BEHAVIOUR OF BITUMINIZED RADIOACTIVE WASTES UNDER IRRADIATION

S.CAMARO, T.GILARDI, P.P. VISTOLI
CEA/DCC/DESD/SEP/LCCM – C.E. Cadarache –F 13108 Saint-Paul Lez Durance

ABSTRACT

Studies are carried out by the CEA in order to predict the behaviour of bituminized radioactive wastes under self irradiation. Bitumen radiolysis produces gas (mainly H_2) which diffuses in the organic matrix. If the hydrogen yield is higher than the diffusion flux through the free surface, hydrogen concentration increases and exceeds its solubility in bitumen. Beyond saturation, bubbles are formed and gas is also evacuated by bubbles drift. The aim of these studies is to evaluate the evacuation capacity of radiolytic gas produced in function of initial bituminized wasteform characteristics. A model was developed to achieve this purpose, by calculating the evolution of bubbles population considering all elementary mechanisms of gas evacuation.

INTRODUCTION

Bituminized waste drums mainly result from the treatment/conditioning of Low and Medium Activity (LMA) liquids produced by the different steps of spent fuel reprocessing. In Marcoule, about 60 000 drums have been produced since 1966, and in La Hague about 10 000 since 1989. 10 000 m^3 of slurries issued from the treatment in the STE2 plant (La Hague) of effluents produced by spent fuel reprocessing from 1966 to 1990, are stored in 7 silos, waiting for conditioning. These slurries are likely to be conditioned in a bitumen matrix.

The main criteria that have led to select bitumen matrix for embedding LMA waste resulting from effluent treatment are : its waterproofing, its low solubility in water, its binding capacity, its implementation ability at moderate temperatures and its chemical inertia.

Treatment of LMA effluents essentially consist in concentrating radionuclides (RN) by evaporation and insolubilization by chemical precipitation. The resulting mix of inactive salts with insolubilized RN is conditioned by embedding with hot bitumen and poured into 200 liters metallic drums. Chemical and radiochemical composition of the waste depends both on effluent's origin and insolubilization's treatment. The evolution of processes from one plant to the other (Marcoule or La Hague) but also with time (in particular between 1966 and 1979), induces a range of waste composition.

Part of the existing drums (Low Activity waste) is destined to surface disposal. For the others (Medium Activity waste), the referential scenario considered for our studies is an intermediate storage likely to be followed by a deep geological disposal. CEA conduct research programs on the long term behaviour of bituminized wastes, both in interim storage and deep geological disposal conditions :

- Under interim storage conditions, radiochemical activity induces bitumen's radiolysis phenomena. Radiolysis gases, mainly H_2 are generated at a production rate depending on the radiochemical spectrum and high enough (a few liters per drum and per year) to cause an hydrogen accumulation in the bituminized wasteform. This phenomenon may generate hydrogen bubbles initiating a swelling of the bituminized wasteform, that may limit the incorporated activity.
- under deep geological disposal conditions, when after a long run, site will be resaturated with water and container will be corroded , bituminized waste will be submitted to the leaching action of liquid water. Long-term behaviour studies performed by the CEA aim to precise performances of bitumen conditioning and their evolution under various environment's factors.

For each mechanism considered in the model phenomenology, the influence of the main parameters was evaluated by different test runs. At the same time, experimental studies were performed in order to precise the values of the parameters supposed to be determining for bituminized wastes swelling, and to test their influence on this phenomenon.

THE PHENOMENOLOGY OF BITUMINIZED RADIOACTIVE WASTES' BEHAVIOUR UNDER IRRADIATION

Previous studies have showed that the swelling of bituminized wastes is very dependent to the number and diameter range of bubbles. This is why in the model JACOB2, the mechanisms controlling the nucleation and the evolution of the bubble population are described using basic characteristics of bituminized wastes. The general phenomenology of swelling defining the model structure can be summarized as follows:

- Under self-irradiation, bitumen radiolysis continuously produces hydrogen which dissolves and then is transported by diffusion in the organic matrix,

- At the free surface, hydrogen is easily evacuated out of bitumen and its concentration remains close to zero. Besides, there is no evacuation flux of hydrogen at the inner wall and at the bottom of the drum. Progressively, a diffusion flux of hydrogen establishes from the lower zone of the bituminized matrix to and through the upper surface. According to the irradiation level, the hydrogen yield related to the radiochemical activity spectrum of the embedded waste may exceed the diffusion flux through the free surface.
- Hydrogen saturation of the bituminized matrix may occur and lead to bubble formation by heterogeneous nucleation in the bitumen matrix.
- After nucleation, the gas produced between the bubbles diffuses towards them and makes them grow.
- The gas pressure is higher in the smaller bubbles due to interfacial tension gas/bitumen (Laplace's law), therefore hydrogen tends to diffuse from the smaller bubbles to the larger ones where the pressure is lower. This phenomenon (Ostwald ripening) contributes to increase the average bubble size.
- Simultaneously, as gas bubbles density is lower than bitumen one, bubbles are submitted to a growing lifting power proportional to their volume (Archimedes' buoyancy), that is slowed by bitumen viscosity. When bubbles reach the upper surface, gas evacuates through the interface air/bitumen. The bubbles velocity results from the compensation of buoyancy and viscosity forces.

SENSITIVITY STUDIES - IDENTIFICATION OF THE MAIN PARAMETERS

First test runs showed that swelling depends on 2 main parameters: Source-term and viscosity. After a time lag due to solubilization, the swelling slope and the source term are proportional. If no movement of bubbles would occur, swelling would go on increasing without slowing down; diffusion would then be the only phenomenon that could evacuate hydrogen so in this case the value of diffusivity would be essential. But even if the drift of bubbles is very slow, it is sufficient to firstly slow down swelling , then to stop it. The higher the viscosity, the later the maximum is reached and the higher the swelling (see fig 1.). The same relation exists between the number of bubbles and swelling (see fig 2.). The number of bubbles created is strictly proportional with the source-term. Then, due to Ostwald ripening, the number of bubbles decreases with time, leading to a limit value after a few years.

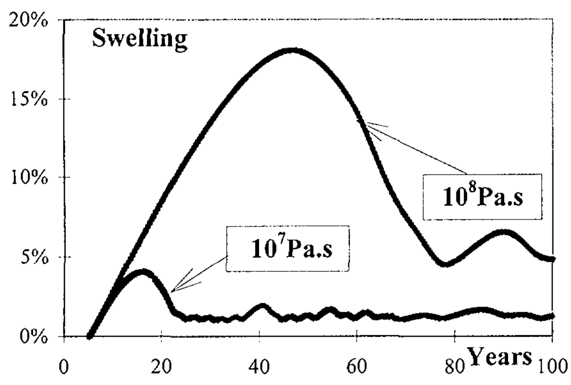

Fig. 1: Swelling dependance with viscosity
C_0=5%, S= 5 $10^{-10}m^3.m^{-3}.s^{-1}$

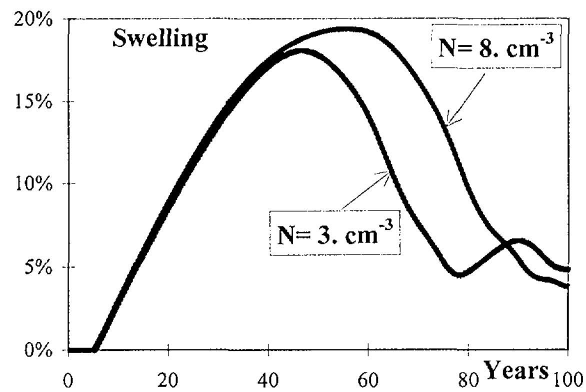

Fig. 2: Influence of the density of bubbles on swelling:
C_0=5%, S= 5 $10^{-10}m^3.m^{-3}.s^{-1}$, η= 10^8Pa.s

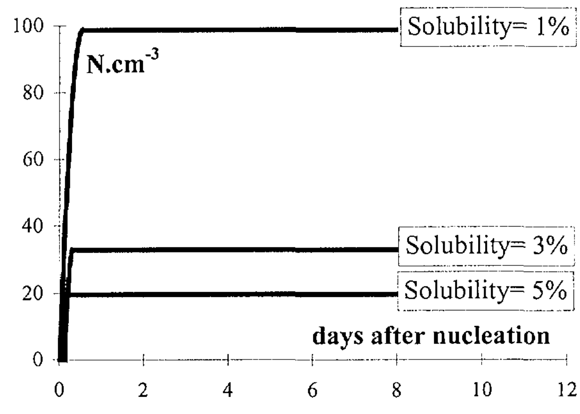

Fig. 3: Effect of solubility on the max number of bubbles
S= 5 $10^{-10}m^3.m^{-3}.s^{-1}$

Other parameters are less important compared to viscosity and source-term. The solubility of hydrogen has an influence on the result for two reasons :

- the time-lag during which no swelling occurs directly depends on it. Notice on fig. 1 that this time lag can last about ten years during which, according to radioactive decay, the source term can be lowered enough to avoid swelling.
- It affects the value of the equilibrium constant K (see forward) and thus the maximum number of bubbles (fig. 3) and its evolution vs time via Ostwald ripening.

Due to the value of the interfacial constant, Ostwald ripening as a significant effect when the source term is lower than $10^{-9} m^3.m^{-3}.s^{-1}$ and when the size of small-sized bubbles is smaller than 100μm.

EVALUATION OF THE THEORETICAL MODELLING BY EXPERIMENTAL STUDIES

The development of this theoretical model was supported by experimental measurements performed on inactive samples at a reduced scale compared to the size of industrial drums. Specific experiments dedicated to the determination of gas evacuation parameters (diffusion of H_2 towards the bitumen surface, migration velocity of bubbles) ,were run out of irradiation. On the other hand, behaviour of pure bitumen and of inactive bituminisate was studied under external gamma irradiation (50 and 300 Gy/h).

DIFFUSION OF HYDROGEN THROUGH BITUMINIZED MATRIX

The diffusion coefficient D of gas in bituminized wasteforms was studied on the base of Fick's law model. When diffusion flow is at equilibrium, the hydrogen concentration C_0 existing in the core of bitumen matrix is maximal and corresponds to the saturation concentration over which hydrogen bubbles are created. These both parameters were determined by following in the time the cumulative gas quantity diffusing through a thin bitumen membrane: after a time-lag proportional to the saturation concentration C_0, a linear evolution of this gas quantity is observed versus time and the corresponding slope value is proportional to the diffusivity coefficient. Gas was analysed by Gas Phase Chromatography.

In the case of pure 70/100 bitumen used at Marcoule and La Hague plants and inactive bituminisates, these parameters were measured by this method at various temperature:
C_0 is about 1.5vol% and increases in bituminisates (up to 5%) and does not seem to vary with temperature. The value of effective diffusion coefficient was found to be 5 $10^{-12} m^2.s^{-1}$ in pure bitumen at 20°C. It increases with temperature (7.5 $10^{-12} m^2$.s-1 at 30°C). It slightly decreases in bituminisates (down to 3 $10^{-12} m^2.s^{-1}$).

MIGRATION OF GAS BUBBLES UPWARDS THE SURFACE OF THE BITUMINIZED WASTE

When the salt content is equivalent to industrial wasteform mass composition (40% of salts, 60% of bitumen), the viscosity of bituminized wastes, is over 1MPa.s at room temperature. The viscosity of the bituminisate slow significantly down the rising velocity of hydrogen bubbles which hardly exceed 1 nm/s. In these conditions, the gas may diffuse from bubbles to the bitumen matrix so that bubbles diameter may decrease before significant moving is measurable. This difficulty was bypassed studying small solid balls sedimentation in bituminisate at 20°C, while air bubbles rising was studied at temperatures over 50°C. Velocity measurements were compared to values predicted from:

- the Stokes's law in the case of balls sedimentation: $U=\frac{D^2\,\Delta\rho\,g}{18\,\eta}$

- and the Hadamard/Rybczynski's law in the case of bubbles rising: $U=\frac{D^2\,\Delta\rho\,g}{12\,\eta}$, where U is the velocity value, D is the ball or bubble diameter, $\Delta\rho$ is the density gap between the spherical object and the bituminisate, g is the gravity acceleration, and η is the dynamic viscosity of the bituminisate. These theoretical expressions are based on the assumption that the bituminisate may be considered as a newtonian fluid.

Balls sedimentation was also followed over 50°C and the measured velocities are, in good agreement with theory, 1,5 time lower than velocities observed for rising air bubbles with equivalent diameter and density gap. Using different balls diameters and various materials, sedimentation speeds at 30°C were confirmed proportional with the square diameter on the one hand and the density gap ($d_{ball} - d_{bituminisate}$) on the other hand. Experimental values of velocities were confronted with values calculated using the viscosity determined by creep shear measurements:

- the Stokes/Hadamard law is representative of measured velocities when temperature is higher than 30°C ($U \geq 100$ nm/s),
- on the other hand, at lower temperatures (20-30°C) measured velocities are about 10 times slower than theoretical predictions and this ratio increases when velocity range is lower.

At room temperature, bitumen cannot be considered as a newtonian fluid: elastic forces are no more negligible compared with viscosity forces and Stokes/Hadamard law is no more directly applicable. Therefore, experimental measurements can be used to determine the corrective factor for the theoretical bubbles velocity predicted by this law.

NUCLEATION OF GAS BUBBLES

Hydrogen is produced by bitumen radiolysis and its concentration increases proportionally to irradiation time. Beyond the saturation concentration C_0, hydrogen is thermodynamically unstable and according to the size and interfacial properties of defects (mainly salt grains) in bitumen, bubbles are formed. Their radius R is defined by:

$$C(R) = C_0 + 2.\gamma / (K.R)$$

where C(R) is the hydrogen concentration round about the bubble,

γ is the interfacial tension bitumen/hydrogen,

and K is the equilibrium constant between the gas phase (P(R) = hydrogen partial pressure) and the dissolved hydrogen concentration in bitumen: P(R) = K.C(R)

The nucleation radius of these bubbles determines their number which must be sufficient to drain all of excess gas. When bubbles are formed, hydrogen can evacuate into them and nucleation is suspended as far as the hydrogen flow drained by bubbles equilibrates the radiolysis yield.

The bubbles population generated by nucleation under gamma irradiation (50 and 300 Gy/h) was characterized in pure bitumen samples. X-rays radioscopy was used to observe the formation of bubbles in bitumen. Microscopic observations were performed on transversal sections of a few samples in order to check the sensibility of non-destructive observations by X-rays radioscopy. Nucleation was observed in pure bitumen samples: less than 1 bubble/cm^3 is formed and the distance between them is greater than 1 cm. Because the excess of gas production is distributed among very few bubbles, each of them drain an important gas flow and grows quickly. On the other hand, if the number of bubbles is larger, the gas flow absorbed by each bubble is lower and diameters increase very slowly.

SWELLING OF BITUMEN UNDER EXTERNAL GAMMA IRRADIATION

Swelling of bitumen samples (S) is defined as the ratio of its volume increase ΔV measured after a given irradiation dose d, reported to its initial volume V_0: $S = \frac{\Delta V}{V_0} = \frac{V(d)-V_0}{V_0}$

Swelling evolution of pure bitumen samples was followed under 300 Gy/h and over a 300 kGy irradiation dose. Experimental measurements are reported on figure 4.

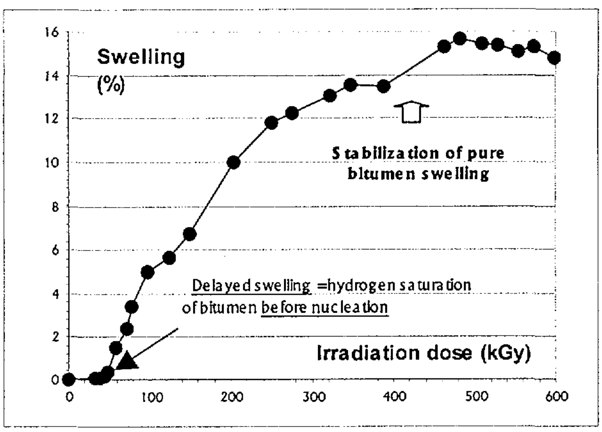

Fig. 4 : Swelling evolution under 300 Gy/h gamma irradiation, of bitumen samples

JACOB2 phenomenology is validated experimentally in the case of pure bitumen:

- swelling starts after a time lag corresponding to hydrogen dissolution in bitumen,
- the swelling stabilization of bitumen observed (after 500 kGy) must be linked with X-rays radioscopy: bubbles diameters increased significantly (≈ 1 cm) and their rising velocity (6 mm/day) is high enough to evacuate bubbles after a few days

Experimental characterization of slightly active samples showed that the texture of bitumen elaborated by the industrial conditioning process in La Hague is homogeneous and without initial bubbles. Because their initial texture is similar it can be considered that the phenomenology described for lab samples is applicable to industrial pure bitumen samples.

CONCLUSION

The main parameters defining the behaviour of bituminized wastes under irradiation have been identified and their values were obtained experimentally. Their influence has been quantitatively evaluated using JACOB2 model, by specific test calculations:

- the nucleation radius, and the H_2 solubility have influence on the number of created bubbles and therefore the bituminisate swelling is very dependent on these parameters,
- the drift velocity of bubbles related to the bituminisate's viscosity also makes a major contribution to gas evacuation

Complementary experiments are in progress in order to precise the H_2 solubility and diffusion coefficient according to the bituminisates composition. Moreover, the influence of salts grains will be examined by studying bubbles nucleation and swelling of inactive bituminisate samples under external irradiation.

Global model calculations must be also validated at industrial scale by comparison with the behaviour of radioactive bituminized waste drums.

Contacts

S.CAMARO:
Tel: 04 42 25 75 97 Fax : 04 42 25 35 45 e-mail: sylvie.camaro@cea.fr

T.GILARDI:
Tel: 04 42 25 70 34 Fax : 04 42 25 77 76 e-mail: thierry.gilardi@cea.fr

P.P.VISTOLI:
Tel: 04 42 25 21 73 Fax : 04 42 25 77 76 e-mail: pierre.vistoli@cea.fr

Softwares used:
Microsoft Word 98
Microsoft Excel 98 (Figures)