ORGANIC WASTE INCINERATION PROCESSES

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ABSTRACT

Nuclear activities produce organic waste compatible with thermal processes designed to obtain a significant weight and volume reduction as well as to stabilize the inorganic residue in a form suitable for various interim storage or disposal routes. Several processes may be implemented (e.g. excess air, plasma, fluidized bed or rotating furnace) depending on the nature of the waste and the desired objectives. The authors focus on the IRIS rotating-kiln process, which was used for the first time with radioactive materials during the first half of 1999. IRIS is capable of processing highly chlorinated and α-contaminated waste at a rate of several kilograms per hour, while limiting corrosion due to chlorine as well as mechanical entrainment of radioactive particles in the off-gas stream. Although operated industrially, the process is under continual development to improve its performance and adapt it to a wider range of industrial applications. The main focus of attention today is on adapting the pyrolytic processes to waste with highly variable compositions and to enhance the efficiency of the off-gas purification systems. These subjects are of considerable interest for a large number of heat treatment processes—including all off-gas treatment systems—for which extremely durable, high-performance and low-flow electrostatic precipitators are now being developed.

Keywords: Incineration, IRIS process, chlorinated organic waste, rotary kiln

INTRODUCTION

Nuclear facilities in routine operation produce waste, that requires maximum weight and volume reduction before interim storage. Incineration is very suitable in this respect for waste with high carbon content, as most of the mass can be decomposed into nonradioactive CO_2 and H_2O, allowing all the radiological activity due to contamination to be concentrated in a solid phase that can be conditioned for disposal.

Incineration raises two major issues. One is related to corrosion of the process equipment, which may be accelerated if the inorganic fraction of the waste forms eutectic mixtures; this occurs, for example, with salt compounds that can associate to dissolve the steel passivation coatings. The second concerns the volatilization or entrainment of some compounds that should remain in the residual solid fraction (ashes or dust).

Various technologies can be adapted to incineration depending on the waste feed volume and on the required final wasteform quality. One of these, IRIS, has the advantage of generating very low-carbon ashes suitable for vitrification, while minimizing corrosion problems at throughputs of several kilograms per hour of highly chlorinated organic waste.

1. DIFFERENT TECHNOLOGIES FOR DIFFERENT REQUIREMENTS

Several incineration methods are available according to the process requirements. The quantity of waste to be processed and the required quality of the final wasteform are the fundamental selection criteria. For example, domestic waste incineration requires facilities with very high capacities—several tons per hour. Large rotating kilns connected to bag filters are generally used for this purpose, as are grate-type furnaces. The furnaces are generally oil- or propane-fired, and solid waste is incinerated in a one-step process. Several types of incineration furnaces widely used industrially are shown schematically in **Figure 1**: (a) rotating kiln; (b) and (c) variants in which the rotating kiln is replaced by a combustion chamber or a conveyor allowing continuous waste feed; (d) a different technology implementing fluidizing of the waste stream, with afterburning of the off-gases, which may occur within the same combustion chamber. In all cases, the process temperature is about 1000°C, and the

recovered bottom ash and slag has very high carbon content. Major corrosion problems can arise if the waste contains various metals or metalloids, requiring intensive and regular maintenance.

In addition to these single-step techniques, other processes involving melting systems are capable of generating a metallic phase and an oxidized phase in which the nonvolatile elements are distributed according to their chemical potential. Plasma torch heating systems can be effective in such systems.

Although these processes are well suited to domestic waste treatment, they must be significantly improved or revised for use with radioactive waste, for which the weight and volume reduction are primordial. The process off-gas stream must be minimized to facilitate subsequent treatment, and secondary waste production must be limited.

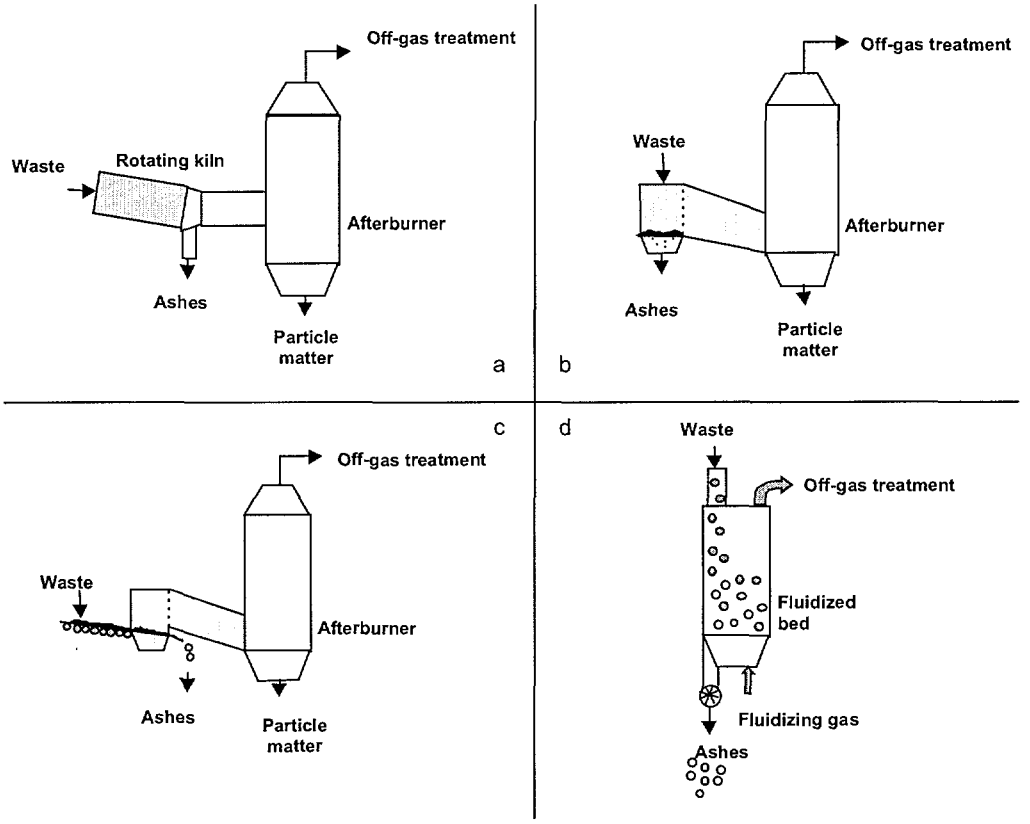

Figure 1. Various technologies suitable for high-rate waste incineration

2. ORGANIC WASTE AND THERMAL DEGRADATION

The principal advantage of thermal degradation of organic waste is to eliminate a large portion of the material in gaseous form. All plastics are polymers; heat and oxygen break down the carbon chains and oxidize all the components as indicated in the following very general relation:

$$C_xH_yO_z + (x + \frac{y}{4} - \frac{z}{2})O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O \quad (1)$$

If all the waste consisted of pure polyethylene –$(CH_2)n$–, all the material would be converted to gas and the weight and volume reduction factors would be infinite. This is not the case, as some compounds such as polyvinyl chloride (PVC) and neoprene contain elements other than carbon and hydrogen. These elements combine during the degradation process, forming the final bottom ash and fly ash depending on the volatility of the resulting products. The weight and volume reduction factors depend mainly on the quantity and quality of the inorganic content in the waste stream, while the bottom and fly ash composition is affected by the physical and chemical conditions of the process. A very important factor is the presence of PVC, degradable at temperatures as low as 150°C, releasing mainly hydrogen chloride, which plays an important role in the incineration process.

Polyvinyl chloride is routinely used for maintenance practices in nuclear facilities, and for handling radioactive materials; technological organic waste can therefore contain large proportions of PVC. This is the case in France, for example, at CEA sites such as Valduc and Cadarache, or at the MELOX fuel fabrication plant.

Hydrogen chloride is a chlorinating agent, and can combine with inorganic matter to form a variety of salt compounds. This is notably the case for structural material components. From the standpoint of thermodynamic equilibria, the chlorination of metals is impeded at higher temperatures, which, on the other hand, favor their kinetics. The main chlorination balance reactions can be summarized as follows:

$$M + n\mathrm{HCl} + \frac{\mathrm{n}}{4}\mathrm{O_2} \leftrightarrow M\mathrm{Cl}_n + \frac{n}{2}\mathrm{H_2O} \quad (2)$$

$$M_x\mathrm{O}_y + 2y\mathrm{HCl} \leftrightarrow xM\mathrm{Cl}_{2y/x} + y\mathrm{H_2O} \quad (3)$$

where M represents the principal metals found in structural alloys.

A thermodynamic study revealed that the oxides of some alloy elements—particularly aluminum—are much less sensitive to hydrogen chloride. It is therefore judicious to use an aluminum alloy, which is protected by a passivation layer formed by superficial oxidation of the aluminum; one such material is Inconel 601®. Moreover, since incineration is a continuous process involving chemical systems under conditions not at thermodynamic equilibrium, the chlorine should be eliminated at low temperatures to retard its diffusion through the oxide passivation layer and to limit the metal oxidation kinetics. These requirements led to the design of dedicated processes.

3. IRIS: A PROCESS SUITABLE FOR HIGHLY CHLORINATED RADIOACTIVE ORGANIC WASTE

IRIS is a three-step process [1] using rotating kilns. The waste is first subjected to oxidizing pyrolysis at 550°C to form a solid residue or pitch, which is then processed by a second calcining step at 900°C under oxygen-enriched atmosphere. The heat treatment off-gas stream containing a volatile hydrocarbon fraction is oxidized at 1100°C in an afterburner. The three process steps are shown schematically in **Figure 2**.

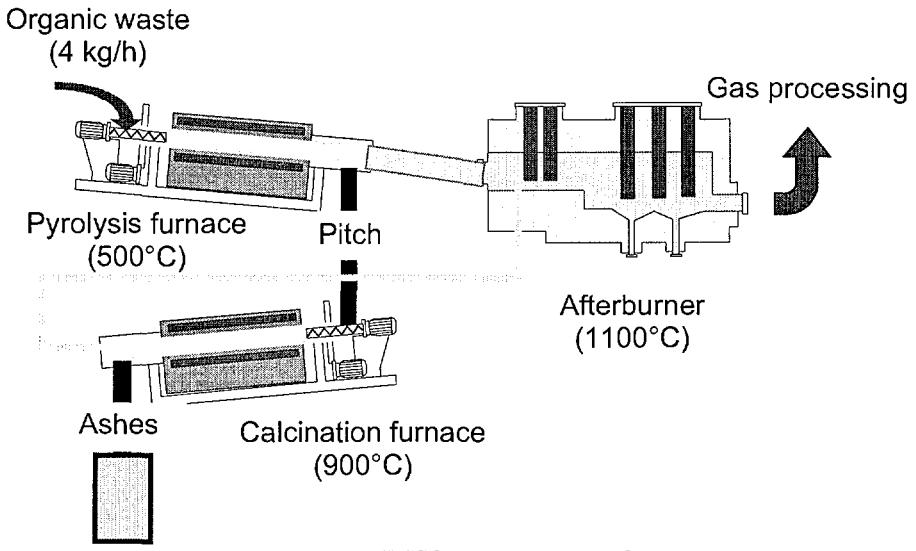

***Figure 2**. IRIS heat treatment cycle*

The multi-step process has two main advantages. Eliminating the chlorine at low temperature in the pyrolyzer minimizes corrosion problems and limits the required glass flows—and thus the entrainment of particle matter. Oxygen enrichment during the pyrolysis step ensures oxidation of the heavy hydrocarbon chains that produce tars and can lead to severe deposits in the process lines.

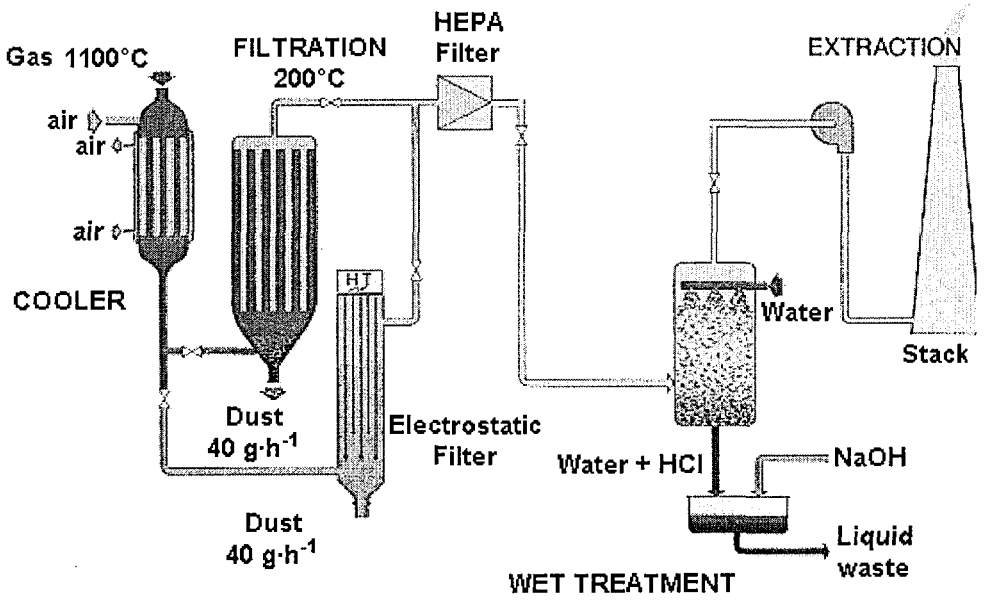

Figure 3. IRIS process off-gas treatment

Following the afterburning treatment, the off-gases are ducted to a high-performance system comprising a series of filtration steps capable of recovering all the solid particles from the airstream, and thus all the α-emitting actinides. The gas stream is then purified of any remaining volatile acidic compounds by sodium hydroxide scrubbing. The main steps in the off-gas treatment are summarized in **Figure 3**.

Although this technology limits corrosion, it does not completely prevent the production of metallic chlorides. The presence of elements such as calcium, zinc or potassium leads to formation of the corresponding chlorides. Nevertheless, thermochemical analysis and experimental results have shown that the presence of oxygen in the process systems favors the formation of silicates or aluminates rather than chlorides. Only volatile zinc chloride is formed in significant quantities, resulting in a very high chlorine concentration in the fly-ash. Generally the presence of an element resulting in the formation of a volatile chloride in the organic waste will have a similar effect, as is the case with zinc, lead or cadmium. Volatile chlorides may lead to serious corrosion problems, particularly when they also revert to liquid form when rehydrated by contact with the atmosphere.

One means of protecting against this risk is to maintain the process equipment at high temperatures even when not in service. Another is to convert the chlorides to more stable and less corrosive compounds such as phosphates [2], which can be formed by adding a compound capable of generating gaseous phosphorus, such as the pentoxide P_2O_5. Tests in the IRIS pilot facility obtained chloride-phosphate conversion yields of nearly 100%, resulting in fly ash of good quality for interim storage. The compositions obtained with and without phosphorus additive in the process are indicated in **Table I**. The studies conducted to date are sufficient to propose an overall degradation mechanism for the IRIS process; a simplified representation is shown in **Figure 4**.

Table I. *Comparative analysis of particle matter obtained with and without phosphatation*

Element	Zn	Cl	P	C	Si	Al	Ca	K
With P additive	47.4	51.4	0.3	0.1	0.2	0.1	0.1	–
Without P additive (ITAP)	26.9	0.2	24.9	0.2	0.1	0	0	4.2

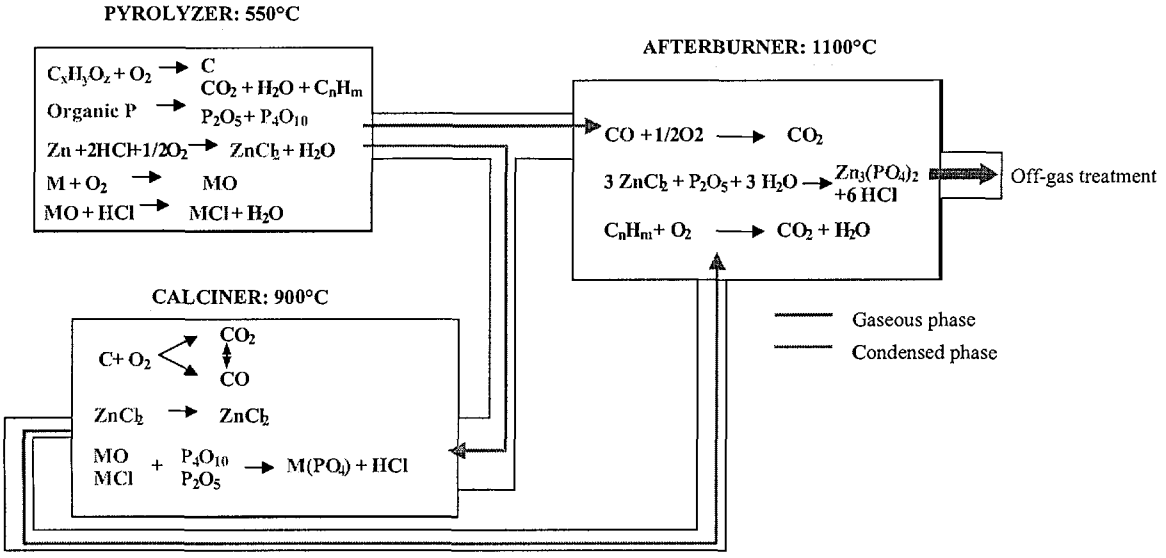

Figure 4. Overall material degradation schematic for the IRIS process

The off-gas treatment system includes two filtration steps to trap all the particle matter. The first uses an electrostatic precipitator that includes no filter medium; this technique not only avoids any pressure drop in the system lines, but also produces no secondary waste. The very high efficiency (better than 99%) prevents clogging of the HEPA filters constituting the second stage. The installation of a sonic wave declogging system allows all the particle matter to be recovered without difficult cleaning operations; the recovery of the particle matter is also facilitated by the phosphatation treatment. The IRIS test results showed that a single-tube precipitator design (**Figure 5**) is sufficient to filter the off-gas stream produced by waste incineration at a rate of 4 $kg \cdot h^{-1}$. With regular declogging, the filter ensures high efficiency.

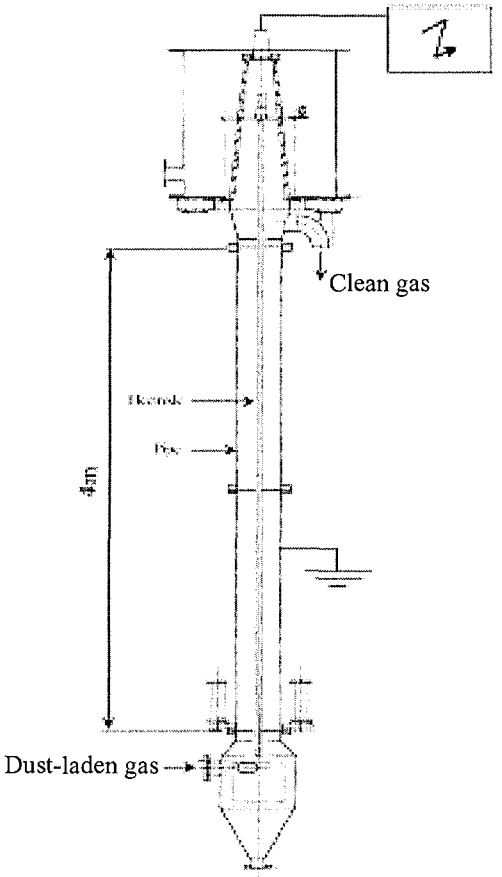

Figure 5. Electrostatic precipitator

4. IRIS PROCESS APPLICATIONS

The CEA's Military Applications Division decided in 1991 to build an incineration facility at the Valduc site. An engineering contract was signed with SGN in 1992, and construction begin in December 1993. All the process equipment was installed in glove boxes in an earthquake-resistant building.

Nonradioactive incineration tests totaling 2500 hours, carried out between January 19978 and December 1998, confirmed the process efficiency and safety, and allowed specific development work. Some 6500 kg of waste were incinerated during this period, producing 310 kg of ashes.

The first radioactive waste was processed on March 10, 1999. The results obtained during the first two production campaigns are indicated in **Table II**.

Table II. Results of the first two radioactive waste incineration campaigns at Valduc

Characterization		First campaign	Second campaign
Weight of incinerated waste	(kg)	395	360
Waste activity	($GBq \cdot kg^{-1}$)	0.185	1.11
Weight of ashes	(kg)	16	20.3
Waste/ash weight ratio		24.7	17.7
Pu in waste stream*	(g)	33.8	179
Pu in bottom ash**	(g)	29.3	162
Pu in fly ash**	(g)	0.03	0.7
Pu recovered after cleaning*	(g)	0.3	3.2

* Measurement uncertainty: ± 20%
** Measurement uncertainty: ± 12%

The Valduc incineration tests from 1997 to 1999 were sufficient to validate the IRIS technology under radioactive conditions. Highly chlorinated and alpha-contaminated wastes were incinerated with fully satisfactory results, yielding excellent weight and volume reduction factors and recovering virtually all the Pu in the ashes. The phosphatation treatment developed at Marcoule resulted in the formation of dry, noncorrosive and stable ashes.

The incineration of 982 kg of waste in 1999 and 1345 kg in 2000, producing 42.8 kg and 73.3 kg of bottom ash, respectively, and 5 kg and 9.4 kg of fly ash. The low gas flow rates ensured recovery of virtually all the plutonium in the ashes.

In addition to the operation of the IRIS process at the CEA's Valduc Center, three other projects are currently at the design stage: one for the ONDRAF in Belgium, the second for the CEA's Cadarache Center in France, and the third for the future Rokkacho Mura plant in Japan. A major effort is thus currently in progress to adapt the IRIS process for the treatment of different types of organic waste. While the Valduc waste contains about 50% PVC and 10% cellulose, for example, ONDRAF waste contains 50% cellulose and 20% PVC; the incineration behavior and the resulting residues are thus very different. It is therefore essential to validate the process today for a wide range of wasteforms.

5. CONCLUSION

While many incineration processes are available today around the world, few are suitable for radioactive waste, which requires not only maximum weight and volume reduction, but also minimum secondary waste production and no release of radioactive substances. Thermal degradation studies conducted by the CEA with chlorinated organic waste led to the development of the two-step IRIS process. The IRIS technology limits corrosion problems due to chlorine release, and minimizes the entrainment of radioactive matter in the process off-gas stream. The technique was proven and refined by extensive nonradioactive testing before a facility was built at the CEA's Valduc Center for use with alpha-contaminated waste. After two years of operation, the process has logged a remarkable record, not only for the volume and quality of the residue produced, but also from a safety standpoint. This experience together with the constant development work on incinerating waste of variable compositions has incited other operators to consider the IRIS process, and should lead to the construction of three additional incineration units.

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