INCINERATION AND VITRIFICATION OF SURROGATE NUCLEAR WASTES BY THERMAL PLASMA

C. GIROLD *, R. CARTIER *, J.P. TAUPIAC **, C. VANDENSTEENDAM [+], J.M. BARONNET [+], T. FLAMENT

* CEA/DCC/DRDD/SCD - BP 171, Marcoule - 32105 BAGNOLS SUR CEZE-FRANCE
** ENTHALPIE - 102, rue Henri Giffard - 87280 LIMOGES-FRANCE
[+] Laboratoire de chimie des plasmas - Université de Limoges - 123, av A. Thomas 87060 LIMOGES-FRANCE
° SGN - 1 rue des Hérons - 78182 SAINT QUENTIN EN YVELINES Cedex-FRANCE

ABSTRACT

The aim of this presentation is to demonstrate the feasibility to substitute a single plasma reactor, where the arc is transferred on a melt glass bath, for existing several steps nuclear technological wastes incinerator. The incineration of wastes, the produced gases treatment and the vitrification of ashes issued from wastes incineration are the three simultaneous functions of this new kind of reactor. The three steps of the work are described : first, the postcombustion in an oxygen plasma of gases generated from the waste pyrolysis, then, the vitrification of ashes issued from calcination of wastes in the transferred plasma furnace and finally, the incineration/vitrification of wastes in the same furnace.

INTRODUCTION

The burnable radioactives wastes are most often composed of cellulose, plastics and rubber. They contain either long period radionuclides (α emitters) or short period ones (β, γ emitters). The incineration aim is to reduce the wastes volume and concentrate the radionuclides in ashes that can be treated further.

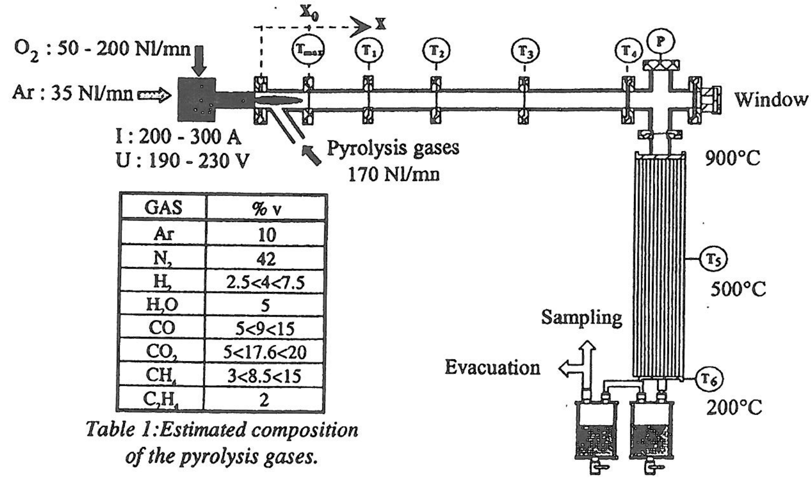
Before studying plasma incineration, SGN [1] and CEA [2] have developed two classical incineration processes ; one in two steps : incineration and postcombustion, and the other in three steps : pyrolysis, calcination and postcombustion. Both have been validated with full-scale pilots and surrogate α wastes.

A new kind of reactor, using thermal plasma with water cooled walls [3], is actually being developed. Aims are to minimize installation size, gasflow, technological wastes by increasing lifetime of the equipment and to confine the radioelements in a glass matrix.

The present report describes the three steps of the new reactor development as follows : postcombustion in an oxygen plasma of gases generated from the wastes pyrolysis and kinetic modeling of the gas treatment in this reactor, then vitrification of ashes issued from calcination of wastes in a transferred plasma furnace and finally, incineration/vitrification of wastes in the same furnace.

I - POSTCOMBUSTION OF PYROLYSIS GASES

Significant advantages can be turned into account by using an oxygen plasma arc in gases postcombustion. Gas temperature and composition can be set independently. Moreover, an oxygen plasma is rich in highly excited molecules and oxygen atoms that increase the combustion kinetic, allowing reactors size reduction. To study the postcombustion in an oxygen plasma arc of gases generated from the pyrolysis of wastes, a water cooled



GAS	% v
Ar	10
N_2	42
H_2	2.5<4<7.5
H_2O	5
CO	5<9<15
CO_2	5<17.6<20
CH_4	3<8.5<15
C_2H_4	2

Table 1: Estimated composition of the pyrolysis gases.

Figure 1 : Sketch of the oxygen plasma postcombustion reactor.

postcombustion reactor was developed. This reactor includes several cylindrical sections made of stainless steel water cooled walls (fig. 1). At one end of the reactor is the plasma torch (Ar/O_2) associated with a mixing module of the plasma with the gases to treat. At the other end, a heat exchanger cools down the gases before exhaust. The reactional volume is about 3 liters and the residence time of gases about few tenths of second.

A tentative description of the combustion in this reactor with a mechanistic kinetic model is proposed. The chemical system is composed of 25 species and radicals and modeled with 132 elementary reactions between them. The gas mixture is submitted to a temperature variation T=f(time), the pressure being constant. The kinetics of the system are governed by (1) [4].

$$\frac{dY_i}{dt} = \omega_i - \left(\frac{Y_i}{\rho} \sum_{i=1}^{25} \omega_i + \frac{Y_i}{T} \frac{dT}{dt} \right) \quad (1) \qquad \omega_i = \sum_{j=1}^{132} k_j \left(\upsilon'_{ji} - \upsilon_{ji} \right) \prod_{i=1}^{25} Y_i^{\upsilon_{ji}} \quad (2)$$

Yi = number of i molecules per volume unit, ρ = number of molecules per volume unit, ω_i = rate of variation for the i species per time unit, νji, $\nu' ji$ = stoichiometric factors, kj = kinetic constants of the reaction j chosen in the litterature according to their determination conditions.

The stiff differential system is solved using a FORTRAN code package : CHEMKIN. For the modeling of the temperature law, mixing of gases and plasma is supposed to be complete at the end of the mixing module ($x = x_0$ on fig. 1), the gases temperature is maximum at this point : Tmax. For a given composition, Tmax can vary with the electrical power supplied to the plasma torch. The gases heating versus time along the mixing module can be known using (3) with v_0 = initial gases velocity. A linear heating of the gas mixture along the mixing module is considered, i.e. k = 0. The quenching law (4) is obtained with the mean enthalpy temperatures calculated (Tmax, T1, T2, T3 and T4 on fig. 1) and with the measured temperatures (T5 and T6).

$$t(x) = \frac{T_0}{v_0} \int_0^x \frac{1}{T_0 + \frac{T_{max} - T_0}{x_0^k} x^k} dx \quad [0<k<1] \quad (3) \qquad T(t) = \left(T_{max} - T_0 \right) e^{-at^2} + T_0 \quad (4)$$

Figure 2 presents the results of modeling for the CH_4 and C_2H_4 degradation in the case of a temperature law with Tmax = 2700 K. Only CH_2, C_2H_2 and C_2H_3 appear during the destruction which is due to the high O_2 ratio. Degradation begins near 900 K for C_2H_4 and near 1300 K for CH_4. The CHx destruction is over in the mixing module for this case, it goes further in the reactor if Tmax is lower.

For a mean composition (tab. 1) of pyrolysis gases and the same O_2 quantities, some combustion modeling results for different Tmax are given in table 2. One case is plotted on fig. 3. It can be seen on this figure that [CO] first increases because of the high rate of CH_x destruction. CO oxidation begins rapidly near 1500 K and further, when temperature goes beyond a limit value (≈ 2300 K for the mean composition plotted), CO/CO_2 equilibrium reverses as far as the quench begins. In the matter of fact, the CO concentration issued from the reactor increases. Table 2 presents the calculated post-treatment NOx concentrations, also increasing with Tmax. The kinetic modeling, unlike thermodynamics equilibrium calculation, allows the prediction of the order of post-treatment NOx concentration. This table also includes experimental values, their difference with modeling results are more important for NOx than for CO. These differences could be explained by the radial gradient of temperature we did not consider in the model.

As can be seen in table 1, the composition of pyrolysis gases can vary with the composition of wastes. Our experimental study has been structured according to the « two levels experiment planification method »[5]. The varying factors are : pyrolysis gases composition (Tab.1), O_2 quantity(50 - 200 Nl/mn), effective power transmitted to the gas mixture, hence the plasma gas + pyrolysis gases temperature (1500 - 2700 K). Sixteen mixtures have been tested, ranging all the composition limits. Pyrolysis gases flowrate was 10 Nm^3/h. Concentrations of CO_2, O_2, CO, NO, NO_2 in gases issued from the reactor, temperatures in several points of the reactor and thermal transfers towards the cooled modules were measured. The most significant results of this study are briefly commented.

Ti [K]	CO [ppm]	NOx [ppm]	CHx [ppm]
2900	60.0	7480	
2900	54	9700	
2700	50.7	7210	
2700	*38*	*8240*	
2500	41.4	5965	
2500	34.7	6530	
1500	8.8	0	
1500	*10*	*800*	*< 200*

Table 2 : Modeling( ) and experimental (■)results for different cases of Tmax and for the same gases composition (170 Nl/mn), with a 140 Nl/mn O_2 flowrate.

Whatever the gas composition is, CO concentrations in exhaust gases are always lower than 87 ppm if the O_2 flowrate is 1.8 time the stoichiometric quantity of oxygen (noted $<O_2>$), needed for a full oxidation of CO and hydrocarbons of the treated gases ; this concentration is under 25 ppm for the lowest net calorific value mixture. When the O_2 flowrate is $2*<O_2>$, [CO] in exhaust gases are always under 70 ppm. For all mixtures tested, the hydrogen content effect on the combustion performances is insignificant if O_2 flowrate is at least $1.8*<O_2>$. It is essentially CO and CH_4 content of the pyrolysis gases that influences the [CO] in exhaust gases. The study indicates also that the reduction of the effective power supplied to the gas mixture lowers [CO], as seen previously in modeling (Tab. 2). [NOx] in treated gases are only a function of the O_2 excess and of the effective power : they increase with these both factors.

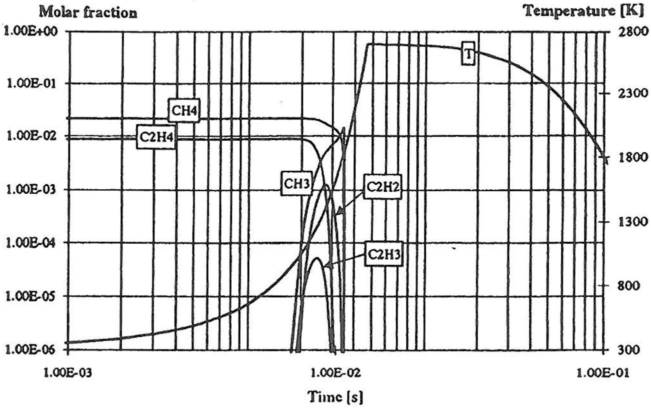


Figure 2 : Composition along the reactor for the CHx with a mean composition of pyrolysis gases and the considered temperature law.

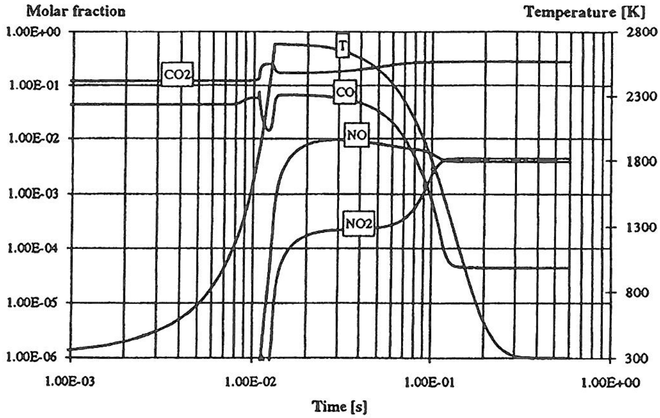


Figure 3 : Composition along the reactor for the NOx and COx with a mean composition of pyrolysis gases and the considered temperature law.

II - ASHES VITRIFICATION

With the final purpose of achieving simultaneous wastes incineration and mineral part vitrification in a plasma furnace, melting/vitrification study of a mixture including 50 % (in weight) of basalt (Tab. 3) and 50 % of ashes issued from calcination of wastes is first presented. Elaborated glass and volatility of some elements are discussed.

	SiO_2	Na_2O	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	K_2O	Ce_2O_3	ZnO
Basalt	50.4	3.0	12.2	11.9	8.8	10.2	2.2	1.2		
Ashes	44.0		28.5	2.1	10.0	4.0	0.2		6.0	4.7
50/50 Mixture	47.2	1.5	20.3	7.0	9.4	7.2	1.2	0.6	3.0	2.3
Elaborated glass	44.9	1.4	21.2	8.7	11.1	7.6	1.3	0.4	3.0	0.7

Table 3 : Basalt, ashes, 50/50 mixture, and elaborated glass composition (weight %)

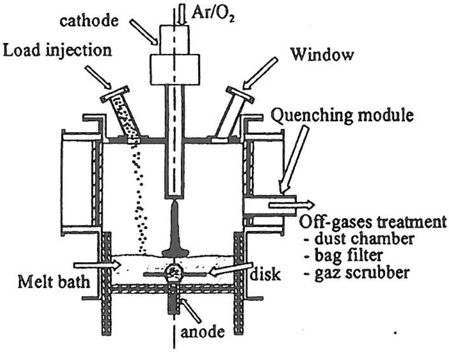


Figure 4 : Sketch of the plasma furnace.

The plasma furnace (Fig. 4) is composed of a principal chamber with a water cooled crucible, a quenching module allowing gases injection, a heat exchanger, two serial dust chambers and two bag filters. The plasma gas (Ar) is introduced in the arc between the cathode tip and an inner sleeve ; an outer sleeve enables oxygen injection for combustion. The anode is made from a starting rod and a disk in molybdene.

When the melted glass quantity is enough to cover up the anode, the arc is transferred on the bath. The arc voltage is about 200 V for a length of 145 mm with O_2 : 15 Nl/mn and Ar : 60 Nl/mn, intensity is about 170 A. 15 kg of load (about 4 kg/h) can be vitrified by trial without tapping.

The elaborated glass is black, glittering and homogeneous with a density near 2.9. As can be seen in table 3, the lattice formative oxides (SiO_2+Al_2O_3) quantity is lower in the glass than in the load ; the main lattice modifier oxides (MgO, CaO) mass ratio increases in the glass, that leads to decrease its viscosity. K, Na and Zn oxides represent 2.5 % of the glass composition versus 4.4 % in the load. Ce oxide quantity is the same in both compositions.

After each trial, the products in each module of the reactor are sampled. Table 4 gives the distribution in the pilot of some elements. Si, Al, Fe, Mg, Ti and Ce do not escape from the principal chamber, they are confined in the furnace and most particularly in the elaborated glass ; only traces are detected in the other water cooled modules. 97.5 % of cerium, are incorporated in the glass matrix. Sodium is found essentially in the glass (87.4 %) but also on the furnace walls (9.3 %) and less in the other water cooled elements (2.2 %) ; 1.1 % reach the bag filter. As far as potassium is concerned, a high ratio is measured on the furnace walls (32.4 %), the bag filter has to stop about 3 %. A small proportion of zinc oxide remains in the glass (39.5 %), ZnO volatilizes and leaves the chamber (3.2 % on the walls) to condense in the other cooled elements (41.2 %) and in the bag filter (16.1 %).

	Zn	Mg	Fe	K	Ca	Ti	Na	Si	Al	Ce
Glass	39.5	97.3	97.1	60.1	97.3	96.8	87.4	97.8	97.5	97.5
Furnace	3.2	2.5	2.5	32.4	2.4	3.2	9.3	1.9	2.5	2
Modules	41.2	0.2	0.3	4.7	0.3		2.2	0.3	<0.1	0.4
Filter	16.1		<0.1	2.9			1.1	<0.1		

Table 4 : Distribution (%) of the elements in the different parts of the pilot.

III - INCINERATION / VITRIFICATION OF WASTES

After the demonstration of feasibility of ashes melting/vitrification with basalt in a transferred plasma arc furnace, incineration/vitrification of wastes in the same reactor has been achieved. A mean composition of technological wastes was chosen : PVC : 48.5 %, cellulose : 9.6 %, neoprene : 17 %, polyethylene : 7.9 %, latex : 17 %, looking like flakes, with a density near 0.2. Isotopes of Sr, Co, Ce and Cr were added to flakes, as nitrates and oxides, to simulate a contamination. 2.5 kg/h of wastes were introduced in the furnace on a 15 kg melted basalt bath. The plasma column radiation is important in the polymers degradation processus : the wastes ignite as early as they are introduced in the furnace and burn in the oxidizing atmosphere.

The distribution of some elements in the pilot is given in table 5. Elements containment in the glass can be compared with the one given in table 4 for ashes vitrification, they are always higher in the present case. As far as tracers are concerned, Ce, Co and Sr are mostly retained in the glass. The off-gas, before they reach the filter, contain only 1 % (in weight) of the introduced tracers. According to low stability of Cs_2O and high volatility of cesium, only a quarter weight (23.5 %) of Cs is in the glass but 52.4 % accumulate on the furnace walls, the remaining quarter leave the chamber and 12.6 % reach the filter.

	Si	Al	Fe	Mg	Ca	Na	K	Ti	Ce	Co	Cs	Sr
Glass	98.0	98.3	97.3	98.2	98.5	95.1	92.7	99.3	98.4	82.4	23.5	96.9
Furnace	1.7	1.5	2.3	1.7	1.2	3.8	5.4	0.5	1.1	9.2	52.4	2.2
Modules	0.3	0.2	0.3	0.2	0.2	0.6	0.7	0.2	0.4	8.1	11.5	0.6
Filter						0.5	1.1		0.2	0.2	12.6	0.4

Table 5: Distribution (%) in the reactor of some elements and tracers added to wastes.

As can be seen in table 6, a good homogeneity of the glass is obtained with this process.

%	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Ce_2O_3	TiO_2	CoO_4	Cs_2O	SrO
Periphery	47.6	12.4	11.9	9.7	9.5	3.0	1.2	0.2	1.8	0.1	0.05	0.05
Bottom	44.3	12.6	11.8	9.4	10.0	3.1	1.2	0.1	2.0	0.1	0.05	0.05
Center	46.1	11.9	11.8	9.7	9.8	3.1	1.2	0.1	2.0	0.1	0.05	0.05
Surface	47.9	12.4	11.8	9.7	9.3	3.2	1.2	0.1	2.0	0.1	0.05	0.05

Table 6 : Composition (%) of glass sampled in different parts of the crucible.

IV - CONCLUSION

Studies were carried out on a plasma postcombustion reactor showing a good efficiency ; an important oxygen excess is not necessary and a moderate temperature is sufficient to ensure a good combustion. Experimental measurements were led with 10 Nm^3/h of pyrolysis gases ; more trials show that the treatment capacity can be at least 35 Nm^3/h. Thermodynamic and kinetic approaches allow the understanding of chemical processes in the reactor and the prediction of experimental results.

The transferred plasma arc reactor with a cold crucible allows the melting/vitrification of more than 15 kg of load (50/50 mixture of basalt and ashes) by trial without tapping. Ashes flowrate is about 4 kg/h with 40 kW of electrical power. The Ar/O_2 plasma is transferred on the melt bath and ensures a quasi-instantaneous melting of the load injected. A good containment in the glass of the chemical elements is obtained with this process.

It has been demonstrated that it was possible to incinerate technological wastes and to vitrify the mineral part in a single compact reactor with water cooled walls. Elements losses and dust accumulation in the cooled modules are very low.

ACKNOWLAGEMENTS

We acknowlage the partial financial support of COmpagnie GEnérale des MAtières nucléaires (COGEMA).

REFERENCES

[1] T. Flament, M. Dupoizat, S. Carpentier, P. Coryn, *Proceedings of the International Incineration Conference*, Houston, USA, 1994.

[2] A. Jouan, J.P. Moncouyoux, R. Boen, R. Cartier, J.J. Vincent and T. Longuet, *Proceedings of the International Incineration Conference*, Bellevue, USA, 1995.

[3] J.P. Taupiac, *Thèse* n° 1566, Incineration de dechets nucléaires en plasma d'arc, Université Paul Sabatier, Toulouse, France, 1993.

[4] E. Meillot, *Thèse n° 234*, Contribution a l'étude d'un plasma d'arc de vapeur d'eau, Université Paul Sabatier, Toulouse, France, 1988.

[5] J. Goupy, La méthode des plans d'expérience, Dunod éditions, 1988.