# INTERMEDIATE LEVEL BURNABLE WASTE VITRIFICATION IN A REFRACTORY FREE FURNACE USING OXYGEN PLASMA

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## ABSTRACT

A new and simplified equipment, using thermal oxygen plasma with water cooled walls, is actually being developed at the Valrho-Marcoule nuclear center (France).

The reactor mainly consists of a cylinder, a roof and a crucible, all made of stainless steel with a water jacket system. A transferred arc plasma system has been preferred to a non-transferred one due to several reasons : the thermal transfer from the arc to the melt is better, the flowrate of plasma forming gas is lower and consequently, the size of the off-gas treatment equipment is smaller. To avoid classical problems induced by a bottom electrode, an oxygen plasma system design with the arc striked between two electrodes has been developped. The DC arc is transferred between two plasma torches above the glass melt which trap the mineral elements. The waste to vitrify is fed between the two electrodes, inside the arc zone so that temperature and turbulence between the two arc columns are higher than near a non-transferred plasma jet and the chemical reactions are enhanced by arc UV radiation. The plasma gas is oxygen, in order to achieve a perfect combustion on the surface.

As it will be shown, control in situ and in real time of the volatility of elements during plasma treatment is feasible. For this purpose, a new Optical Emission Spectroscopy method to probe metallic vapors above the melt has been experimented. It allows the measurement of the volatility of some elements according to the running parameters. The evolution of cesium leaving the melt is presented for exemple versus time and as a function of several treatment atmospheres.

## INTRODUCTION

Burnable radioactive waste management patterns are often in favour of the vitrification due to their volume reduction, resulting in cost saving for transport and storage. More, the interest is also to obtain a best radioactivity immobilization in a long-lasting matrix.

Significant advantages can be obtained by supplying burnable waste to treat directly into an **oxygen arc plasma** [1] to proceed both their volume reduction and their vitrification : the reached temperatures are very high and so is the efficiency of the combustion in the exited free oxygen rich atmosphere. Moreover, oxygen plasma can participate to a good oxidizing of the glass.

In order to minimize installation size, gasflowrate, technological waste (such as refractories) and to confine the radioelements in a glass matrix, a new and simplified equipment, using thermal oxygen plasma with water cooled walls, is actually being developed at the Valrho-Marcoule nuclear center (France).

## EXPERIMENTAL SET-UP

### Twin-torch transferred arc system

A transferred arc plasma system has been preferred to a non-transferred arc one due to several reasons the thermal transfert from the arc to the melt is better, the flowrate of plasma forming gas is lower and consequently the off-gas treatment size is smaller, the temperature and the turbulence between the two arc columns are higher than near a non-transferred plasma jet, the chemical reactions are enhanced by arc UV radiation. To avoid

problems induced by a bottom electrode, a plasma system design where the arc is striken between two electrodes has been preferred.

The twin-torch transferred arc system comprises two plasma torches of opposite polarity ( see Fig.1 ). The cathode torch consists of a thoriated tungsten water cooled pointed electrode. Two water cooled nozzles, feeding argon and oxygen, provide a shroud of plasma forming gas around the cathode and confines the arc attachment to the cathode. The anode torch is similar to the cathode one, however the anodic electrode is a high-purity water cooled button of copper. A spherical bearing arrangement allows variation of the angle between the torches and the inter-electrode gap, i.e. the distance between axis of the torches at their nozzle exits.

Two transferred arc plasma jets from opposite polarity electrodes are generated which impinge in a region located between the torches. In this remote location, termed the coupling zone, current can either be transferred through the plasma phase when the jets are coupled together, or through an external conductor which is introduced between the two plasma torches, such as the glass bath.

Arc intensity is from 150 to 300 A, distance between the tungsten cathode tip and the copper anode end is from 5 to 10 cm and the same between electrode tips and the melt surface. Plasma forming gas flow-rate is in the range of 20 to 200 Nl/mn for each electrode.

## The Reactor

The reactor mainly consists of a cylinder, a roof and a crucible, all made of stainless steel with a water jacket system. The inside diameter of the combustion chamber is 600 mm and the crucible diameter is 400 mm. The total heigh is about 800 mm. Two openings in the roof allow the entry of the twin plasma torches with an angle between them from 70 to 20°. Openings allow the feeding of the waste to treat directly in the plasma coupling zone or of the glass frit. The waste can be solid and/or liquid.

The gases are exhausted through a water cooled wall pipe and forwarded to the stack throug a high temperature filter and a wet scrubber using water and soda.

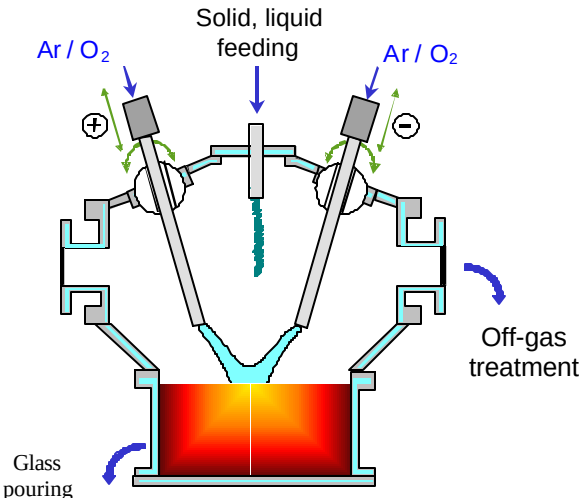


Fig. 1. Plasma furnace

## Running Parameters

The combustion vitrification of various kind of waste have been studied, such as: Ion Exchange Resins, cellulose, plastics, graphite sludge, alone or mixed with minerals (ashes, zeolite, …) or metallic particles.

The crucible recieve about 30 kg of glass frit, which composition is to be choosen according to the kind of waste to be treated. This frit is first melted during about 3 hours in order to obtain a sufficient glass bath. The temperature of the glas in the middle of the bath is held around 1200°C for an arc intensity of 200 A and a voltage of 100 V. Then, the waste is processed by direct feeding in the plasma. As the plasma columns radiation is very important, the waste generally ignite as early as it is introduced in the furnace and burn in the oxydizing atmosphere. The arc voltage increases during feeding, up to 250 V. With a moderate feeding flowrate of about 10 kg/h (depending of the waste), a perfect combustion is achieved in the oxygen plasma, on the surface of the bath, without accumulation. Glass pouring is possible after treatment. After each run, the products in each module of the installation are sampled and a material balance is made ; it shows a good transfert in the glass of the mineral elements of the waste. The elaborated glass is dark, glittering and very homogeneous in composition. Oxygen fugacity measurement in the elaborated glass shows that the oxygen plasma atmosphere above the molten glass seems to influence its oxidation degree ; i.e. glass is not reduced by combustion on the surface.

## OES DIAGNOSTIC OF THE BOUNDARY LAYER ABOVE THE MELT

A new optical emission spectroscopy method to probe metallic vapors above the melt has been experimented. This method may be runned, without sophisticated tomographic system, in the situation of non-homogeneous and optically thin plasma which exhibits a symmetry plane.

A numerical model, based on thermodynamic equilibrium at high temperature, on a twin resolution of radiative transfer equations for argon and metallic lines and on the plasma temperature profile in the direction of the measurement, has been developed. This plasma temperature profile is deduced from the ratio of two integrated intensities of argon lines and from an absolute value of one of them. To reach local concentrations of the metallic vapors in the plasma, the ratio of integrated intensities of an argon line and a metallic one, which are both measured above the melt, is used.

### Optical Emission Spectroscopy Measurement Arrangement

The twin-torch coupling zone at the surface of cold crucible has been imaged on the entrance slit of a monochromator with a reduction by a factor of 3 using a system of mirrors and lenses. The monochromator (Jobin-Yvon THR 1000, Czerny-Turner type) has 1 m focal length, F/9 aperture and 1200 grooves/mm holographic grating. The emission spectra of the plasma have been detected at the monochromator exit plane by a silicon intensified target (SIT Vidicon OMA 2 PAR 1254) driven by PAR 1216 controller. The controller and the monochromator are interfaced with a HP 9000 computer.

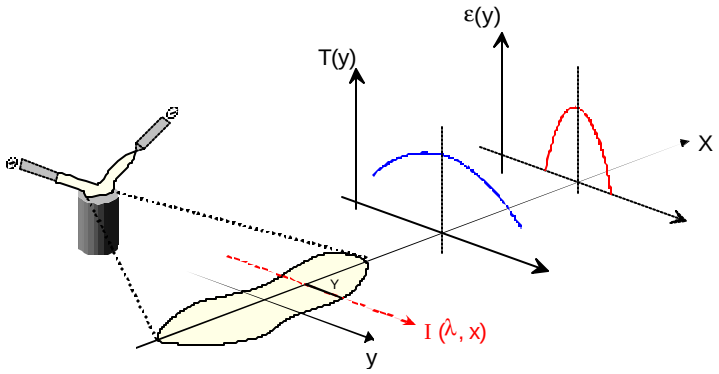


Fig. 2. OES diagnostic parameters

The observation direction y, has been chosen to be perpendicular to the plane of both torches ( see Fig. 2 ). The twin-torch image has been oriented in such a way, that the line connecting both nozzle exits (x-coordinate in Fig. 2) is parallel to the entrance slit edges. In this manner, a distribution of spectral radiation intensities for the twin-torch plasma thin layer along x coordinate have been measured. Positioning of the twin-torch image is accomplished with a He-Ne laser and external optics with a micrometric transfer system. A tungsten ribbon lamp is imaged onto the entrance slit by rotation of the mirror system to provide a radiation energy calibration.

A mean wavelength interval, recorded by the OMA detector, is about 9 nm. The recording system dynamic range (normally $5\times10^2$) has been increased up to $10^5$ using a set of calibrated neutral optical filters. The intensity measurement error is estimated to be ±10%. The spectral apparatus function of the system has a Lorentzian profile with the half-width of 0.08 nm. A time resolution of the system is determined by the OMA target reading time, which has been varied in the interval 70 - 300 ms.

An axial symmetry approximation, commonly used for OES measurements in arcs and plasma jets is not applicable to the twin-torch plasma under study. The approximation and common Abel inversion technique, can only be used for measurements of the plasma local emissivity near the electrode zones of the twin-torch, where the twin-torch arc is similar to a common transferred arc. For other twin-torch plasma regions, especially for the jet coupling zone, the approximation is not valid.

For the twin-torch configuration shown in Fig. 2, the electrode axes are in a common plane and the spatial distribution of the plasma parameters can be presented as having a plane symmetry, i.e. the plasma temperature has a maximum in the plane and decreases monotonously either side of it. For low-temperature thermal plasmas with such parameter distributions, one can use the technique of local parameter measurements in plasmas having no axial symmetry, developed in [2]. The technique is based on a fast (exponential) decrease of thermal plasma emissivity with a plasma temperature drop, at a constant pressure. This approach avoids an Abel inversion and simplifies the experimental data treatment in optical diagnostics of plasmas having axial symmetry. This technique can be also used to measure the parameters of plasmas with arbitrary temperature distributions, provided the distribution satisfies the above condition in the observation direction [2].

## Local Measurement Fundamentals

The radiation intensity $I(\lambda,x)$ of an optically thin plasma volume of plane symmetry, which is measured in a direction y perpendicular to the symmetry plane, is given by :

$$I(\lambda, x) = 2 \int_0^{y_{lim}} \varepsilon(\lambda, y)\, dy \qquad \text{(Eq. 1)}$$

where $\varepsilon(\lambda, y)$ is the plasma emissivity. The volumic emission coefficient $\varepsilon(y)$ of an atomic line at position y is given by :

$$\varepsilon(y) = \int_{profil} \varepsilon(\lambda, y)\, d\lambda \qquad \left(\frac{W}{m^3\, sr}\right) \qquad \text{(Eq. 2)}$$

The plasma volume is supposed to have an arbitrary monotonous temperature profile along the line of sight ( y ) having the maximun temperature ( $T(x,y=0) = T_0$ ) in the plane symmetry. The profiles can be presented in the following way :

$$T(y) = T(x,0)\, \frac{1}{1+(y / y_0)^{l}} \quad \text{with } 1 \le l < \infty \qquad \text{(Eq. 3)}$$

$y_0$ is a parameter determining the volume dimension along y: $y_0$ is the distance from the symmetry plane where temperature is $T_0 / 2$. l gives the profile form: from a linear ( l = 1 ), plasma with a steep temperature gradient) to a rectangular one one ( $l = \infty$, homogeneous plasma ); parabolic profil ,i.e. l = 2, has been showed to be the best value to satisfy the experimental results. So, the temperature profile is fully determined by $T_0$ and $y_0$ .

For a close-to LTE plasma, the spectral line emissivity can be expressed in theform:

$$I(x) = 2\, \frac{1}{4p}\, \frac{h\, c\, A\, g}{l} \int_0^{y_{lim}} \frac{N(T(y), a(y))}{Q(T(y))} \exp\left(\frac{-E_m}{kT(y)}\right) dy \qquad \text{(Eq. 4)}$$

where g and Em are respectively the statistical weight and energy of the upper level of the optical transition under consideration with a transition probability A; N and Q are the total density and partition function of emitting particles; $\lambda$ is the spectral line wavelength; c, h and k are the velocity of light, Planck's constant and Boltzmann's constant, respectively.

N, here density of the considered metallic element, is a function of the position y, of the local temperature T(y) and, overall, of the local chemical composition described by $\alpha(y)$ which is the ratio of considered metal nucleus ( Pb, Pb+,...) volumic densities on argon (Ar,Ar+,...) volumic density. In the followings, this parameter $\alpha(y)$ has been considered as nearly constant on the observed part of the melt surface and equal to a mean value $\alpha$. **The measurement objective is to reach a.**

A spectral line emissivity has a maximum value at a so-called "norm temperature" $T_m$.[3] .At $T < T_m$ the particle total density N(T) changes with temperature slower than the Boltzmann exponent, and an approximation can be used [4].

$$e(\mathrm{T(y)}) \propto \exp\left[-\frac{\mathrm{Em}}{\mathrm{kT(y)}}\right]. \qquad \text{( Eq. 5 )}$$

According to Eq. (3), for plasma volumes with a monotonous fall of temperature from the maximum value $T_0 = T(y = 0)$ at the symmetry plane to the periphery, the measured intensity I(y) is due mainly to a small plasma layer where the temperature reaches its maximum T(x,y=0). So I(y) can be expressed using local plasma characteristics in the symmetry plane volume.

For the plasma volumes under consideration, with a parabolic temperature profil, if Em satisfies Em >> k.T(x,0), and it is the situation for the used argon lines, it has been shown [4, 5] that the "line-of-sight" radiation intensity I(x), at x coordinate, can be approximated using the emissivity (maximum) value, at y = 0, as follows:

$$I(x) = e\left(T(x,0)\right)\ \mathrm{y_0}\ \sqrt{p}\ \left(\frac{k\,T(x,0)}{E_m}\right)^{1/2} \qquad \text{( Eq. 6 )}$$

For metallic lines,such as used lead lines, it ahs been numerically showed, via Eq. (4), that I(x) is also proportional to $y_0$. Consequently, the ratio of intensities of an argon line and of a metallic line is independent of $y_0$.

By measuring the intensities of two spectral lines of the same atom, which are due to transitions from levels with energies $E_{m1}$ and $E_{m2}$, one can find from Eq. (6) the maximum plasma temperature value, $T_0(x)$, in the symmetry plane, along the observation line, at x :

$$\mathrm{T(x,0)} = \frac{\mathrm{E_{m2} - E_{m1}}}{\mathrm{k}} \left\{ \mathrm{Ln}\left[ \frac{\mathrm{I_2(x)\ A_1\ g_1\ \lambda_2}}{\mathrm{I_1(x)\ A_2\ g_2\ \lambda_1}} \left(\frac{\mathrm{E_{m2}}}{\mathrm{E_{m1}}}\right)^{1/2} \right] \right\}^{-1} \qquad \text{( Eq. 7 )}$$

Note that $y_0$ could be obtained from Eq.(6).

From Eq.(7), it is seen that the measured temperature value will be so much accurate as the energies $E_{m1}$ and $E_{m2}$ will be different. Besides, in order to avoid energy calibration versus wavelength, and to be free from plasma fluctuations, the two lines are selected to be on the same target, i.e. the wavelength difference of the two lines must be less than 80 nm. So, ArI,696.5 nm and ArI,703 nm lines have been selected.

Vapor phase composition is computed, assuming LTE, via Saha equation, mass balance, electrical neutrality and Dalton law. It will be showed that inside the plasma phase, the metal densities are very much lower than argon densities ( 4 or 5 order of magnitude).So plasma is supposed constituted of Ar, Ar+, e- and only of M and M+, where M represents the metal under consideration; its lines emissivities are supposed not to be modified by other metallic vapors densities; this approximation will be justified a posteriori.

Previously, with an $y_0$ arbitrary value, for a set of temperatures from 7000 to 13000 K, the ratio of selected argon and metal lines intensities are computed versus metallic vapor content, represented by $\alpha$ ( see Fig. 2 ). Practically, Eq.(4) is summed from 0 to $y_{lim}$ as $T(y_{lim}) = 2000$ K.

Experimentaly, the two argon lines first and selected argon line and metallic line secondly are registered; for each line of sight along (y) at position (x), T(x,y=0) is measured using the two argon lines. Then from the measured ratio of argon line and metallic line intensities, via an iterative method, $\alpha$ is reached.

In the symmetry plane where $T_0$ is about 11000 K, an error of 5 % on temperature leads to an error of 200 % on metal vapor density, but it is the magnitude of order which is important.

## Experimental Results

The interest of the plasma diagnostic concern all the metalic elements volatility. The study presented here was carried out with a natural basaltic glass including cesium as tracer, incorporated during elaboration at 1350°C for one hour in a resistance heated furnace.

The used lines are 672.32 nm for CsI and 667.72 nm for the composition calculation associated ArI line. The following figures present the 1/a ratio, that is the ratio [Cs]+[Cs+] / [Ar]+[Ar+] in the plasma. The arc intensity is

always 250 A and differents plasma atmospheres are tested, the arc voltage is a function of these gases but is about 70 V.

The knowledge of the plasma temperature ($T_0$ in the symetry plane) is the first step necessary for the calculation of the plasma composition. Figure 3 presents a $T_0$ measurement, we can see that the cathodic jet shift to the anode the plasma geometry due to its higher quantity of motion.

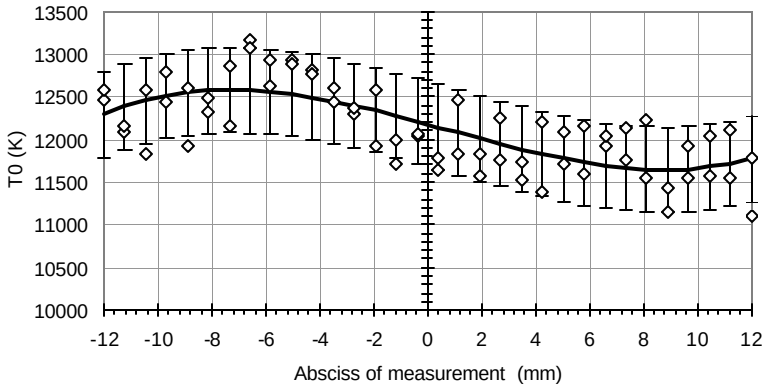


Fig. 3. Temperature of the plasma in the symetry plane

Figure 4 shows the evolution of cesium volatility versus time in the case of a neutral atmosphere (Ar). An exponentail decrease of cesium above the melt can be observed. This phenomenon can fit with a global depletion of cesium in the liquid phase or a surface depletion due to a diffusionnal limitation of Cs in the glass. However, EDS analysis of the glass along its deepness did not confirm one or the other of theses hypothesis because of the analysis device detection limit.

The influence of an oxidizing atmosphere is clearly displayed on figure 5. After 18 minutes, 20 l/min of oxygen are introduiced in the plasma, an order of magnitude increase of the cesium volatility can immediately be observed.

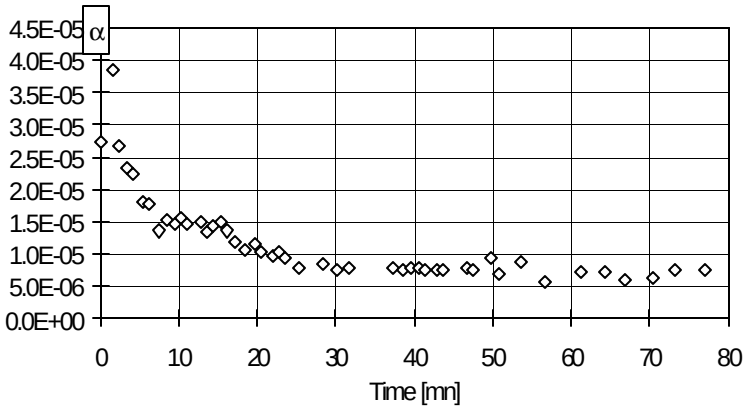


Fig. 4. Evolution versus time of Cs vapors concentration in the plasma.above the melt

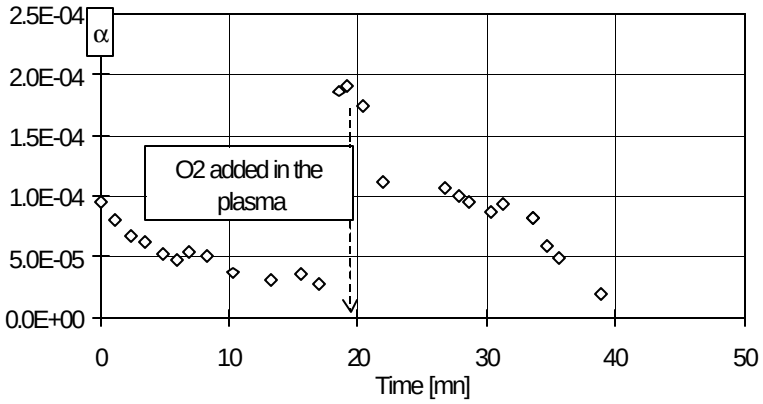


Fig. 5. Influence of oxygen on Cs volatility

We have also shown that the introduction of a small amount of hydrogen in the plasma leads to the same effect. The volatility of cesium increase in the case of a reducing atmosphere very likely by the reduction of the cesium oxide and metal release whereas in the case of a Ar/O2 plasma, it is the formation of a very volatil cesium peroxide that leads to increase the volatility.

## CONCLUSION

The transferred Twin-torch oxygen plasma arc system associated with a cold crucible actually been developped at the Valrho-Marcoule nuclear center (France), allows the melting/vitrification of several kg/h of various burnable and/or non burnable waste. The $O_2$ plasma ensures a quasi-instantaneous melting of the load injected and combustion of the waste. All the treatment of the waste is the achieved in a small refractory free single reactor : combustion, vitrification and gas burning.

As far as the volatility of the glass elements is concerned, it appears that a tool to probe in real time and in-situ the vapors above the melt is highly required. For this, a new optical emission spectroscopic method has been experimented. The evolution versus time of metallic vapors concentrations during melting have been followed. By the same, the influence of various parameters such as the plasma forming gases composition on metals vaporisation has been studied. It has been shown that steep variation of the volatility of some elements are induced by low reducing potential of the plasma atmosphere. In the particular case of cesium, we could also observe the increase of the volatility in the case of an oxidizing atmosphere.

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