Incineration of organic liquid waste

by underwater thermal plasma

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Abstract: This work deals with incineration of (radioactive) organic liquid waste using an oxygen thermal plasma jet, submerged under water. The results presented here are focused on incineration on the one hand of a mixture of tributylphosphate (TBP) and dodecane and on the other hand of a perfluoropolyether oil (PFPE). 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 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 99.9 % for phosphorous as for fluorine. No zirconium trace has been found in the condensed residues.

Keywords: Underwater thermal plasma, liquid waste incineration, TBP, zirconium, perfluoropolyether oil.

1. Introduction

Radioactive organic liquid waste is a special category of radioactive waste precisely because of their organic nature which makes them often flammable, non-miscible with water. Therefore they are systematically separated from other liquid waste, stored and processed separately. Several techniques for conditioning organic radioactive waste have been developed.

Incineration and wet oxidation are attractive techniques, 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[1].

Up to now, a very few works [2] 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. However 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. The 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.

Recently, new processes based on plasma technologies 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. Moreover, underwater thermal plasma jet [3, 4, 5] 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 a widely used 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 [6], steam-assisted
pyrolysis system [7], submerged combustion technique [8], pebble bed pyrolysis [9] and a few
others. Some remaining problems and the characteristics of this particular waste were an
incitation 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/dodécane 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 HNO$_3$ concentration is 4M, after equilibration, the HNO$_3$ concentration in organic phase is 0.7 M
[10]. Water is simultaneously extracted from aqueous phase: solvent adduct in form of a Lewis
acid-base complex is formed:

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

TBP(HNO$_3$)$_{1.3}$(H$_2$O)$_{0.6}$ and TBP(HNO$_3$)$_{1.8}$(H$_2$O)$_{0.6}$ are proposed in [11].

Then a determined quantity of zirconium carbonate (SA ref:14616) (typically a few g of zirconium / L)
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)$_2$(NO$_3$)$_2$(TBP)$_2$, ZrOH(NO$_3$)$_3$(TBP)$_2$ and Zr(NO$_3$)$_4$(TBP)$_2$ [11]. 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 [11].

The basic principle of the process may be summarized by:

\[
\text{thermal plasma} \quad \text{TBP} + \text{dodecane} + \text{Zr} \quad \rightarrow \quad \text{CO}_2 + \text{H}_2\text{O} + \text{H}_3\text{PO}_4 + \text{Zr(?)}
\]

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 specie: zirconium oxide or zirconium phospate?

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:

\[
(C_2O_{1.1}F_{4.2})_{liq} + 0.4 \text{O}_2 + 2.1 \text{H}_2\text{O}_{liq} \quad \rightarrow \quad 2 \text{CO}_2 + 4.2 \text{HF}
\]

3. Experimental set up

The experimental set up is presented on figure 1; it consists essentially on a water-jacket reactor filled
with water, at the base a plasma torch, 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 control the solution temperature, we added a cooling loop which includes a pump and a heat exchanger.

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 [12].

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 equilibrium thermodynamics. If we accept this assumption, with typical running parameters, CO content is in the range of 10 %; then if the jet enters the solution, CO is immediately quenched. So to reduce the CO content in the off-gas, first, oxygen is injected downstream, secondly, a cooling nozzle is added to moderate the quenching rate before the jet enters in the solution. So, CO content in the off-gas is less than 1 %.

CO₂ and CO contents in the exhaust gas are continuously measured. Samples, periodically taken from the solution, are analyzed by appropriate chemical methods: pH, contents in total organic carbon (TOC), phosphorus, fluoride and nitrates are measured. Condensed residues are characterized by RX diffraction and SEM with EDS.

4. Results

4.1 Operating parameters

The gas flow rates for a typical assay of our work 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 and 100 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 66 %.

Once the arc is established, the reactor and the loop are filled with water ~ 23 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.

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

4.2 TBP/dodecane

Mass rate of the charge is ~ 1.9 kg/h ( 2.4 L/h); the zirconium concentration was 10⁻⁵ M. 2.8 L are processed during the test run detailed here. The combustion of TBP/dodecane produces 24 kW besides 33 kW effectively delivered by the plasma torch. So a total power of 57 kW is delivered inside only 10 cm³. 15 kW are transferred in the cooling stage, 11 kW in the reactor walls and condenser, the rest is found in the cooling circuit of the loop.

Given the flow rates of oxygen, argon and charge, supposing complete thermodynamic equilibrium at each step and all the water and phosphoric acid condensed inside the reactor, CO₂ content in the off-gas is calculated to be around 15 %. Measurements give 14.5% for CO₂ and 0.45% for CO.

The combustion efficiency defined by: [CO₂]/([CO₂]+[CO]) is ≈ 97%; pH falls rapidly to below 1.8.

At the end of the test, the amount of TOC content in the whole solution may be estimated at about 1.22 g; while 1677 g of carbon were introduced: So we can inferred a destruction rate better than 99.9 %, within measurement accuracy.
The amount of phosphorus content in the solution is ~ 78.23 g while the mass of phosphorus introduced was 77.8 g. Thus, the trapping rate of phosphorus is evaluated at 100%, within measurement accuracy.

Nitrate content in the solution vary like phosphorus content (figure 2 where nitrate content is given in mg of nitrogen/L). Nitrogen mass balance shows nitrogen lose which may be explained by NO formation in the plasma: NO might escape in the off-gas.

\[ \text{Figure 2: Phosphorus and nitrogen contents (test 20101119)} \]

No zirconium trace in condensed residues has been detected by RX diffraction, neither by SEM with EDS.

4.2 PFPE

Mass rate of the charge is ~ 0.83 kg/h (0.44 L/h). 0.266 L are processed during the test run. The combustion of PFPE produces only 2.1 kW besides 33 kW effectively delivered by the plasma torch; so the total power is 35 kW. 7.5 kW are transferred in the cooling stage, 5.5 kW in the reactor walls and condenser, the rest is found in the cooling circuit of the loop.

Given the flow rates of oxygen, argon and charge, supposing complete thermodynamic equilibrium at each step and all the water and fluoride acid condensed inside the reactor, CO₂ content in the off-gas is calculated to be around 2%. Measurements give 1.95% for CO₂ and 0.07% for CO.

The combustion efficiency is ≈ 96%.

At the end of the test, the amount of TOC content in the whole solution is estimated at about 0.37 g; while 102 g of carbon were introduced: So we can inferred a destruction rate better than 99.7%, within measurement accuracy.

The amount of fluorine content in the solution is ~ 341 g while the mass of fluorine introduced was 333 g. Thus, the trapping rate of fluorine is evaluated at 100%, within measurement accuracy.

5. Conclusions

Incineration of used TBP/dodecane with zirconium as plutonium surrogate and PFPE oil was demonstrated. Process efficiency 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 99.9% for phosphorus as for fluorine. No zirconium trace have been found in the condensed residues. In future, trials of longer duration will be undertaken to assess the corrosion problems.

References

[10] Moisy P. CEA/DEN/DRCP private communication