Incineration of radioactive organic liquid wastes by underwater thermal plasma

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Abstract. This work deals with incineration of radioactive organic liquid wastes using an oxygen thermal plasma jet, submerged under water. The results presented here are focused on incineration of three different wastes: a mixture of tributylphosphate (TBP) and dodecane, a perfluoropolyether oil (PFPE) and trichloroethylene (TCE). To evaluate the plutonium behavior in used TBP/dodecane incineration, zirconium is used as a surrogate of plutonium; the method to enrich TBP/dodecane mixture in zirconium is detailed. Experimental set-up is described. During a trial run, CO2 and CO contents in the exhaust gas are continuously measured; samples, periodically taken from the solution, are analyzed by appropriate chemical methods: contents in total organic carbon (COT), phosphorus, fluoride and nitrates are measured. Condensed residues are characterized by RX diffraction and SEM with EDS. Process efficiency, during tests with a few L/h of separated or mixed wastes, is given by mineralization rate which is better than 99.9 % for feed rate up to 4 L/h. Trapping rate is also better than 99 % for phosphorous as for fluorine and chlorine. Those trials, with long duration, have shown that there is no corrosion problems, also the hydrogen chloride and fluoride have been neutralized by an aqueous solution of potassium carbonate.

1. Introduction
Radioactive organic liquid waste is a particular category of radioactive waste precisely because of their organic nature. Therefore they are systematically separated from other liquid wastes, stored and processed separately. They consist of:
- used solvents, implemented especially in combustible cycle installations. The main solvent is TBP (tributylphosphate) used diluted with a hydrocarbon, typically dodecane. TBP evolves under irradiation, giving rise to degradation products, mono and dibutylphosphates.
- solvents used in decontamination operations. These solvents are often halogenated (trichlorethylene, perchlorethylene, freon, ...).
- lubricating oils of various mechanical devices used in workshops or nuclear installations and which may be contaminated.
- liquids of scintillation.

Several techniques for conditioning organic radioactive waste have been developed like incineration and wet oxidation, but the combustion of solution containing waste produces corrosive products for the process, and leads to off-gas purification problems. Moreover, combustion generates relatively large volumes of radioactive gaseous, liquid and solid wastes. Wet oxidation also generates various undesirable secondary waste byproducts.

Also few works [1] are devoted to submerged quench incineration: combustion takes place in a chamber above a liquid surface, and the products of combustion are introduced through a downcomer into the liquid bath for a rapid quench. It is an effective means to exchange heat and to absorb components of combustion products and inorganic salts while cooling and scrubbing the flue gas.
hydrogen chloride and fluoride are soluble in water and can be easily scrubbed and removed in the form of weak acid and (or) neutralized by an aqueous solution of sodium or potassium hydroxide.

New processes based on plasma technologies [2] appeared and proved their efficiency to decontaminate aqueous effluents: intense UV radiation emission and very high concentrations of radicals allow to mineralize persistent organic pollutants.

Since a few years we are working about a new process of oxidation of organic compounds by an outflow of an oxygen thermal plasma jet into the bulk of a liquid [3, 4]. Under these conditions, the gas-liquid system has an intense turbulence resulting in a rapid degradation of the jet into small sized gaseous inclusions. This ensures high rates of mass transfer processes and has the possibility of transport of dissociated entities to the gas-liquid interface and their subsequent participation in chemical reactions with the liquid phase components. This kind of processes [5-7] have many advantages:

- high temperature but cold reactor in bulk,
- high concentrations of radicals,
- clean reactor without thermal inertia,
- high chemical reaction rates,
- mineral radioactive pollutants may be trapped in the solution.

2. The wastes of interest

2.1. TBP / dodecane

The first aim of this work was to incinerate a mixture of tributylphosphate (TBP)(Sigma Aldrich(SA) ref:158615) and dodecane(SA ref:44030).

TBP is an extraction solvent involved in nuclear fuel reprocessing, and particularly in the Purex process to recover uranium and plutonium from spent fuel. Additionally, it is listed among the highly radioactive liquid wastes which must be mineralized before conditioning. Different kind of processes are around the world under investigation to improve treatment of used TBP/dodecane, such as glidarc [8], steam-assisted pyrolysis system [9], submerged combustion technique [10], pebble bed pyrolysis [11] and a few others. Some remaining problems and the characteristics of this particular waste were an incitement to test our process with it.

To understand the behavior of radioactive elements, especially plutonium, in the process, zirconium was chosen as a surrogate. Nevertheless to enrich TBP/dodecane with zirconium needs a particular method. An 1M TBP/dodecane solution (with 30 % TBP in volume) is contacted in 1 : 1 phase ratio with nitric acid 4M (SA ref:438073) during 30 minutes with intensive agitation. In these conditions, if the initial HNO₃ concentration is 4M, after equilibration, the HNO₃ concentration in organic phase is 0.7 M [12]. Water is simultaneously extracted from aqueous phase : solvent adduct in form of a Lewis acid-base complex is formed :

$$\text{TBP}_{\text{org}} + x \text{HNO}_3_{\text{aq}} + y \text{H}_2\text{O}_{\text{aq}} \rightarrow (\text{TBP(HNO}_3)_{x}(\text{H}_2\text{O})_y)_{\text{org}}$$

$$\text{TBP(HNO}_3)_{1.3}(\text{H}_2\text{O})_{0.6} \text{ and TBP(HNO}_3)_{1.8}(\text{H}_2\text{O})_{0.6} \text{ are proposed in [13].}$$

Then a determined quantity of zirconium carbonate (SA ref:14616) (typically few g of zirconium ) is dissolved in nitric acid 4M. Then this aqueous phase is contacted, in 1 : 1 phase ratio, with the pre-equilibrated organic phase, during 45 minutes with intensive agitation. Zirconium is supposed extracted in the form of di,tri, or tetra nitrate complex : Zr(OH)₂(NO₃)₂(TBP)₂, ZrOH(NO₃)₃(TBP)₂ and Zr(NO₃)₄(TBP)₂ [13]. Taking into account the aqueous phase molarity –4 M-, the distribution coefficient of Zr by TBP 30 % in dodecane may be estimated to 0.144 [13].

The basic principle of the process may be summarized by:

$$\text{TBP} + \text{dodecane} + \text{Zr} + \text{thermal plasma} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{H}_3\text{PO}_4 + \text{Zr}$$

(1)
Carbon is burnt into CO$_2$ which exits in the off-gas, hydrogen to H$_2$O vapor which is immediately condensed inside the solution, phosphorus is presumed trapped inside the solution in the form of H$_3$PO$_4$ since pH is rapidly less than 2. A question remains: is zirconium dissolved in the solution as zirconium nitrate or phosphate, or, if it is condensed, in what species: zirconium oxide or zirconium phosphate?

2.2. Perfluoropolyether oil  
The second aim is to evaluate the efficiency of the process on a very particular waste: a pump oil, which is, unlike TBP/dodecane, non-flammable. It is a perfluoropolyether oil (PFPE). Their thermal stability and oxidation resistance are exceptional, as well as their resistance to fire: they are completely fireproof. They have a very high chemical inertia. These properties justify their use in the transfer pumps for UF6, by example.

The ratio of carbon, oxygen and fluorine in this oil may be approximated in a pseudo formula - C$_2$O$_{1.1}$F$_{4.2}$ - used to strike the mass balance. Besides a pseudo formation enthalpy may be calculated, using bonds energies, giving -536 kJ for a pseudo mole C$_2$O$_{1.1}$F$_{4.2}$. So incineration of this oil may be schematized by:

$$(C_2O_{1.1}F_{4.2})_{liq} + 0.4 \ O_2 + 2.1 \ H_2O_{liq} \rightarrow 2 \ CO_2 + 4.2 \ HF \quad (2)$$

2.3. Trichloroethylene (TCE)  
Trichloroethylene (C$_2$HCl$_3$ or TCE) is also known by a variety of chemical and trade names: Trimar, Trilene ...Due to its effectiveness, non corrosivity, non flammability and ease of recycling, few solvents matched the performance of TCE in cleaning and degreasing.

A wide variety of entities used TCE, including the electronics, defense, chemical, rail, automotive, boat, food processing, textile, and dry-cleaning industries. Although TCE works best on fats, grease, and waxes, it is also a powerful solvent for a large variety of natural and synthetic substances [14].

Moreover, this waste has been heavily used in the nuclear industry. But its separated incineration involves some difficulties in standard processes in particular for certain co-products. Today the production and use of this solvent are prohibited but stocks of spent solvents exist and must be destroyed.

We can simplify the decomposition reaction product in the reactor as:

$$(C_2HCl_3)_{liq} + 1.5 \ O_2 + H_2O_{liq} \rightarrow 2 \ CO_2 + 3 \ HCl_{liq} \quad (3)$$

3. Experimental set-up

3.1. The process  
The process is based on a non-transferred arc torch of an original design producing a plasma jet of oxygen.

The torch, with gas-vortex stabilization of the arc column is made of a tungsten cathode, a copper anode, between both a diaphragm. The cathode tungsten tip is protected by a stream of argon. Oxygen is the main gas, it is injected downstream the diaphragm. The change in diameter inside the nozzle anode creates a zone of the recirculation flow, colder thus more electrically resistive, fixing the anodic spot behind the ledge [15].

The liquid waste is injected, with a peristaltic pump, at the nozzle exit inside the jet; mean enthalpic temperature is about 3500 K. At this temperature the oxidation reactions are fast enough to reach immediately thermodynamic equilibrium.

The plasma torch is disposed vertically to the base of a water-jacket reactor filled with water (see figure 1). At the top, we find a condenser/mist eliminator to trap water, a heat exchanger to cold the gas flow and to decrease the steam partial pressure, a cyclone to trap residual water, then a demister to improve the water balance.
To control the solution temperature, we added a cooling loop which includes a pump and a heat exchanger. To trap any solid particles in the solution, we placed upstream of the heat exchanger, two filters, positioned in parallel.

A tube placed in the axis at the top of the reactor, can take a sample of gas. It crosses a pretreatment device for trapping dust or liquid droplet before reaching the analyzer. The principle of analysis is by infrared absorption which allows to give the gas content of CO and CO₂.

3.2. Operating parameters
The gas flow rates for a typical trial are:
- 30 NL / min of argon at the cathode
- 180 NL / min of oxygen at the anode
- 7 NL / min of argon to inject the waste
- 40 NL / min of oxygen in the stage of dilution.

The current intensity of the arc is 200 A, the tension is ~ 250 V; the thermal efficiency of the torch is about 62 %. Once the arc is established, the reactor and the loop are filled with water ~ 30 liters; the flow-rate in the loop is 2 m³/h; after a few minutes the waste is introduced via a peristaltic pump.

The solution temperature is maintained below 40°C and the off gas temperature after the heat exchanger is about 20°C. Over the course of the trial, samples are taken at the bottom of the reactor for earlier analysis.

At the end of the test, the reactor is evacuated before the arc is switched off.

4. Results
4.1. TBP/dodecane
The simulated waste was prepared with 30% in mass of TBP and the zirconium concentration is estimated to 1.2 g/L. During the trial described here, waste was fed at ~ 1.2 kg/h (1.5 L/h). In other studies, it can reach 2.4 kg/h (3 L/h).

At high temperatures, the oxidation reactions are sufficiently fast so it can be assumed that thermodynamic equilibrium is reached. So a predictive model [16] shows that we find argon, oxygen
in excess and CO\textsubscript{2}; water in excess and phosphoric acid are supposed to be completely condensed in the reactor. Thus the CO\textsubscript{2} content in the outlet gas should be around 11 \%.

The combustion of TBP/dodecane produces 15 kW besides 30 kW effectively delivered by the plasma torch. So a total power of 45 kW is delivered inside only 10 cm\textsuperscript{3}. 6 kW are transferred in the cooling stage, 10 kW in the reactor walls and condenser, the rest is found in the cooling circuit of the loop.

Measurements during waste injection give 11.2 \% for CO\textsubscript{2} and 0.07 \% for CO. The combustion efficiency defined by: \([\text{CO}_2]/(\text{CO}_2+\text{CO})\) is \(\approx 99\%\); pH falls rapidly to below 2.

At the end of the trial, the amount of TOC content in the whole solution was \(\sim 0.2\) g; while 778 g of carbon were introduced: So we can inferred a destruction rate better than 99.9 \%, within measurement accuracy.

The simulated waste introduced contains 36.15 g of phosphorus while the amount of phosphorus content in the final solution is \(\sim 35.97\) g. Thus, the trapping rate of phosphorus is evaluated at 99.5\%, within measurement accuracy. Nitrate content in the solution varies like phosphorus content (figure 2 where nitrate content is given in mg of nitrogen/L). Nitrogen mass balance shows nitrogen loss which may be explained by NO formation in the plasma: NO might escape in the off-gas.

![Figure 2. Phosphorus and nitrogen contents](image)

No zirconium trace in solid residues has been detected by RX diffraction, neither by SEM with EDS. In the liquid phase, we detected by ICP/MS only 0.32 g of Zr, while the Zr introduced mass is estimated at 1.56 g! Besides, analyzes of Zr content, on the one hand in the raw solution and in the other hand in the filtered solution, showed a difference of almost one order of magnitude. We therefore plan to filter the remaining solution and analyze the obtained powder by plasma emission spectrometry. In all instances, further trials must be carried out with a larger amount of Zr and especially we must check the real mass of Zr in the commercial product (zirconium carbonate) whose purity does not exceed 40%.

4.2. PFPE

Waste was fed at \(\sim 3.5\) kg/h (1.8 L/h), 0.350 L are processed during the test run.

The combustion of PFPE produces 8.6 kW besides 31 kW effectively delivered by the plasma torch; so the total power is \(\sim 40\) kW. 3.2 kW are transferred in the cooling stage, 7.4 kW in the reactor walls and condenser, the rest is found in the cooling circuit of the loop.

Supposing complete thermodynamic equilibrium at each step and all the water and fluoride acid condensed inside the reactor, CO\textsubscript{2} content in the off-gas is calculated to be around 7.9 \%. Measurements give 7.6 \% for CO\textsubscript{2} and 0.3 \% for CO: The combustion efficiency is \(\sim 96\%\).

At the end of the trial, the amount of TOC content in the whole solution is measured at about 0.3 g; while 131 g of carbon were introduced: So we can inferred a destruction rate better than 99.75 \%, within measurement accuracy.
The amount of fluorine content in the solution is ~ 411 g while the mass of fluorine introduced was 436 g. Thus, the trapping rate of fluorine is evaluated at 94.1 %, within measurement accuracy.

![Fluorine and TOC contents](image)

**Figure 3.** Fluorine and TOC contents

4.3. TCE

In the case of a highly chlorinated waste, following the Deacon equilibrium

$$2 \text{ HCl} + \frac{1}{2} \text{ O}_2 \rightarrow \text{ Cl}_2 + \text{ H}_2\text{O}$$

(4)

in order to trap the chlorine as HCl condensed in the solution rather than in the form of Cl₂ gas, we must shift the equilibrium in the endothermic direction and increase the partial pressure of water vapor, that we do by re-injecting a fraction of the solution (see figure 5).

Mass rate of the charge is ~ 2.9 kg/h (2 L/h) so 0.5 L are processed during the test run.

The combustion of TCE produces only 2.9 kW besides 31 kW effectively delivered by the plasma torch; so the total power is ~ 34 kW. 7 kW are transferred in the cooling stage, 7.2 kW in the reactor walls and condenser, the rest is found in the cooling circuit of the loop.

CO₂ content in the off-gas is calculated to be around 6.4 %. Measurements give 6.5 % for CO₂ (see figure 4 which highlights the stability of the process under steady injection conditions) and 0.04 % for CO. The combustion efficiency is ~ 99.38%.

![CO₂ evolution during TCE trial](image)

**Figure 4.** CO₂ evolution during TCE trial

At the end of the trial, the amount of TOC content in the whole solution is estimated at about 0.09 g; while 133 g of carbon were introduced: So we can inferred a destruction rate better than 99.93 %, within measurement accuracy.

The amount of chlorine content in the solution is ~ 586 g while the mass of chlorine introduced was 592 g. Thus, the trapping rate of chlorine is evaluated at 98.98 %, within measurement accuracy.

4.4. PFPE/TCE

In the practice, liquid wastes are rarely pure products, so it is important for evaluating the process efficiency to test it on a mixture of model products. The trial described here is focused on the
incineration of a mixture of PFPE oil and TCE with neutralization of the solution using potassium carbonate K₂CO₃.

For this, we have included a tank filled with potassium carbonate in the recirculation loop (see Figure 5), a volume of K₂CO₃ have been periodically injected to neutralize the solution.

![Figure 5. Neutralisation device.](image)

1. Solution racking
2. K₂CO₃ injection
3. Reinjection of a part of solution volume
4. Cooling loop

So, if the injection flow rate of the mixture is 1 L/h and if we inject 1 L of K₂CO₃ every 10 min, number of moles of CO₂ in the off-gas is calculated to be around 43.5 moles. Measurements give 41.6 moles of CO₂. CO content is about 0.05 % but it increases (0.15%) each time we inject the solution of K₂CO₃.

We have injected in excess the volume of K₂CO₃ required for the neutralization of HCl and HF to finally get a basic solution: pH ~ 9.

The destruction rate is better than 99.88 % while the trapping rate of fluorine and chlorine are respectively better than 93.2 % and 76 % (see figure 6).

![Figure 6. Fluorine and chlorine contents](image)

5. Conclusion
Incineration of used TBP/dodecane with zirconium as plutonium surrogate was demonstrated without zirconium trace in the condensed residues. Process efficiency is also shown by the incineration of other wastes such as TCE and PFE, separately or mixed.

We have proved that:
- Mineralization rate better than 99 % for feed rate up to 4 L/h.
- High trapping rate for phosphorous as for fluorine and chlorine.
- Possibility of neutralization without great difficulty.

The next step consists to strengthen analysis of the solution and specify the measurement uncertainties and to compare thermodynamics and chemical kinetics.
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