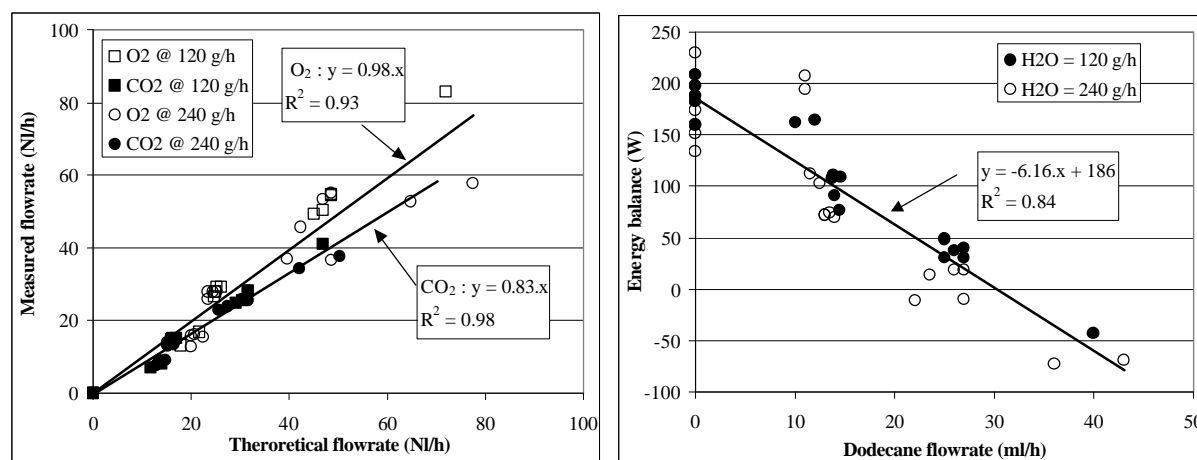


Figure 3 : steady state CO₂ and O₂ outlet concentrations (left) and energy balance (right).

This inline measurements, although they are relatively precise, are not used to prove the efficient combustion of the initial input. For this goal, the TOC measurements of the aqueous effluents are performed. The results are given on Figure 4.

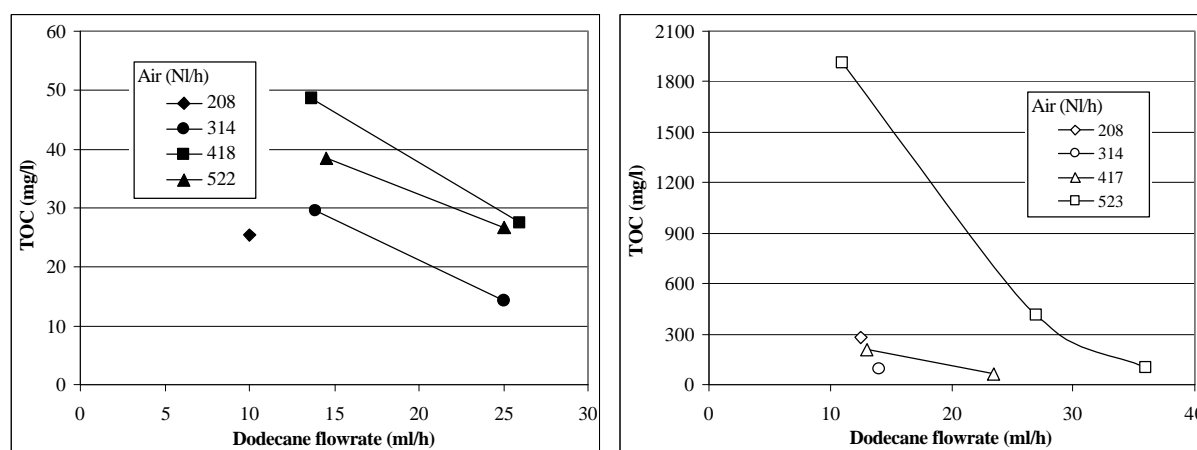


Figure 4 : steady state TOC measurements on the aqueous effluent at 120 g.h⁻¹ water (left) and 240 g.h⁻¹ (right).

This results show that at given air and water flowrates, an increase in the dodecane flowrate enhances the combustion. At a moderate water flowrate the effluent TOC values always remains lower than 50 ppm. At a maximal water flowrate, this value can drastically increase ; but except for the worst case the combustion yield, based on the TOC abatement, is always better than 99.1 %. In the best conditions, it reaches a 99.99 % value.

B. First treatment of contaminated TBP/TLA

The operating conditions for the treatment of the alpha contaminated TBP/TLA residue were 30 MPa, 500°C with the following flowrates : 200 Nl/h (air), 120 g/h (water) and 10 g/h (solvent). The runs (1-12) correspond to the daily treatment of the residue. When the CO₂-O₂-thermal steady state is reached, the aqueous effluents are sampled, for alpha activity, TOC and PO₄ determination, which results are given on Figure 5.

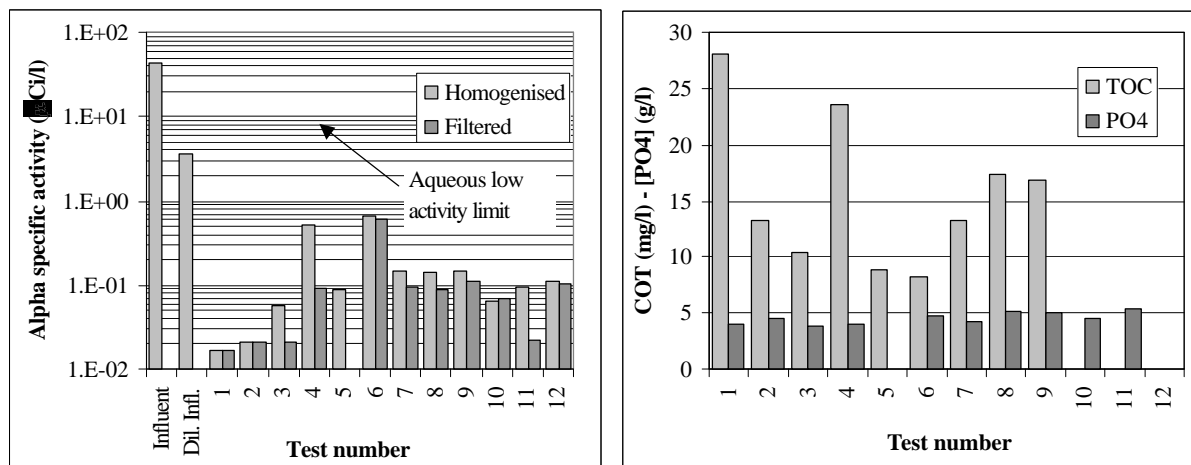


Figure 5 : tests results for the treatment of alpha contaminated TBP/TLA – alpha specific activity, TOC and PO₄ concentration of the aqueous effluents.

The TOC values are lower than 30 mg/l and PO₄ concentrations remain roughly constant around 4-5 g/l and are in good agreement with the total P determination (not figured), but the total P determination of the organic influent has to be carried out to lead to the P balance. The alpha activity, which was determined on homogenised and 0.22 µm filtered samples is always 10 times smaller than the theoretical value, which can be estimated by dilution (Dil. Infl.) of the initial influent activity (Influent). The filtration exhibits no particular effect, although small deposits could be observed on the sample tubes. Further investigations have to be carried out. The effluent activity increased during the first active experiments, but after several runs it reached a stable value, which could make it possible to send the aqueous effluents to the low activity output of the Atalante facility.

CONCLUSION

A SCWO process has been successfully integrated into a contaminated solvents treatment process called Mini-DELOS. The first results of the mineralization of contaminated TBP/TLA confirm the high CO₂ conversion yields of the organic matrix obtained during the qualification tests. The organic effluents which are currently treated are contaminated with alpha emitting radioisotopes, which make it difficult to set up the contamination balance, due to the available methodologies. The foreseen organic effluents will also contain fission products. We are currently developing a titanium liner for the SCWO process in order to treat mixed halogenated and contaminated solvents. The design options exhibit several degrees of freedom that will be used for the future scale-up of the pilot.

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