



DEVELOPING ALTERNATIVE OXIDATION PROCESSES FOR THE TREATMENT OF ORGANIC RADIOACTIVE WASTE

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Abstract

An electrogenerated silver (II) mediated oxidation process is currently under development in the *Atalante* facility of the French Atomic Energy Commission, as an operation of the DELOS unit, with the aim to mineralize α -contaminated solvents with respect to the principles of nuclear safety. This process is a wet oxidation one involving a powerful mediator (Ag(II)/Ag(I) : 1.92 V/NHE), but its throughput is mainly limited by technological constraints. Hydrothermal oxidation (HTO) has been investigated and proved by inactive studies as to be a versatile and powerful process, which could help destroying the contaminated solvents (dodecane, TBP, TLA...) produced by the spent nuclear fuel reprocessing research and industry. The current development aims to set up a continuous HTO pilot in a standard glovebox, in order to solve both technological and safety difficulties and to treat small volumes of contaminated solvents. This paper discusses the main results of the silver(II) oxidation and HTO process development works.

Introduction

Several operations of the nuclear fuel cycle 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 solvents that must be discarded.

These effluents combine both fire and contamination hazards, which are critical from a nuclear environmental standpoint. Because of their different chemical natures and properties, no multipurpose process can ever deal with all of them. Incinerators in particular, which provide a satisfactory tradeoff between industrial cost and efficiency in common waste treatment, cannot be used in the nuclear reprocessing environment because of the complexity and cost of the subsequent fly-ash treatment.

The French Atomic Energy Commission (CEA) first developed a technology based on electrochemical oxidation involving a strong oxidizing agent, silver(II). This technology is an outgrowth of a former decontamination process using silver(II) to dissolve plutonium in solid waste. However, silver(II) oxidation of organic solvents is subject to several limitations. An alternative solution is therefore being investigated in the CEA's high-level radioactive research laboratory, *Atalante*, where a small-scale hydrothermal oxidation unit is currently under development. This unit is

a demonstration step and will also be used to treat small problematic volumes of contaminated solvents.

Silver(II) electrolysis

Oxidation with electrogenerated silver(II) occurs at low temperature (20-50°C) under atmospheric pressure in an aqueous medium, and is therefore suitable for use in the nuclear environment. This oxidizing agent is strong enough to perform a complete mineralization of organic compounds, i.e. complete conversion of organic carbon into carbon dioxide.

Silver nitrate (0.5 to 1 mM) is dissolved in nitric acid (4 to 6 M), which forms the anolyte of a two-compartment electrolyzer in which the catholyte is concentrated nitric acid (15 M); the compartments are divided by a silicon nitride separator. The organic compound is added to the anolyte. Ag(I) is oxidized to Ag(II) at the anode surface (where the current intensity is maintained constant), and then homogeneously reacts with the organic compound. TBP, dodecane and TLA have been studied as model waste. The reaction chemistry is relatively complex, and mechanical studies have been performed, showing some effects occurring on the anode surface. A demonstration has been performed on an actual contaminated organic liquid waste sample (diluted Trilaurylamine contacted with spent nuclear fuel, see Fig. 1).

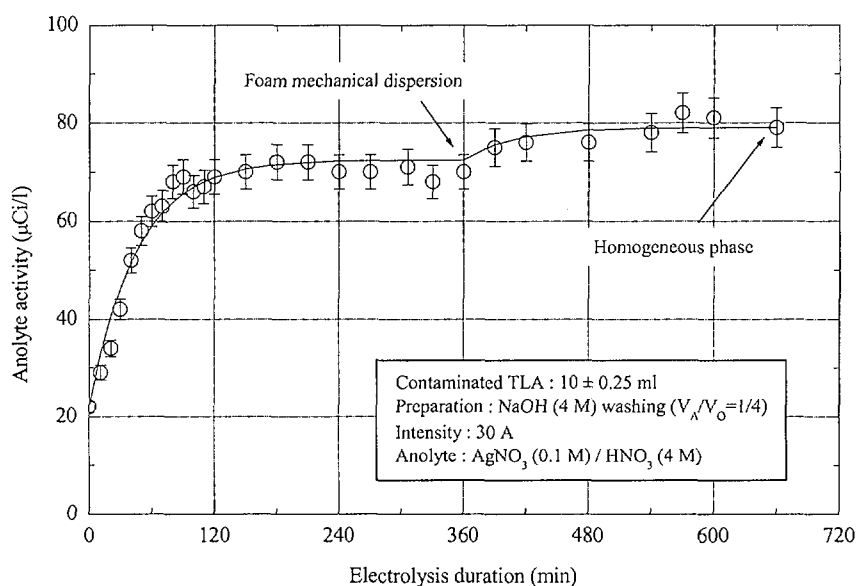


Figure 1 : α activity of the anolyte during the electrolysis of a contaminated solvent sample

A transfer of α activity from the organic phase to the anolyte can be observed. It is strongly correlated to the total mineralization of the organic matrix. This mineralization is also observed during inactive experiments, where the degradation rate is quantified through FTIR analysis of the gases (CO , CO_2), which are extracted from the anolyte by an inert gas flow (Ar). This method enabled us to detect the presence of traces of volatile alkyl nitrates, which are explosive compounds. Moreover, the chemical pathways in the presence of nitric acid can lead to the production of volatile alkyl nitrates, which are explosive compounds. Nevertheless, this risk has been managed by inline thermal cracking.

Although this process has several limitations, one of which being the reaction rate due to the maximum available current (300 A), it has been chosen as the reference one for the design of a treatment unit called DELOS, which is currently under construction. It is the most powerful process involving wet oxidation.

Hydrothermal oxidation (HTO)

Following the studies performed by the CEA at Pierrelatte on the POSCEA inactive bench-scale unit, which demonstrated that hydrothermal oxidation can treat most of the organic wastes produced by nuclear fuel reprocessing, we decided to take a further step by designing and building a 1:10 scale model of POSCEA, compatible with actual contaminated radioactive waste.

POSCEA is based on a tubular design. Water (up to $2 \text{ kg}\cdot\text{h}^{-1}$), oxidant gas (O_2/N_2), and organic waste (up to 10% of the water flowrate) are fed at the inlet of the plug-flow reaction tube, where the HTO conditions are performed ($P > 221 \text{ bars}$, $T > 374^\circ\text{C}$). Since supercritical water dissolves gas and organic compounds into a homogeneous mixture, it enables a total combustion of the organics, which is then not limited by any interfacial transfer. Acetic acid, which is difficult to be oxidized under sub-critical conditions, is completely destroyed under supercritical conditions with a residence time shorter than 1 min. Under this conditions, dodecane (see Fig. 2), TBP, TLA, aromatic and aliphatic solvents are also totally mineralized. On Fig. 2, the destruction yields obtained on POSCEA are calculated using DCO measurements. Further Total Organic Content and Gas Chromatography determinations have shown that the remaining organic traces never exceed 100 ppm (TOC, CH_4 , CO). A temperature profile along the reaction tube (Fig. 3) shows the presence of a combustion flame within the supercritical water medium.

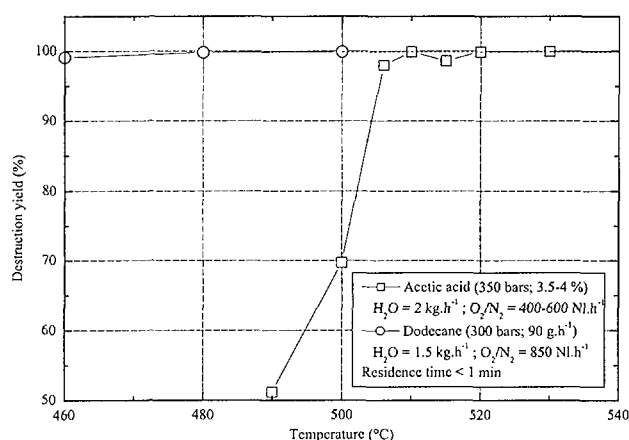


Figure 2 : destruction yields (effluent DCO determination) of acetic acid and dodecane vs. temperature during HTO experiments on POSCEA

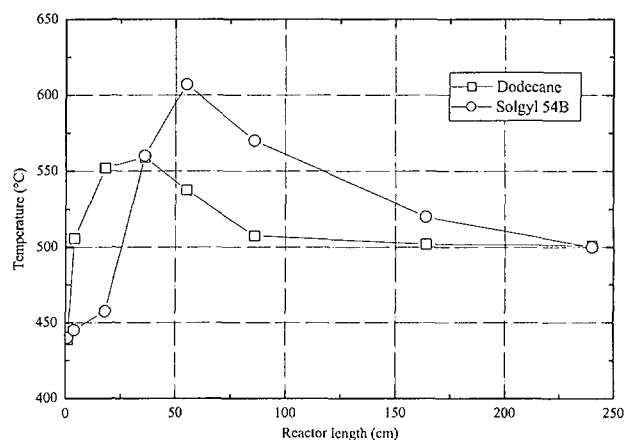


Figure 3 : temperature profiles observed on the tubular reactor of POSCEA during the complete combustion of dodecane and Solgyl 54B (tertiobutylbenzene)

The unit is designed to be inserted in an existing standard glove box (1 m^3) in *Atalante*. We decided to use a continuous reactor, to avoid developing a batch reactor that could not have been scaled up later without major design changes. Using the results obtained on the model wastes of the previous studies performed at Pierrelatte, we established that a 100 ml reaction volume, including a preheating

zone, a reaction zone and a cooling zone, was sufficient to perform a complete reaction on selected compounds with a reaction time of less than 1 minute. The typical flowrates of the pilot under development are 400 ml.h⁻¹ of water, 400 Nl.h⁻¹ of air (used as oxidant), 10 ml.h⁻¹ of organic liquids. The main design principles are given on Fig. 4.

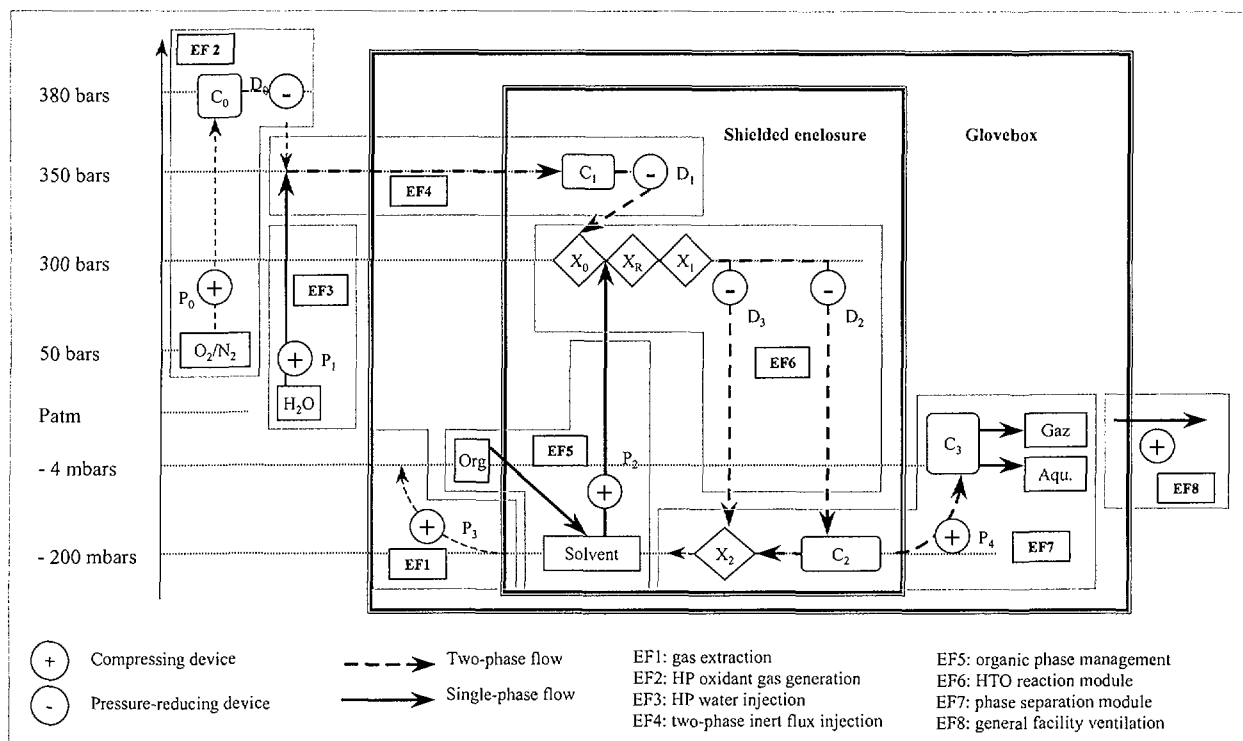


Figure 4 : design principles for the hydrothermal oxidation (HTO) pilot inserted in a glovebox

The major difficulty in designing this unit is to ensure the safety of the process under pressure and temperature, in a confined environment, of a limited volume. Therefore, the parts of the process which are contaminated and under pressure are set up in a shielded enclosure which is inserted in the glovebox. This enclosure enables to guarantee the integrity of the glovebox against incidental volume expansions or parts projections.

Conclusion

Both electrogenerated Ag(II) oxidation and HTO processes are being investigated in order to solve the problem of contaminated organic solvents in *Atalante*. Mediated Ag(II) oxidation is a simple and powerful wet oxidation technique, but with a relatively low processing rate due to technological and chemical limitations. HTO appears to have the flexibility of incinerators, with a reaction time short enough to allow the process to be scaled down and implemented in a confined nuclear enclosure. Our intended demonstration should prove that it can be fully compatible with nuclear operation and will help eliminate part of the present contaminated organic waste.