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TRANSPORTATION OF RADIOACTIVE WASTE CONTAINING ORGANIC MATERIALS: NEW METHODOLOGY BASED ON OXYGEN CONSUMPTION

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ABSTRACT

The French Atomic Energy and Alternative Energies Commission carries research programs in various nuclear fields, including radioactive waste management. These activities require transport of different types of radioactive materials with a wide range of transport packages. CEA packaging are designed, constructed and operated to meet safety and regulatory requirements. Application for package approval requires a complete and thorough safety demonstration in which flammable gas generation mechanism have become a major issue in the last few years.

Depending on the type of waste and conditioning, CEA has developed different approaches. One of the critical problems concerns organic materials within waste packages and conditioned in closed containers, where gas release is limited by diffusion through a barrier such as a polymer film or a cement matrix. Then, hydrogen produced by organic materials radiolysis accumulates in the interstices between the waste, occurring potential flammable conditions. Most of current safety studies focus only on the production of flammable gas, which is often too conservative: in parallel to hydrogen release, oxygen consumption leads to the depletion of the combustive. CEA laboratories have developed a methodology based on the concomitant production of hydrogen and oxygen consumption by radiolysis of organic materials. This approach was applied to transport packages used for some cemented waste produced in CEA waste treatment facilities.

Using a simple mathematical model, a generic non-flammable criterion is deduced. It depends principally of the ratio of the mean hydrogen radiolytic yield to the mean radiochemical yield of oxygen consumption for waste materials.

Generally this criterion is rather easy to fulfill for gamma or beta irradiation, but not always for alpha irradiation. A specific experimental program was developed to evaluate hydrogen emission and oxygen consumption for organic materials in contact with alpha particles in intermediate-level long-lived waste. Simulation of alpha particles was performed using high energy swift heavy ions. This presentation will precise situations in which this demonstration applies, present the different hypothesis and justify the choice of irradiation conditions to simulate alpha particles. Finally the effect of parameters such as temperature, dose rate and atmosphere will be discussed.

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INTRODUCTION

This work aims to demonstrate the absence of inflammation risk in historical waste mainly contaminated by alpha emitters (Pu-238, Pu-239, Pu-240, Pu-242, Am-241) in their oxide forms. The activity is about a few GBq/g of Pu oxides. Only radiolysis due to alpha particles is discussed in this document, since beta particles and gamma radiation represent only 2% of total power.

The first part describes how we can determine a non-flammable criterion in given situations with different hypothesis. This methodology is based on oxygen consumption in parallel to hydrogen production by radiolysis.

The second part presents the experiment program carried on different materials (polyvinyl chloride, neoprene, polyethylene, cellulose and polypropylene) that are the most present in radioactive waste produced by CEA facilities.

We justify the choice of irradiation conditions to simulate alpha particles and give results for studied materials.

Finally the effect of parameters such as temperature, dose rate and atmosphere will be discussed in relation with the non-flammable criterion.

DEFINITION OF A NON-FLAMMABLE CRITERION

Methods

Let's consider some wastes containing several components k contained in a volume surrounding by an envelope such a plastic bag or a cement matrix. The amounts of H_2 and O_2 within the volume are calculated from the following equations:

$$\frac{dN_{H_2}}{dt} = \sum_k G_{H_2}^{\alpha,k} \times P_{abs}^{\alpha,k} - Q_{H_2}$$

with: N_{H_2} : moles of H_2 within the volume
  $G_{H_2}^{\alpha,k}$: H_2 formation radiolytic yield of component k (mol/J)
  Q_{H_2} : H_2 permeation rate through the envelope (mol/s)

$$\frac{dN_{O_2}}{dt} = -\sum_k G_{-O_2}^{\alpha,k} \times P_{abs}^{\alpha,k} - Q_{O_2}$$

with: N_{O_2} : moles of O_2 within the volume
  $G_{-O_2}^{\alpha,k}$: O_2 consumption radiolytic yield of component k (mol/J)
  Q_{O_2} : O_2 permeation rate through the envelope (mol/s)

$P_{abs}^{\alpha,k}$ is the component k absorbed power. We suppose that it can be written: $P_{abs}^{\alpha,k} = f_k^\alpha \times P_{abs}^\alpha$, where $P_{abs}^{\alpha,k}$ is the absorbed power by all the components within the volume.

The two previous equations can then be written:

$$\frac{dN_{H_2}}{dt} = \overline{G}_{H_2}^\alpha \times P_{abs}^\alpha - Q_{H_2} \qquad \text{with:} \quad \overline{G}_{H_2}^\alpha = \sum_k f_k^\alpha \times G_{H_2}^{\alpha,k}$$
$$\frac{dN_{O_2}}{dt} = -\overline{G}_{-O_2}^\alpha \times P_{abs}^\alpha - Q_{O_2} \qquad \text{with:} \quad \overline{G}_{-O_2}^\alpha = \sum_k f_k^\alpha \times G_{-O_2}^{\alpha,k}$$

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The above equations simply express that, within the volume:
- hydrogen is produced by radiolysis and it diffuses out through the membrane;
- oxygen is consumed by radiolysis and it diffuses from outside.

The ratio χ is defined as follows: $\qquad \chi = \dfrac{\overline{G}^{\alpha}_{-O_2}}{\overline{G}^{\alpha}_{H_2}}$

H_2 and O_2 permeation rates through the envelope are proportional to partial pressures difference between the inside and the outside of the envelope:

$$Q_{H_2} = A_{H_2} \times \left(p^{int}_{H_2} - p^{ext}_{H_2}\right)$$

with: A_{H_2} :   proportionality constant
          $p^{int}_{H_2}$: H_2 partial pressure within the envelope
          $p^{ext}_{H_2}$: H_2 partial pressure outside the envelope

$$Q_{O_2} = A_{O_2} \times \left(p^{int}_{O_2} - p^{ext}_{O_2}\right)$$

with: A_{O_2} :   proportionality constant
          $p^{int}_{O_2}$: O_2 partial pressure within the envelope
          $p^{ext}_{O_2}$: O_2 partial pressure outside the envelope

H_2 and O_2 partial pressures within the envelope are expressed as a function of their respective amounts within the envelope:

$$p^{int}_{H_2} = \frac{N_{H_2} \times R \times T}{V_L} \qquad \text{and} \qquad p^{int}_{O_2} = \frac{N_{O_2} \times R \times T}{V_L}$$

with: R :   molar gas constant
          T :   temperature
          V_L : free volume within the envelope which is assumed to be constant

We assume that:
- initial oxygen partial pressure within the envelope is equal to partial pressure outside, so we can write: $p^{ext}_{O_2} = p^0_{O_2} = \dfrac{N^0_{O_2} \times R \times T}{V_L}$,
  where $N^0_{O_2}$ is the initial O_2 amount within the envelope;
- the volume outside the envelope is large enough to consider that $p^{ext}_{H_2} \approx 0$.

The hydrogen percentage within the envelop can be written: $\%H_2 = \dfrac{N_{H_2}}{N_T}$, where N_T is the total amount of gases.

After a transitional period, a steady state will be established: $\dfrac{dN_{H_2}}{dt} = \dfrac{dN_{H_2}}{dt} = 0$,

then we calculate $N^{\infty}_{H_2}$ and $N^{\infty}_{O_2}$:

$$N^{\infty}_{H2} = \left(\frac{\overline{G}^{\alpha}_{H2} P^{\alpha}_{abs}}{A_{H2}}\right) \frac{V_L}{RT}$$

$$N^{\infty}_{O2} = N^0_{O2} - \left(\frac{\overline{G}^{\alpha}_{-O2} P^{\alpha}_{abs}}{A_{O2}}\right) \frac{V_L}{RT}$$

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$N_{O_2}^{\infty}$ expression has meaning only if the O_2 partial pressure is greater than or equal to 0:

$$\frac{\overline{G}_{-O2}^{\alpha} P_{abs}^{\alpha}}{A_{O2}} \leq \frac{N_{O2}^{0} RT}{V_L} = p_{O2}^{0}$$

Let's define the following quantity: $\mu = \dfrac{Q_{O_2}^{max}}{\overline{G}_{-O_2}^{\alpha} \times P_{abs}^{\alpha}}$.

$Q_{O_2}^{max} = A_{O_2} \times p_{O_2}^{0}$ represents the maximum rate of oxygen permeation through the membrane. We can distinguish the three following cases:

- $\mu \geq 1$: O_2 permeation rate is greater than its consumption rate;
- $\mu < 1$: O_2 permeation rate is less than its consumption rate;
- $\mu = 0$: the envelope behaves like a closed and hermetic container.

ΔN_{O_2} is proportional to N_{H_2}: $\Delta N_{O_2} = N_{O_2}^{0} - N_{O_2} = r \times N_{H_2}$

Given that: $N_T \leq N_T^0 - \Delta N_{O_2}$, we can deduce an upper limit to $\%H_2$:

$$Max\ (\%H_2) = \frac{1}{r} \times \frac{\%O_2^0 - \%O_2(t)}{1 - \%O_2(t)} \times \frac{1}{1 - \%O_2^0}$$

with: $\%O_2^0$:   initial O_2 percentage within the envelope
$\%O_2(t)$: O_2 percentage within the envelope at time t

We calculate the evolution of $N_{O_2}(t)$ and $N_{H_2}(t)$ in order to determine the following expression for $\%H_2$:

$$\%H_2 \leq \frac{\overline{G}_{H_2}^{\alpha} \times P_{abs}^{\alpha}}{A_{H_2} \times p_{O_2}^{0}} \times \left(\frac{N_{O_2}^{0}}{N_T^0 - N_{O_2}^{0}} - \frac{N_{O_2}}{N_T} \right) \times \left[1 - \left(1 - \frac{p_{O_2}^{ext} \times A_{O_2}}{\overline{G}_{-O_2}^{\alpha} \times P_{abs}^{\alpha}} \right)^{\alpha} \right]$$

Let's define the ratio of membrane permeability coefficients: $\nu = \dfrac{A_{H_2}}{A_{O_2}} = \dfrac{P_{H_2}}{P_{O_2}}$.

$\%H_2$ upper limit can be written: $Max\ (\%H_2) = \frac{1}{\chi} \times g(\mu, \nu) \times \frac{\%O_2^0 - \%O_2(t)}{1 - \%O_2(t)} \times \frac{1}{1 - \%O_2^0}$

with: $g(\mu, \nu) = \frac{1}{\nu} \times \frac{1}{\mu} \times [1 - (1 - \mu)^{\nu}]$

We can now deduce a criterion for non-flammability. H_2 percentage should not exceed the Lower Flammable Limit (LFL) before O_2 percentage is less than the Minimum Oxygen Concentration (MOC), defined as limiting concentration of oxygen below which hydrogen combustion is no more possible.

$$\%H_2 < LFL \iff \chi = \frac{\overline{G}_{-O_2}^{\alpha}}{\overline{G}_{H_2}^{\alpha}} > g(\mu, \nu) \times \frac{1}{LFL} \times \left(\frac{\%O_2^0}{1 - \%O_2^0} - MOC \right)$$

Table 1 below gives the different results for this criterion.

Table 1: criterion for non-flammability in a plastic envelop

LFL = 3.6% [1] $\%O_2^0 = 20.6\%$	Criterion for χ
MOC = 0%	$\chi > 7.2 \times g(\mu, \nu)$
MOC = 4.5% [2]	$\chi > 5.9 \times g(\mu, \nu)$

[1] The LFL considered here is the lower flammability limit of hydrogen in air at 85°C. It can be underlined that this statement is very disadvantageous as it does not consider the LFL increase while the oxygen concentration in the air decreases.

[2] Based on the INRS work [1], there is no hydrogen explosion hazard when the oxygen proportion in the air is below 4.5% (MOC = 4.5%).

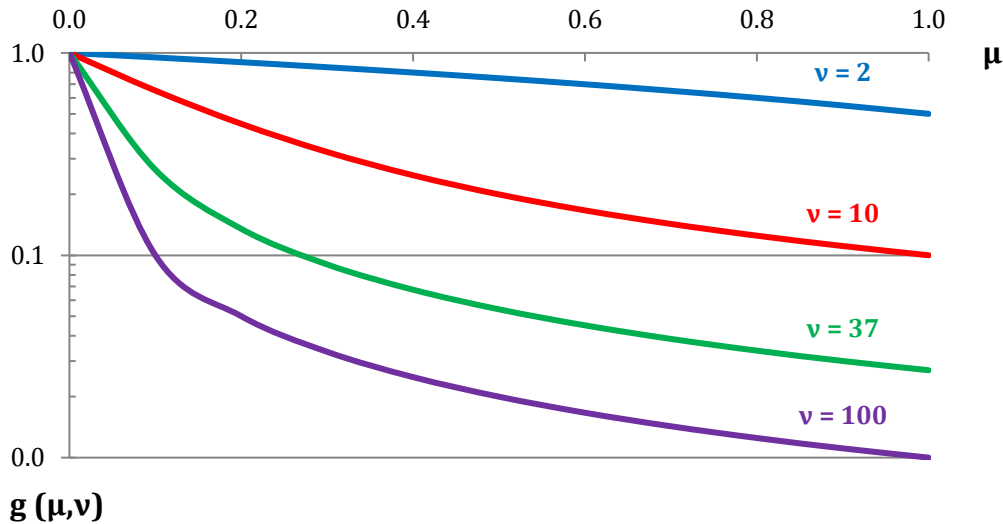Figure 1 shows the variation of the function g for different values of ν and μ.

Figure 1 : Variation of the function g for different values of ν and μ

The function g(μ,ν) can be simplified when for μ ≥ 1 and μ = 0.

If μ ≥ 1: $g(\mu, \nu) \le \frac{1}{\nu}$. In that case, the non-flammability criterion can be written:

$$\%H_2 < \text{LFL} \iff \chi = \frac{\overline{G}_{-O_2}^\alpha}{\overline{G}_{H_2}^\alpha} > \frac{1}{\nu} \times \frac{1}{LFL} \times \left(\frac{\%O_2^0}{1 - \%O_2^0} - \text{MOC} \right)$$

If μ = 0: $g(\mu, \nu) = 1$. In that case, the non-flammability criterion can be written:

$$\%H_2 < \text{LFL} \iff \chi = \frac{\overline{G}_{-O_2}^\alpha}{\overline{G}_{H_2}^\alpha} > \frac{1}{LFL} \times \left(\frac{\%O_2^0}{1 - \%O_2^0} - \text{MOC} \right)$$

<u>Results</u>

Observing that:

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- H$_2$ permeation is always greater than O$_2$ permeation ($\nu > 1$);
- g(μ,ν) is always less than 1, for any value of μ and ν;

we deduce that the criterion corresponding to $\mu = 0$ is the most penalizing (the volume behaves like a closed and hermetic container):

There is no risk of flammability in the volume when the ratio χ is greater than 5.9.

The following diagram presents an approach to determine the relevant flammability criterion.
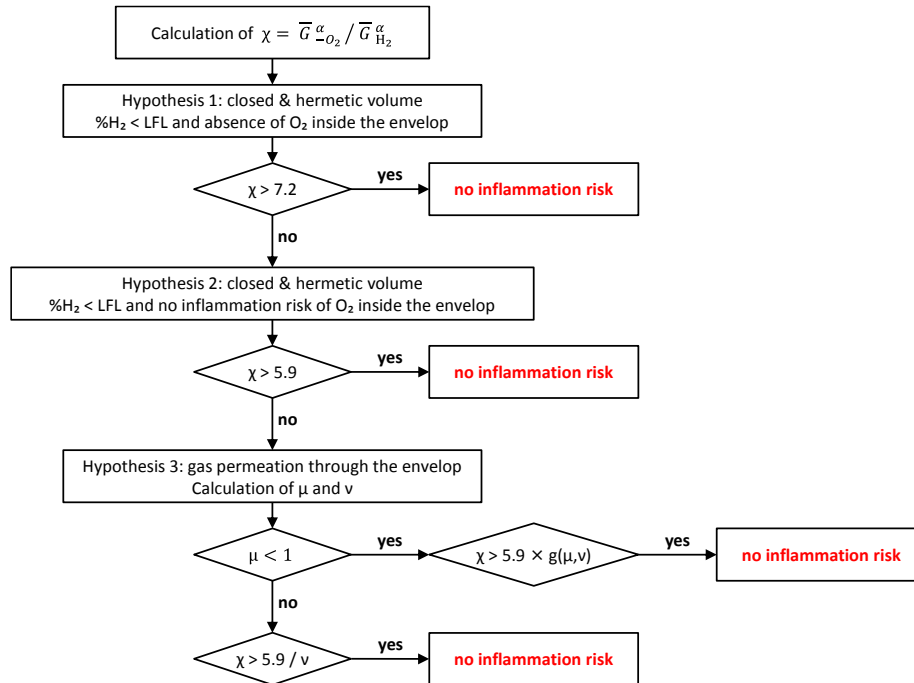

Figure 2: Determination of a relevant non-flammable criterion

IRRADIATION EXPERIMENTS

Given the limited available data on alpha irradiation of polymers in oxidizing conditions, a specific experimental program was performed to evaluate hydrogen emission and oxygen consumption for polymers representative of the materials in nuclear wastes, such as PVC or cellulose.

Irradiation conditions

In order to be representative of actual irradiation conditions in alpha wastes, the irradiation simulation needs to be carried out with particles with linear energy transfer (LET) similar to alpha particles (500-2000 keV/µm) and under oxidizing conditions. The relative high LET of alpha particles exacerbates energy deposition heterogeneity and increases the local concentration of primary radiolysis products.

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Heavy ions simulating alpha particles are chosen such that their stopping power is close to the maximum stopping power calculated for alpha particles emitted by most actinides. As the materials were packaged in sealed glass ampoules we chose sufficiently energetic particles (mainly Ar-36 ions of 95 MeV/A) to pass through the ampoule glass while maintaining a constant LET in the irradiated materials contained in the ampoule. These constraints led us to carry out the irradiations at the GANIL facility. The temperature was between 20°C and 25°C. Due to a lack of time allowed on the high energy line, it has been chosen to use high dose rates, of the order of 500 kGy/h.

Several samples in the form of thin films are stacked and simultaneously irradiated (see Figure 3 below). Material thickness has been determined by imposing homogeneous oxidation while samples number has been set such that the energy deposition variation in each film does not exceed 25%.
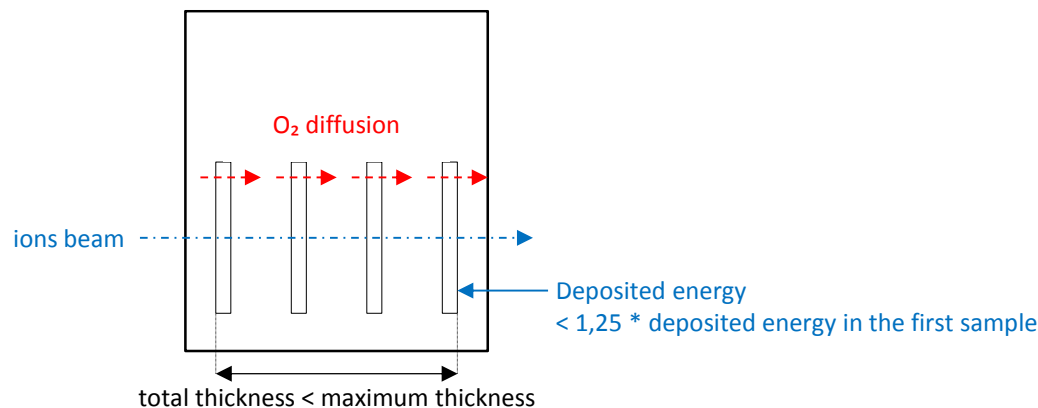

Figure 3: Schematic representation of films superposition in an ampoule

Polymers have been packaged in ampoules under 800 mbar of reconstituted air pressure with krypton tracer for gas analysis (20.2% O_2, 74.77% N_2, 5.03% Kr).

The ampoules were analyzed after irradiation using high resolution mass spectrometry.

Results

Table 2 below summarizes the irradiations characteristics for each material and gives gases radiolytic yields. Some results for gamma irradiation (Co-60) are added for comparison.

Table 2: Radiolytic yields from polymers irradiated with heavy ions simulating alpha particles

Material	Thickness (μm)	Irradiation type / ions	LET (keV/μm)	Dose (kGy)	Temperature	Radiolytic yields (10^{-7} mol/J)		χ
						$\overline{G}^{\alpha}_{H_2}$	$\overline{G}^{\alpha}_{-O_2}$	
Polycarbonate	1800	gamma	0.19	50	25°C	0.02	1.3	65.0
	15	alpha	283	2019	25°C	0.10	2.3	23.0
	15	alpha	283	4060	25°C	0.07	1.2	16.9
Polyvinyl chloride	20	gamma	0.19	81	25°C	0.31	8.3	26.8
	20	gamma	0.19	24	80°C	0.79	68.0	86.1
	20	alpha / Ar-36	286	473	25°C	0.69	6.20	9.0
	20	alpha / Ar-36	329	924	25°C	0.62	6.2	10.0

Material	Thickness (μm)	Irradiation type / ions	LET (keV/μm)	Dose (kGy)	Temperature	Radiolytic yields (10⁻⁷ mol/J)		χ
						$\overline{G}^{\alpha}_{H_2}$	$\overline{G}^{\alpha}_{-O_2}$	
	20	alpha / Ar-36	329	2013	25°C	0.49	5.2	10.7
Neoprene®	160	alpha / S-32	221	904	25°C	0.25	7.4	29.6
Polyethylene	20	alpha / Ar-36	239	524	25°C	4.3	8.8	2.0
Cellulose	15 to 30	alpha / Ar-36	339	3870	25°C	1.4	2.5	1.8
Polypropylene	47	alpha / S-32	185	1010	25°C	3.5	19.6	5.6

DISCUSSION

LET influence

Deposition of energy induced in materials differs between beta particles and gamma radiation on the one hand, and alpha particles and neutrons on the other hand. Alpha and neutrons lead to a 1000 times stronger LET than beta/gamma. The main effect of LET is to exacerbate the energy deposition heterogeneity, and to increase the primary radiolysis products local concentration.

Dély and al. ([2]) show that an increase of the LET leads mainly to a reduction of the oxidation consumption.

We verified this result for two materials: polycarbonate and polyvinyl chloride (see Table 2). The χ ratio obtained with gamma radiations is approximatively 3 times higher than those measured for heavy ions.

Dose influence

For polymers, dose effect on gas radiolytic yields is relatively well documented in inert atmosphere. A global decrease of hydrogen yields is observed for common polymers.

Ferry and col. ([3]) extend this result to oxidizing conditions. They show that radiochemical yields of hydrogen formation and oxygen consumption of polyethylene decrease when the dose increases. This decrease is explained by a protective effect of radio-induced defects. These defects act as energy sink.

Results, presented in Table 2 for PC and PVC, confirm that hydrogen production and oxygen consumption yields decrease and reveal that the ratio χ tends to increase with the dose.

Dose rate influence

In oxidizing conditions two different dose rate effects have been observed, the first is related to the kinetics of oxidation and the second to the diffusion of oxygen.

Chemical effect of dose rate on polymer oxidation

The oxidation of irradiated polymers proceeds via a well-known chain reaction ([4]). It results high G_{-O_2} values that depend of the dose rate and are described by the following equation ([5]): $G_{-O_2} = \alpha + \beta/\sqrt{d}$

In conclusion:
- At high dose rate (> 400 kGy / h), oxygen consumption yield tends towards a constant;

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- At low dose rate, a dose rate effect is observed: in the absence of effective radical capture, polymer oxidation increases while the dose rate decreases.

Physical effect of dose rate on polymer oxidation

Under oxidizing conditions, oxygen diffusion inside the polymer must be considered: oxygen diffusion from outside the material has to be fast enough to compensate for its consumption. For a given oxidation rate, a critical thickness can be determined beyond which the inner material is not homogeneously oxidized ([6]).

In our experiments the thickness of the films was always less than the critical thickness, in order to observe phenomena in a context of material homogeneous oxidation.

Atmosphere influence

Simulation irradiations have been carried out under oxidizing conditions, in order to be representative with wastes stored in air. The oxidized layer in the material depends on the oxygen permeation coefficient and the oxidation kinetics but also for alpha particles on the range of the particles in the material. In the case of polymer contaminated with Pu oxides the critical oxidized layer thickness is estimated to be greater than the mean range of alpha particles which is only a few tens of μm. Thus, in real conditions, polymer oxidation is not limited by the oxygen diffusion.

Temperature influence

There is almost no data available on the effect of temperature on alpha irradiation for polymers. On the basis of the results obtained with gamma irradiation for different polymers such as polyethylene, polyvinyl chloride, etc. it is concluded that temperature effect is generally moderate on the dihydrogen production but it accelerates greatly polymer oxidation. Above room temperature the radiation-induced oxidation is controlled by chain propagation. Then the activation energy of the oxygen consumption yield is expected to be between 30 and 50 kJ/mol.

The decomposition of unstable oxidized products (hydroperoxides, peracids, peresters, etc.) can also contribute to the acceleration of the oxidation rate with temperature.

In Table 2 the values measured for gamma-irradiated PVC at 80°C in air are reported. The results confirm the significant increase in the ratio χ with temperature.

CONCLUSION

A generic non-flammable criterion is deduced for waste packages containing organic materials that release gases, whose diffusion is limited by an envelope such as a polymer bag or a cement matrix. It depends on the ratio of the mean hydrogen radiolytic yield to the mean radiochemical yield of oxygen consumption for waste materials and on the ratio of the permeation rates of hydrogen and oxygen through the envelope.

Given the lack of data available on alpha irradiation of polymers in presence of oxygen, a specific experimental program was performed to evaluate hydrogen emission and oxygen consumption for polymers representative of the materials in nuclear wastes, such as PVC or cellulose.

Simulation irradiation parameters (particle type, dose rate, atmosphere and temperature) have been chosen in order to minimize the ratio of oxygen consumption to dihydrogen production.

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Experiments carried out on the GANIL high-energy line showed that the most binding non-flammability criterion (hermetic container) is verified for PVC, PC and neoprene®.

There is no explosion risk even if hydrogen proportion reaches the LFL of hydrogen in air: oxygen proportion will be too low to induce a risk of explosion.

For other materials, such as cellulose, polyethylene and polypropylene, the non-flammability criterion is not verified in a closed hermetic volume. The absence of explosion risk will then depend on the characteristics of the envelope in which wastes are conditioned.

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