



# The modelling of fuel volatilisation in accident conditions

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## Abstract

For oxidising conditions, at high temperatures, the pressure of uranium vapour species at the fuel surface is predicted to be high. These vapour species can be transported away from the fuel surface, giving rise to significant amounts of volatilised fuel, as has been observed during small-scale experiments and taken into account in different models. Hence, fuel volatilisation must be taken into account in the conduct of a simulated severe accident such as the Phebus FPT-4 experiment. A large-scale in-pile test is designed to investigate the release of fission products and actinides from irradiated UO<sub>2</sub> fuel in a debris bed and molten pool configuration. Best estimate predictions for fuel volatilisation were performed before the test. This analysis was used to assess the maximum possible loading of filters collecting emissions and the consequences for the filter-change schedule. Following successful completion of the experiment, blind post-test analysis is being performed; boundary conditions for the calculations are based on the preliminary post-test analysis with the core degradation code ICARE2 [J.C. Crestia, G. Repetto, S. Ederli, in: Proceedings of the Fourth Technical Seminar on the PHEBUS FP Programme, Marseille, France, 20–22 March 2000]. The general modelling approach is presented here and then illustrated by the analysis of fuel volatilisation in Phebus FPT4 (for which results are not yet available). Effort was made to reduce uncertainties in the calculations by improving the understanding of controlling physical processes and by using critically assessed thermodynamic data to determine uranium vapour pressures. The analysis presented here constitutes a preliminary, blind, post-test estimate of fuel volatilised during the test. © 2001 Published by Elsevier Science B.V.

## 1. Introduction

Significant amounts of volatilised fuel have been observed in small-scale experiments [1–4], and have been taken into account in different models [5,6]. Hence, fuel volatilisation must be taken into account in the conduct of a simulated severe accident such as the Phebus FPT-4 experiment.

Phebus FPT-4 is a large-scale in-pile experiment designed principally to investigate the release of actinide and fission product species from irradiated UO<sub>2</sub> fuel in a debris bed and molten pool configuration. As part of the pre-test calculations, best estimate predictions were made for the maximum extent of volatilisation of uranium during the experiment.

Following successful completion of the experiment, further degradation calculations have been made [7] in order to interpret the experimental data, in particular the thermal history of the debris bed. Using results from post-test degradation calculations, revised blind post-test calculations have been made for fuel volatilisation. The methodology and results from both pre- and post-test calculations are described here.

## 2. Test description

The starting configuration of FPT-4 was that of a debris bed, approximately 70 mm diameter and ~360 mm in height. The lower 120 mm comprised depleted uranium and the upper two-thirds of the debris bed contained a mixture comprising ~3200 g of fragments of irradiated uranium dioxide fuel (~4 mm diameter) and ~800 g of fully oxidised shards of Zircaloy. The initial bed porosity was approximately 50%.

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During the experiment a mixture of 80 mol% steam/ 20 mol% hydrogen was injected through the bed at a flow rate of  $0.5 \text{ g s}^{-1}$ . The gas leaving the debris bed was passed through a battery of filters located in the upper part of the in-pile test package: these will be analysed as part of the post-test analyses in order to determine the release from the bed of fission products and fuel.

By increasing the power of the PHEBUS reactor in a controlled sequence, the temperature of the debris bed was increased until a stable molten pool was obtained. Six temperature ramps and hold periods were planned for the experiment. In particular, in order to obtain quantitative information on actinide and fission product (Ba, Sr, La, Ce, ...) release, and to see the effect of the solid to liquid transition on the release, it was planned:

- to hold the fuel at a constant power for  $\sim 3000 \text{ s}$  with a maximum temperature in the bed of  $\sim 2700 \text{ K}$  ( $\langle\langle\text{P6 plateau}\rangle\rangle$ ), i.e. while the fuel is still in an intact geometry,
- to achieve a stable molten pool at  $\sim 2900 \text{ K}$  ( $\langle\langle\text{P7 plateau}\rangle\rangle$ ), after which the test was to be terminated.

The temperature ramp and hold sequence was achieved satisfactorily, although the final temperature plateau was terminated earlier than planned due to the test-shutdown criteria being achieved (strong and rapid increase of measured temperatures in the bundle in both radial and axial directions).

### 3. Methodology

The maximum rate of volatilisation is limited by the equilibrium pressure of the volatile uranium species and the mass flow rate of the steam-hydrogen bulk gas which is injected through the debris bed. The equilibrium vapour pressures of the volatile uranium species can be calculated using the thermodynamic data. Possible rate limiting mechanisms due to mass transfer of the uranium vapour into the bulk gas or surface reaction kinetics have been considered as part of the pre-test calculations.

### 4. Pre-test calculations

The rate of fuel volatilisation is controlled by two mechanisms which occur in series: the rate of reactions at the surface and mass transfer from the fuel surface to the bulk gas. The driving force for the former is the difference between the partial pressure of volatile uranium species at the fuel/gas interface and their equilibrium vapour pressures. The driving force for the latter is the difference between the bulk vapour pressure and the vapour pressure at the fuel/gas interface.

The uranium molar flux can be expressed as

$$J_U = \frac{\beta}{RT}(P_{\text{eqm}} - P_i) = \frac{k_U}{RT}(P_i - P_b) = \frac{K}{RT}(P_{\text{eqm}} - P_b), \quad (1)$$

where  $J_U$  ( $\text{mol cm}^{-2} \text{ s}^{-1}$ ) is the uranium molar flux,  $R$  ( $\text{atm cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ ) is the perfect gas constant,  $T$  (K) is the fuel temperature,  $P_i$  (atm) is the  $\text{UO}_3(\text{g})$  pressure at the fuel/gas interface,  $P_b$  (atm) is the  $\text{UO}_3(\text{g})$  pressure in the bulk gas,  $P_{\text{eqm}}$  (atm) is the  $\text{UO}_3(\text{g})$  equilibrium pressure,  $K$  ( $\text{cm s}^{-1}$ ) is the combined coefficient of mass transfer and surface reactions,  $k_U$  ( $\text{cm s}^{-1}$ ) is the mass transfer coefficient for  $\text{UO}_3(\text{g})$  and  $\beta$  ( $\text{cm s}^{-1}$ ) is the surface reaction coefficient for volatilisation.

For the Phebus FPT4 experiment,  $\text{UO}_3$  can be considered as the dominant volatile uranium species to the exclusion of other volatile forms of U. This is discussed further below.

$K$  ( $\text{cm s}^{-1}$ ) can be expressed as

$$\frac{1}{K} = \frac{1}{\beta} + \frac{1}{k_U}. \quad (2)$$

The mass transfer coefficient  $k_U$  can be calculated for the debris bed using a suitable correlation [8]. In contrast  $\beta$  must be determined based on the analysis of well-characterised experiments, such as those of Mansouri [4], for which the experimental mass transfer coefficient can be calculated with reasonable accuracy.

In order to determine  $P_b$  for  $\text{UO}_3(\text{g})$  at an elevation  $z$  in the debris bed, the following equation, which is based on mass balance principles, is integrated:

$$\frac{Q}{AP_{\text{tot}}} \frac{dP_b}{dz} = \frac{K}{RT}(1 - \varepsilon) \frac{S}{V}(P_{\text{eqm}} - P_b), \quad (3)$$

where  $Q$  ( $\text{mol s}^{-1}$ ) is the injected gas flow rate,  $P_{\text{tot}}$  (atm) is the total pressure of the system,  $A$  ( $\text{cm}^2$ ) is the cross-sectional area of the surface of the cylindrical debris bed, ( $A = \pi D^2/4$  if  $D$  is the diameter of the bed),  $\varepsilon$  is the debris bed porosity (non-dimensional) and  $S/V$  ( $\text{cm}^{-1}$ ) is the effective surface area to volume ratio of a fuel fragment.

The effective surface area to volume ratio of a fragment was considered to be three times the geometrical value: it is assumed that fuel volatilisation occurs at the fragment surface (note that a different assumption was considered by other authors [5]), increased by an empirical factor of 3 to account for surface roughness. A similar approach is often used to model fuel oxidation [9].

The initial condition for Eq. (3) is  $P_b(z=0) = 0$ .

It was considered that the extent of fuel volatilisation from the debris bed prior to the P6 plateau (2700 K) would be negligible compared with that released during the P6 and P7 plateau (melt phase). Therefore fuel volatilisation prior to the P6 plateau was ignored for the

pre-test calculations. Temperatures for four specific times representing the transient from the start of P6 to the end of P7 were selected. The fuel was considered as two parts of equal mass (a central cylinder and an external annulus), to take some account of non-uniform radial temperatures. The temperatures at these two radial positions, varying as a function of elevation, were obtained from the degradation code ICARE2 (the maximum axial temperature was considered in the pre-test analysis).

To see if mass transfer is limiting, the temperatures obtained from ICARE2 for the two radial positions were used in conjunction with Eq. (3) and substituting  $k_U$  for  $K$ , the pressure  $P_b$  of  $UO_3(g)$  in the bulk gas was calculated for all elevations. The results of these calculations indicate that the bulk gas becomes saturated with  $UO_3(g)$  over the length of the debris bed. Hence it was concluded that mass transfer is not limiting for fuel volatilisation for FPT-4 test conditions.

Then it was determined whether surface reaction kinetics is a rate-controlling process. Based on the experiments of Mansouri [4], values for  $\beta$  at different temperatures between 1672 and 1873 K have been obtained. In the absence of data at higher temperatures, these have then been extrapolated to temperatures between 2200 and 2700 K. At 2700 K,  $\beta$  has a value of  $\sim 6 \text{ cm s}^{-1}$ , which is much less than the value of  $89 \text{ cm s}^{-1}$  calculated for  $k_U$ ; therefore surface reaction kinetics will be the rate determining factor. When  $\beta$  and  $k_U$  are known, the  $UO_3(g)$  vapour pressure in the bulk can be calculated using Eq. (3). The results indicate that the  $UO_3(g)$  vapour pressure in the bulk is very close to the equilibrium vapour pressure. Therefore it was concluded that the surface reaction is also not a limiting process and that equilibrium between the debris bed and the bulk gas is reached.

The volatilisation rate (in S.I. units) can then be expressed as

$$\dot{m}_{UO_3} = \frac{P_{UO_3}^{eqm}}{P} M_{UO_3} \left( \frac{\dot{m}_{H_2O}}{M_{H_2O}} + \frac{\dot{m}_{H_2}}{M_{H_2}} \right), \quad (4)$$

where  $M_i$  is the molecular mass of species  $i$ ,  $\dot{m}_i$  is the mass flow rate for species  $i$ ,  $P_{UO_3}^{eqm}$  is the  $UO_3(g)$  equilibrium pressure and  $P$  is the total pressure.

In order to estimate the equilibrium pressure of  $UO_3(g)$ , thermodynamic calculations were performed with the MTDATA code [10] in conjunction with a database assembled and assessed by the AEA Technology for the U–Zr–O–H system [11,12].  $UO_3(g)$  can be considered as the dominant volatile uranium species for FPT4 conditions for the following reasons:

- $pUO(g)$  and  $pUO_2(g)$  are much smaller than  $pUO_3(g)$ ,
- $UO_2(OH)_2(g)$  compound is important only at high pressure [13],

- $pUO_2(OH)(g)$  could be higher than  $pUO_3(g)$  by a factor of 10–100 according to thermodynamic calculations, but this is not supported by any experimental evidence (similar volatilisation rates measured in steam [2,4] or in experiments performed in  $CO/CO_2$  by AEA-T where  $UO_3$  is necessarily the dominant species), and, in addition, large uncertainties exist in the thermodynamic data concerning  $UO_2(OH)(g)$  [14].

Each radial zone was treated separately for the thermodynamic calculations. The input parameters are the number of moles of  $UO_2$  and  $ZrO_2$ , the temperature, and the volume of gas assumed to pass through each part of the bed during the period of time for each calculation. The following simplifications were made:

- for the first temperature ramp and plateau P6 ( $T_{max} \sim 2700 \text{ K}$ ), half the gas is assumed to pass through the central cylinder and outer annulus,
- from the last temperature ramp up to the end of the transient (P7 plateau, melt phase), all the gas is assumed to flow through the outer annulus, because of liquefaction which is assumed to have occurred in the central region.

The cumulative mass volatilised at the end of the transient is predicted to be about 1 kg ( $\sim 170 \text{ g}$  at the end of P6, i.e.  $T_{max} \sim 2700 \text{ K}$ ).

It must be emphasised that the amount of fuel volatilisation calculated here represents the maximum mass of fuel volatilised *within* the debris bed, but not necessarily that, which will be transported to the filters. The decrease in axial temperature near the top of the bed has not been taken into consideration during these calculations and this may lead to a large condensation of  $UO_3(g)$ ; a separate thermodynamic calculation shows that the amount of fuel predicted to be in vapour form at the top of the debris bed (with a reduced temperature,  $\sim 500 \text{ K}$  lower) was only 5 g.

## 5. Post-test calculations

Using the results from post-test degradation calculations performed with the ICARE2 code [7] for the thermal hydraulic history of the debris bed, revised blind post-test calculations have been made up to the end of P6, i.e.  $T_{max} \sim 2700 \text{ K}$ . In order to achieve a good correlation between the measured degradation with the ICARE2 code, it was necessary to assume that there was a gas bypass through the exterior thermal insulation.

The debris bed has been nodalised in 12 zones of equal mass: two radial zones (a central zone and an outer annulus) with six elevations. The initial distribution of  $UO_2$  and  $ZrO_2$  in each node is assumed to be 1/12 of the initial inventory. Given the temperature, system pressure (0.22 MPa), and the amounts of  $H_2O$  and  $H_2$

Table 1  
Post-test calculations of mass of UO<sub>2</sub> volatilised during P5 and P6

Elevation (mm)	Central zone		External ring	
	$\Delta$ mass UO <sub>2</sub> at the end of P6 (g)	Mass of fuel as vapour (g)	$\Delta$ mass UO <sub>2</sub> at the end of P6 (g)	Mass of fuel as vapour (g)
140	-0.2		-0.04	
180	-3.6		-3.6	
220	-1.5		-14.8	
260	-8.3		-16.3	
300	-1.0	14.5	-12.1	46.8
340	+0.04	14.5	+5.9	40.8

calculated by ICARE2, a thermodynamic calculation is performed for each node at a given time step.

Based on the values of temperature and the amounts of steam and hydrogen calculated for each time step by ICARE2, a series of iterative thermodynamic calculations have been made to calculate the amount of uranium vapour which forms under equilibrium conditions. The transport of vapour from one elevation to the next level above and its impact on the chemistry at higher elevations has also been taken into consideration during these calculations. It has been assumed that for time step  $T_n$ , at elevation  $L_y$ , U and Zr present in the vapour phase are transported into elevation  $L_{y+1}$  at the beginning of time step  $T_{n+1}$ . Consequently, for time step  $T_{n+1}$  at elevation  $L_y$ , the amount of U and Zr that was calculated to be present in the vapour phase for the previous time step at the same elevation has been removed from the input inventory. This is treated consistently for all six elevations and all times, except for the very first time step where no previous transport into a higher elevation could have occurred. For simplicity, it is assumed that the inner cylinder and outer annulus are treated independently.

In addition to amending the amount of uranium and zirconia present in the condensed phase at the beginning of each time step, the previous oxidation state (extent of hyperstoichiometry) of the fuel is also maintained. Thus there is a conservation of mass within the system.

In total thirty thermodynamic calculations corresponding to different time steps have been calculated for each node, giving a total of 360 thermodynamic calculations. The results of these iterative series of calculations are presented in Table 1.

As can be seen in the table, for each elevation the volatilised mass has been calculated with time. It can be seen that re-condensation (indicated by a positive change in mass) begins at level 340 mm in the post-test analysis which corresponds to almost the top of the debris bed.

Assuming no re-condensation at cooler elevations in the debris bed, at the end of P6, the best estimate of volatilised uranium is ~61 g. This value is lower than the

~170 g predicted at the end of P6 by the pre-test calculations (see discussion below).

## 6. Discussion

As already emphasised in §4, the amount of fuel volatilisation calculated represents the maximum mass of fuel volatilised *within* the debris bed, but not necessarily that, which will be transported to the filters.

Calculation of the mass released *from* the debris bed is a complex issue. A preliminary assessment has shown that there will be competition between condensation on debris and aerosol formation (both homogeneous and heterogeneous nucleation), where condensation would lead to greater retention in the debris bed since the aerosol size formed by nucleation and agglomeration could be too large for Brownian retention to be efficient, but too small for efficient trapping by impaction.

The best estimate of the minimum mass leaving the debris bed, i.e. assuming equilibrium at the surface with total re-condensation of UO<sub>3</sub>(g) and no aerosol formation, would be much lower than the mass predicted to be volatilised inside the debris bed (~5 g in the pre-test analyses). The upper value of 61 g calculated in the post-test analyses is lower than the ~170 g predicted at the end of P6 by the pre-test calculations. The reasons for this are lower average temperatures due to taking into consideration the axial temperature variation in the bed instead of the maximum temperature as well as slightly shorter times at the hotter temperatures than had been assumed for the pre-test calculations. Additionally, the volatilisation calculations presented here are also sensitive to the mass flow of steam/hydrogen assumed to flow through the debris bed and it is this parameter which has the greatest influence on the results. The assumption of a gas bypass in the insulation in the ICARE2 calculations is therefore particularly important since it reduces the mass flow of gas through the debris bed. Also, it is the lower mass flow of steam through the central zone which explains why this has a lower prediction of fuel volatilisation, when compared with the exterior ring, despite

having higher temperatures in the inner region. Hence, as part of the post-experiment examinations, it will be important to establish where the gas bypass through the insulation begins and correlate this with the ICARE2 calculations.

In addition, it should be noted that the simplified approach adopted here has not considered the feedback effects of fuel volatilisation on the degradation process (in particular, influence on the debris bed temperature). Any physical process that leads to a reduction of the fuel temperature within the debris bed, such as the relocation of mass within the bed, will also limit the extent of fuel volatilisation.

## 7. Conclusions

Phebus FPT-4 is a large-scale in-pile experiment designed principally to investigate the release of actinide and fission product species from irradiated  $\text{UO}_2$  fuel in a debris bed and molten pool configuration. As part of the pre-test calculations, best estimate predictions were made for the maximum extent of volatilisation of uranium during the experiment. Following the successful completion of the experiment, blind post-test analysis of release is being performed; the boundary conditions for the calculations are based on the preliminary post-test analysis with the ICARE2 code.

The volatilisation calculations are very sensitive to the mass flow of  $\text{H}_2\text{O}/\text{H}_2$ : the assumption of gas bypass in the ICARE2 calculations has a great influence on the results.

The best estimate of the amount of fuel volatilised within the debris bed at the end of P6 is 61 g. The amount of fuel transported to the filters is likely to be much lower than this, but is difficult to predict, because of the competition between condensation on debris and aerosol formation. Condensation on the debris would lead to greater retention in the debris bed as the aerosol retention could be less efficient. Pre-test analyses showed that about 5 g of uranium leave the debris bed, if

equilibrium at the surface with re-condensation of  $\text{UO}_3(\text{g})$  and no aerosol formation are assumed.

Feedback effects of fuel volatilisation on bed temperatures have not been considered and this may even reduce the amount of fuel volatilised in the debris bed.

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