

Organic Waste Treatment by Incineration and Coupled Incineration/Vitrification Processes – 14059

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ABSTRACT

Nuclear fuel recycling requires separation and waste treatment in facilities that generate alpha-contaminated organic secondary wastes. Organic wastes are not suitable for long-term storage due to their behavior under irradiation. Two processes have been developed by French nuclear research laboratories to propose solutions for the removal of the organic fraction before storage. The IRIS process involves three electric furnaces operating successively at different temperatures to perform pyrolysis (and chlorine removal) at medium temperature, calcination of the residue at 900°C, and post combustion of the off-gas in an afterburner. In the SHIVA process, all three steps are conducted in a single reactor with plasma torches; the high temperatures made possible by the plasma improve the kinetics and allow the use of a more compact reactor. Both processes have advantages and drawbacks depending on the type of waste, the level of contamination, and whether the objective is confinement or recycling.

INTRODUCTION

Nuclear power plants produce high-level radioactive waste arising from fuel irradiated in the reactor. Recycling of uranium and plutonium can be achieved with separation processes in recycling plants such as La Hague in France. Vitrification process can then immobilize non-reusable waste (actinides and fission products) in a leach-resistant glass matrix tailored for radionuclide containment.

Although recycling limits the quantities of high-level waste in the fuel cycle, separation and waste treatment generate alpha-contaminated intermediate-level. The main problem is the wide range of wasteforms, which can be organic (gloves, bags), inorganic (refractory bricks), or metallic.

Organic wastes are particularly unsuitable for long-term storage. Organic molecules are sensitive to radiation from the radionuclides. Decomposition of these molecules generates gases including H₂ or HCl that jeopardize the integrity of the metal drums by swelling and corrosion. Intermediate molecules can form soluble complexes with actinides that favor their dissemination in the environment. For all these reasons, nuclear waste containing organics cannot be candidates for long-term storage.

The CEA (French atomic energy research agency) is developing processes to remove the organic fraction from nuclear waste. Thermal treatment is a promising way to achieve this aim and reduce the waste volume. Two thermal processes developed at the Innovative Containment Process Laboratory (LPIC) are described and compared. The advantages and drawbacks of each process are discussed, and suitable wasteforms for each process are enumerated.

IRIS PROCESS

The first incinerator is a succession of three electrically heated furnaces at increasing temperatures (**Figure 1**). The pilot facility named IRIS (Installation for Research on Incineration of Solids) heats waste successively to three different temperatures to achieve the decomposition of all types of organic products.

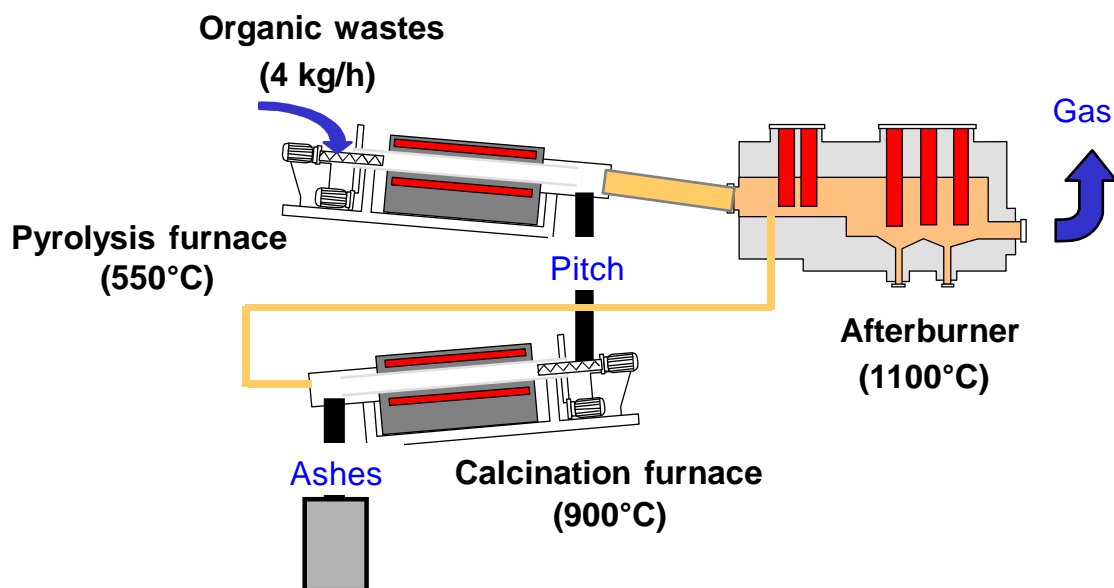


Figure 1. Schematic of the IRIS process, composed of three furnaces

Pyrolysis step

Waste is first fed to a resistance-heated rotating kiln at a temperature of 550°C. This stage is the seat of pyrolysis reactions that occur at low temperature. Although oxygen is not involved in the pyrolysis reaction mechanism, an oxidative atmosphere is required in the first kiln to avoid plugging. Thermodynamic analysis and experimental results show that oxygen favors the formation of silicates and aluminates rather than chlorides. Oxides which remain solid at intermediate temperatures exhibit suitable behavior in the rotating kiln. The presence of oxygen avoids heavy hydrocarbons which could form tar deposits.

A residence time of 5 minutes is necessary to ensure complete reactions. Increasing the temperature in the kiln could improve the reaction kinetics and thus shorten the residence time or increase the throughput. However, chlorine is removed from the condensed phase of the waste during this step and eliminated in the off-gas stream. The temperature must be as low as possible to limit corrosion of the reactor walls.

This first step produces pitch with high carbon content but without chlorine. The solid output mass flow is divided by a factor of six compared with the waste feed mass.

Calcination

The second part of the process is similar to the first, and again takes place in a resistance-heated rotating kiln. The main differences are the temperature (900°C) and the residence time (2 h).

This furnace is fed with the pitch produced in the pyrolyzer. The aim of calcination is complete oxidation of the carbon content in the solid. Oxygen plays a major role in these reactions. Oxidation of the pitch is enhanced by an oxygen-enriched atmosphere and high temperature. Despite the high kinetic rates, an extended residence time is necessary to produce carbon-free ashes. Under these conditions, the carbon content of the solid residue is less than 1 wt%. The mass flow is divided by five during this stage, resulting in an overall mass flow reduction factor of 30.

Post combustion

The temperature is higher in the final afterburning step with a setpoint of 1100°C. This furnace is dedicated to off-gas treatment. The gas flows exiting the pyrolyzer and calciner are injected in a post combustion chamber with pure oxygen or air and heated to 1100°C for at least 2 seconds. These conditions are required by authorities to ensure complete oxidation of the combustion gases.

The afterburner is composed of refractory walls and heated by electrical resistors inserted in wells. Because of the very high temperatures and refractory walls, deposits are negligible, which limits the maintenance requirements.

Phosphatation of metal chlorides

Chlorine is the main contributor to corrosion in the process. Although halogen removal is conducted at low temperature in the pyrolysis step in presence of oxygen, some metals such as zinc can form volatile metal chlorides. Zinc chloride formation raises problems because this compound condenses in every cold part of the process. It is very hygroscopic and highly corrosive in the presence of water.

The solution developed is to substitute phosphate ions for chloride ions to obtain zinc phosphate rather than zinc chloride. Zinc orthophosphate ($\text{Zn}_2(\text{PO}_4)_3$) is stable at high temperature in solid form. The chloride is thus eliminated in the off-gas stream and zinc phosphate can be recovered by particle filtration.

Phosphorus additives in the waste feed stream or in the calciner have been tested [1] in the form of tributyl phosphate (TBP) or a plastic material with high phosphorus content. Analysis of the filter dust and deposits showed that the phosphatation reaction occurs in the afterburner at high temperature. Particles are composed of several zinc phosphates such as $\text{Zn}_2\text{P}_2\text{O}_7$, $\text{Zn}_5(\text{P}_3\text{O}_{10})_2$ and the targeted orthophosphate. The proportion of each phosphate is governed by the equilibrium in the gas phase. This equilibrium can be modified by varying the proportions of zinc and phosphorus. A P/Zn molar ratio of 0.7 has been identified as the optimum value for producing $\text{Zn}_3(\text{PO}_4)_2$. Other phosphates are favored if phosphorus is introduced in excess, but they are liquid at intermediate temperatures, resulting in deposits in the off-gas treatment facility and obstructing the process lines.

SHIVA PROCESS

The second process, SHIVA, implements plasma torch technology coupled with induction-heated melting. Both of these technologies have been integrated in a single reactor (**Figure 2**) to perform organic waste treatment.

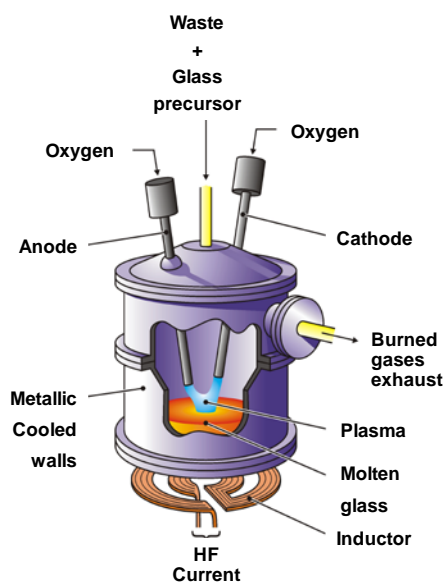


Figure 2. Schematic of SHIVA high-temperature reactor

Induction system

High frequency induction is an efficient method for maintaining a molten bath of glass above 1000°C without contact. This technology is commonly used for vitrification of high-level radioactive waste. The latest development is the cold crucible melter in which the reactor wall is cooled by a water jacket. A thick layer of glass solidifies in contact with the cold wall, protecting the metal shell from corrosion by the molten bath.

Plasma torches

Electric arcs are used in the glass industry to melt and prepare batches of glass before pouring. In our concept, an electric arc is formed in the gas phase in the upper part of the reactor. The arc heats the surrounding gas and generates a plasma at the center of the reactor. The energy of the plasma is transferred to the surrounding gas and to the molten glass below (**Figure 3**).

The Waste Confinement and Vitrification Service (SCDV) has developed plasma torches compatible with nuclear requirements and allowing efficient combustion of organic materials. Graphite rods are used for the cathode and anode. These electrodes are consumed during operation by thermal and chemical erosion but are continuously advanced into the reactor to offset the tip erosion. A system of nipples is used to attach fresh graphite rods to the outer end of the operating electrode. The lifetime of the graphite electrodes is thus virtually unlimited.

Both torches allow angular and linear movements in the reactor to shift the plasma zone if necessary. The distance between the plasma zone and surface of the melt determines the heat exchange between the two phases and allows control of the molten glass surface temperature.

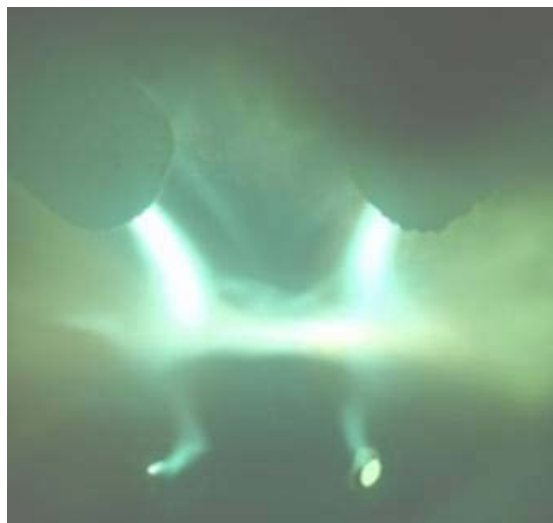


Figure 3. Photo of twin torches (left: cathode, right: anode) and plasma zone

Milled organic waste is fed to the center of the reactor via a solid screw conveyor. The waste passes through the plasma zone where it is quickly heated to high temperature in the presence of oxygen. Combustion reactions occur in the plasma zone with good kinetics due to the high temperature. The mineral fraction and ashes containing radionuclides, which are stable at high temperature, fall into the molten bath below the torches and are incorporated in the glass.

OFF-GAS TREATMENT

Both combustion processes generate a significant quantity of off-gas that must be treated before discharge into the environment. The off-gas treatment facility shown in **Figure 4** is the same for both processes described above.

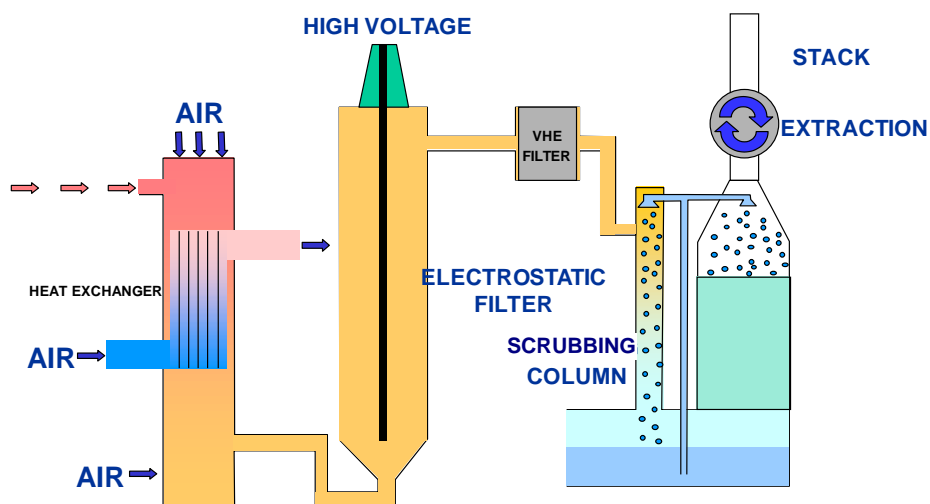


Figure 4. Schematic of off-gas treatment facility

The first step is to cool the gas by quenching in air, via a heat exchanger with dilution in room-temperature air. The second step is to filter the particles entrained in the off-gas stream. An

electrostatic precipitator is first used to collect most of particles: an electrode connected to a high voltage generator is placed at the center of a metal tube. The electrostatic field induced by voltage drop causes the particles to adhere to the wall. Complete filtration is achieved by Very High Efficiency filters.

Halogens in plastics such as PVC or neoprene are converted to acidic gas which must be neutralized. The gas stream therefore flows through a scrubbing column to wash the acidic gas with a basic solution before stack discharge.

PROCESS COMPARISON

Both processes described here can achieve combustion of organic waste to reduce its volume and remove the organic fraction. The waste must be pure organic and milled before treatment. Both processes have successfully processed ion exchange resins, sludge from water treatment stations, and bitumen. Complete combustion of the organic fraction has been demonstrated in several tests for all types of wastes.

The IRIS process produces ashes containing concentrated radionuclides. This form of residue allows further treatment including separation of compounds to recycle a fraction of the ashes. If confinement is required, a wide choice of matrices is available and is independent of the combustion process. The waste volume reduction factor can reach a maximum of 30 depending on the initial waste composition. The progressive temperature elevation in different furnaces minimizes equipment corrosion. The high temperature of the afterburner facilitates complete conversion of metal chlorides to stable phosphates. All three furnaces, and particularly the afterburner, have large volumes that can easily absorb a local pressure rise due to combustion. A negative pressure gradient, which is required in nuclear installations, can be maintained. However, the large equipment volume is a drawback for implementation in hot cells and for remote maintenance. The waste feed capacity of the IRIS process is limited in order to allow the use of devices of reasonable size.

The SHIVA process based on plasma torches and very high temperatures is complementary to the IRIS process. The combustion chamber volume can be limited without decreasing the waste feed rate because the process kinetics are enhanced by the high temperatures. With a continuous feed of milled organic waste, post combustion of the off-gas can be complete, making the afterburner (the largest equipment item) unnecessary. Compactness is obtained by using pure oxygen as the oxidizing agent, and thereby reducing the total gas flow. Incineration and glass melting in a cold crucible avoids the need for a second process to treat the residue and transfer radionuclides from one process to another. It allows “in situ” radionuclide incorporation, reducing contamination and secondary waste production. The SHIVA process receives contaminated waste and produces glass incorporating radionuclides with very limited secondary waste production. Dust collected in electrostatic filters can be recycled in the reactor and incorporated in the glass matrix.

CONCLUSION

The CEA has developed two processes for organic waste treatment based on different heating technologies. The IRIS process uses robust electric furnaces to produce ashes and dust composed of metal phosphates to avoid corrosion by metal chlorides. The SHIVA reactor combines plasma torches assuring complete combustion of milled organic waste in a small volume with induction-

heated melting in the crucible to produce a stable residue composed of glass incorporating the ashes and radionuclides. Both processes have advantages and drawbacks depending on the type of waste, the level of contamination, and whether the objective is confinement or recycling.

REFERENCES

1. Lemont F., Management of metal chlorides in high temperature processes – Application to nuclear waste treatment, *J. of Hazardous Materials* (2012), Vol. 213-214, pp 38-45.