

Analysis of tritium release from LiAlO_2 in the TEQUILA experiment, using the MISTRAL code

A. Badawi, A.R. Raffray and M.A. Abdou

University of California, Los Angeles, Department of Mechanical, Aerospace and Nuclear Engineering, Los Angeles, CA 90024-1597, USA

The tritium release behavior from LiAlO_2 samples in the TEQUILA experiment was analyzed using the MISTRAL code. This was done in order to benchmark the code for analyzing the performance of a LiAlO_2 blanket test section under ITER-like conditions. Material property data available from the experimental sample microstructure characterization and from the literature were used as input to the code. The microstructure characterization was quite thorough and included the pore size distribution which was used to estimate the pore diffusion coefficient. In the case of the bulk diffusion coefficient, since single crystal experimental measurements are not available, two different values from different experimental data were used.

The strategy was to model four different transients for the same sample and to use the property data, in particular the diffusion coefficient, which will better reproduce all four transients. The transients studied were: two temperature transients, in which the temperature changed by $+50^\circ\text{C}$ and -50°C and two hydrogen concentration transients in the purge, in which the concentration changes from 0.1% to 1% and from 1% to 0.1%. The results showed that the assumed bulk diffusion coefficient can change the output substantially. For each case, the effects of other parameters, such as the adsorption activation energy and pore diffusion coefficient, were also considered. The results are discussed in the paper.

1. Introduction

In order to analyze the tritium release behavior, using the MISTRAL code [1], of a helium-cooled LiAlO_2 blanket test module, under cyclic conditions relevant to ITER and NET, the material property parameters were first calibrated. The calibration was based on the analysis of tritium release data for LiAlO_2 samples irradiated in the TEQUILA experiment [2]. The P-type LiAlO_2 samples were selected since their microstructure is similar to the proposed blanket LiAlO_2 material. The strategy was to model different TEQUILA temperature and purge hydrogen content transients for the same LiAlO_2 sample at temperature levels relevant to the blanket operation, and to find the material property parameters which would best reproduce the experimental results.

2. Input data

The input data include the breeder microstructure characteristics and parameters defining the different

tritium transport processes. Table 1 summarizes the input data used for the calculations. The microstructure of the TEQUILA P-type LiAlO_2 sample was quite thoroughly characterized, including the grain size, specific surface area and pore size distribution [3]. The latter is a key factor from which the average effective pore diffusion coefficient, D_{peff} , can be estimated, as follows [1,4]. First, the average pore diffusion coefficient, D_{pave} , is estimated from the pore size distribution using eq. (1).

$$D_{\text{pave}} = \frac{\left[\sum_{j=1}^n (\epsilon_{pj}/r_{pj}^2) \right]^2}{\sum_{j=1}^n (\epsilon_{pj}^2/r_{pj}^4 D_{pj})}, \quad (1)$$

where ϵ_{pj} , r_{pj} and D_{pj} are the porosity, average radius and pore diffusion coefficient associated with pore size j . In addition, the diffusive process is slowed down because of the effect of a series of contractions and expansions associated with the different pore sizes. Michaels [5] considered two cylindrical pores, one of

Table 1
Main parameters used for tritium calculations for the LiAlO₂ solid breeder for the TEQUILA experiment

Volume (m ³)	2.36 × 10 ⁻⁶ [2]
Thickness (mm)	5 [2]
LiAlO ₂ sample	S2 [2]
Tritium generation rate (atoms/s m ³)	8.45 × 10 ¹⁸ [2]
Standard temperature (°C)	510 [2]
Open porosity (%)	20 [2]
Average grain diameter (μm)	0.3 [2]
BET surface area (m ² /kg)	2600 [2]
LiAlO ₂ theoretical density (kg/m ³)	2610 [1]
Average pore radius (μm)	0.074
Grain diffusion coefficient: pre-exponential (m ² /s)	8.9 × 10 ⁻⁷ [6]; 1.99 × 10 ⁻⁹ [7] ^a
activation energy (kJ/mol)	198 [6]; 90.4 [7] ^a
Pore diffusion coefficient factor: $f_{D_p} = D_{peff} / D_p$	0.1 to 1
Adsorption activation energy (kJ/mol)	50 [1], 30, 15 ^a
Hydrogen concentration in purge	0.1-1% ^a
Pore diffusion coefficients for tritium and hydrogen (m ² /s); see ref. [1]	

^a Different values were used.

radius r_{p1} and length l_{p1} and the other of radius r_{p2} and length l_{p2} and derived the following equation:

$$\frac{D_{pave}}{D_{peff}} = 1 + \frac{L_p(R_p^2 - 1)^2}{(L_p + 1)^2 R_p^2}, \quad (2)$$

where L_p and R_p are the ratios between the two pore radii and lengths, respectively.

From the pore size distribution of eq. (1), D_{pave} was estimated as being 1.4 times the pore diffusion coefficient, D_p based on the overall average pore radius (0.074 μm).

Calculation of the effect of a series of contractions and expansions in the interconnected pore system for this particular case is difficult since the pore size distribution is not bimodal. However, an estimate can be made of the range of values of (D_{pave}/D_{peff}) from eq. (2) assuming different values for R_p based on the pore sizes.

The ratio, $f_{D_p} = D_{peff}/D_p$ can be estimated for the different assumed ratios of binary pore sizes by combining the factor of 1.4 obtained from eq. (1) with the different values of D_{pave}/D_{peff} from eq. (2), and is found to range from about 0.15 to 0.85. Other factors such as partial pore closure might also affect f_{D_p} , but for this study it seems reasonable to explore the effect

on the tritium release predictions of varying f_{D_p} values, particularly in the range between 0.1 and 1.

Key parameters for the bulk diffusion and surface adsorption/desorption processes are the bulk diffusion pre-exponential and activation energy, and the adsorption and desorption activation energies. In the case of the bulk diffusion coefficient, very limited data from single-crystal experimental measurements seem to be available, and estimates based on experiments using multi-grain LiAlO₂ samples tend to vary widely.

For this study, it was decided to use both sets of values from refs. [6] and [7] in modeling the tritium release transients and to determine which one would provide a better fit to the TEQUILA experimental data under different conditions.

The activation energy for adsorption (E_{ads}) tends to be quite low compared to that for desorption (E_{des}). For this analysis, E_{ads} is assumed to be constant and the corresponding E_{des} for each coverage is obtained from the following expression:

$$E_{des} = Q_{ads} + E_{ads}, \quad (3)$$

where Q_{ads} is the heat of adsorption.

To ascertain the effect of the choice of E_{ads} on the tritium release, calculations were done for $E_{ads} = 50, 30$ and 15 kJ/mol, respectively. It should be noted that the operating temperature of the TEQUILA sample of interest oscillates about 510°C which is lower than the temperature at which Q_{ads} was determined from ref. [8], which was used to estimate the heat of adsorption as a function of coverage. It might be that at lower temperature, the desorption process is different resulting in different activation energies. For example, ref. [9] suggests that, at low temperature, desorption might be of the first order instead of the second order as assumed here and in ref. [8]. However, previous use of the Q_{ads} values from ref. [8] for analysis of cases with purge hydrogen content transients seemed to yield reasonable results [1], and, thus, these values are used here.

3. Experimental cases considered

The strategy was to model four different transients for the same sample and to determine the set of property data, in particular D_{go} , E_d and f_{D_p} , which will better reproduce all four transients. The sample of interest is S2 since its standard temperature of 510°C is closer to the expected operating temperature of the LiAlO₂ in the test module. The transients initially

Table 2
TEQUILA experiment's cases considered for tritium transport analysis [2]

Case no.	Sample	Temp.	H ₂ in purge
1.18	S2	460–510°C	1%
1.17	S2	510–460°C	1%
1.16	S2	510°C	0.1%–1%
1.19	S2	510°C	1%–0.1%
1.3	S2	510–560°C	0.1%

chosen for the study consist of a temperature increase transient, a temperature decrease transient, a purge H₂ concentration increase transient, and a purge H₂ concentration decrease transient, as shown in table 2. In addition, a temperature increase case at higher temperatures and with a lower H₂ purge concentration (case 1.3) was also analyzed to test the ability of the model to analyze temperature transients over a range of temperatures and purge H₂ content where the relative importance of the various transport mechanisms might vary.

4. Results and discussions

The temperature and H₂ concentration profiles were obtained from the experiment [3] and used as an input in the code. Each case was analyzed separately to determine which parameters affect the tritium release significantly. For the sake of computing time, only those property data that were expected to affect the tritium release were changed in each case.

4.1. Case 1.17

In this case the H₂ content in the purge remained constant (1%) while the temperature was decreased from 510 to 460°C, as shown in fig. 1. The bulk diffusion coefficient was expected to be the key parameter in this low temperature and high hydrogen content case, and, therefore, the release was calculated using two different values of D_g (see table 1) that differ by a factor of $\approx 10^5$ at 460°C. The tritium release is shown in fig. 2. From this figure, the higher diffusion coefficient case results in a relatively small decrease in the tritium release followed by a quick return to steady state (within about one hour). The lower diffusion coefficient case models the experimental results quite well showing a sharp and prolonged decrease in the tritium release following the transient. This seems to

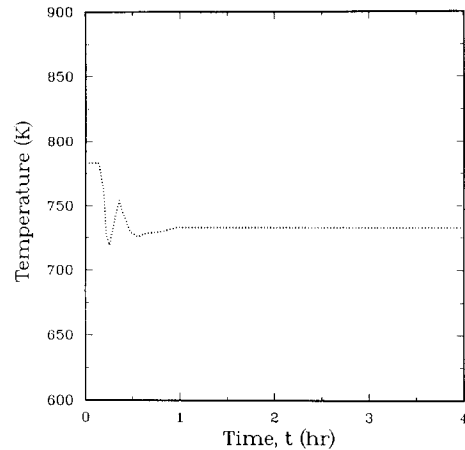


Fig. 1. Temperature history of LiAlO₂ S2 sample for case 1.17 of the TEQUILA experiment.

indicate that grain diffusion is rate-controlling based on the assumed parameters. f_{D_p} was also changed to see its effect on the tritium release for both low and high D_g cases. The effect of f_{D_p} was found to be small for the low D_g case but much more pronounced for the high D_g case. This is in agreement with the indication that for the low D_g case, grain diffusion is rate-limiting and, thus, the tritium release behavior is less affected by changes in other tritium transport parameters. For the high D_g case, in order to obtain a significant change in the release profile, f_{D_p} has to be about 0.01, which is very low and probably not realistic. This suggests that the low bulk diffusion coefficient in this

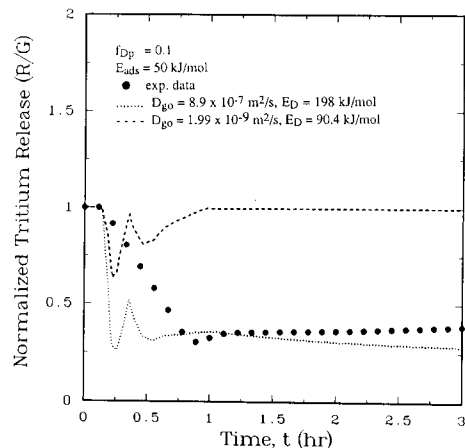


Fig. 2. Calculated tritium release history from the LiAlO₂ S2 sample for case 1.17 of the TEQUILA experiment for different values of the bulk diffusion coefficient.

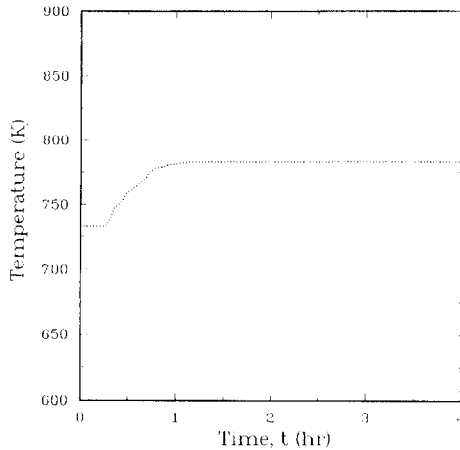


Fig. 3. Temperature history of the LiAlO_2 S2 sample for case 1.18 of the TEQUILA experiment.

case might be more realistic. However, a choice for the value of f_{D_p} cannot be made yet from those results.

4.2. Case 1.18

This is a case of constant H_2 concentration in the purge (1%) in which the temperature was increased from 460°C to 510°C , as shown in fig. 3. Again the bulk diffusion was expected to be rate limiting at this low temperature range and therefore was changed to see its effect on the tritium release. However, since the temperature was higher than that in case 1.17, the effects of both f_{D_p} and E_{ads} were also examined. Fig. 4 shows the normalized tritium release history for the

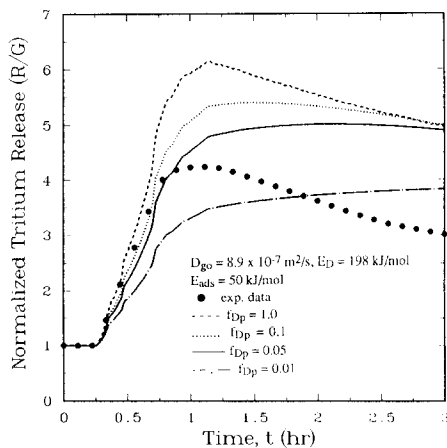


Fig. 4. Calculated tritium release history from the LiAlO_2 S2 sample for case 1.18 of the TEQUILA experiment for different values of effective pore diffusion coefficient.

low value of D_g for different values of f_{D_p} . D_g seems to be a key factor in determining the tritium release profile. For the low diffusion coefficient case, for $f_{D_p} = 0.1$, the tritium release after four hours is still higher than steady state and the resulting profile is similar to that obtained experimentally. However, the tritium release peak is about 30% higher than the experiment in this case. The same case was also run with the high bulk diffusion coefficient. The tritium release only increased to about 1.1 before returning to steady state, indicating once more that the low diffusion coefficient is more appropriate in reproducing the experimental data. The effect of f_{D_p} is more significant than for the previous case (1.17). Using a high f_{D_p} tends to increase the peaking in the tritium release and decrease the time required for the release to reach a normalized value of one. However, for cases with $f_{D_p} > 0.1$, the initial tritium release peak from the model is significantly higher than the experimental one. For this case, E_{ads} was also changed from 50 to 30 kJ/mol and was found to have little effect on the tritium release behavior.

4.3. Case 1.16

In this case the temperature was constant (510°C) while the H_2 concentration in the purge was increased from 0.1% to 1%. The transient in the experiment occurred over a 4 minute time period [3]. Figs. 5–7 show the tritium release profiles obtained for different values of D_g , f_{D_p} , and E_{ads} , respectively. Fig. 5 shows the effect of D_g on the tritium release, which is not as

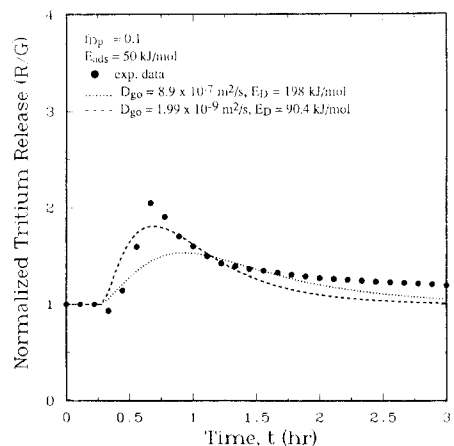


Fig. 5. Calculated tritium release history from the LiAlO_2 S2 sample for case 1.16 of the TEQUILA experiment for different values of the bulk diffusion coefficient.

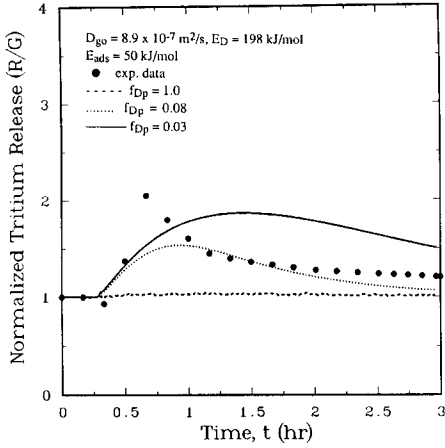


Fig. 6. Calculated tritium release history from the LiAlO_2 S2 sample for case 1.16 of the TEQUILA experiment for different values of the effective pore diffusion coefficient.

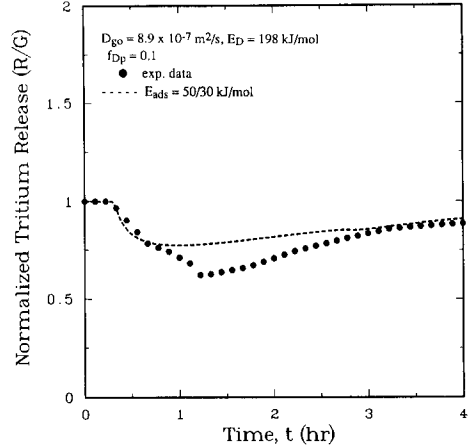


Fig. 8. Calculated tritium release history from the LiAlO_2 S2 sample for case 1.19 of the TEQUILA experiment for different values of the adsorption activation energy.

important in this H_2 concentration transient case as in the previous temperature transient cases. This is because the H_2 concentration transient affects mainly the surface and pore inventories and not the grain inventory, which indicates that changing f_{D_p} and E_{ads} should have larger effects on the tritium release. Fig. 6 shows the tritium release histories for different values of f_{D_p} (0.03–1). Decreasing f_{D_p} below 0.1 tends to flatten the tritium release peak and increase the time required for the normalized tritium release to return to unity. For higher values of f_{D_p} (of the order of 1), no peak is observed. This can be explained by the fact that al-

though the tritium response is faster in this case, there is very little inventory to begin with. Therefore, when more hydrogen is added to the purge, only a small amount of surface tritium is available for isotope exchange. Fig. 7 shows the tritium release for $f_{D_p} = 0.5$ and $E_{ads} = 15, 30$ and 50 kJ/mol, respectively. The tritium release profile for $E_{ads} = 50$ kJ/mol is flat, whereas the profile obtained for $E_{ads} = 15$ kJ/mol has a shape similar to the experimental results but returns to steady state much faster. Combining the indications from figs. 6 and 7 suggests that using $E_{ads} = 30$ kJ/mol and a value of f_{D_p} of about 0.1 can reasonably reproduce the experimental results.

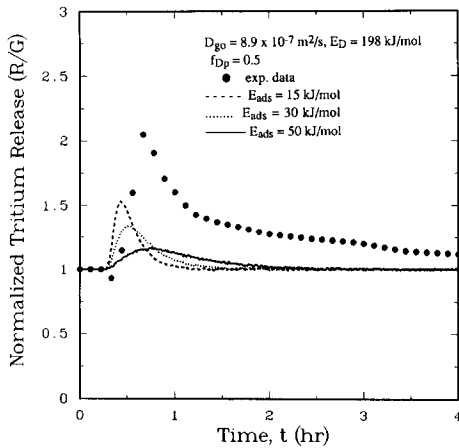


Fig. 7. Calculated tritium release history from the LiAlO_2 S2 sample for case 1.16 of the TEQUILA experiment for different values of the adsorption activation energy.

4.4. Case 1.19

In this case the temperature was constant (510°C) and the H_2 concentration was decreased from 1% to 0.1%. Since the time over which this transient occurs was not given, it was assumed to be four minutes as in case 1.16. For this case, only the effect of E_{ads} was investigated and the results are shown in fig. 8 for $f_{D_p} = 0.1$ and for $E_{ads} = 30$ and 50 kJ/mol. The tritium release profile in both cases was virtually identical showing an initial tritium release dip not as marked as the experimental one but showing a gradual return to steady state in accordance with the experimental data. When a value of $f_{D_p} = 0.5$ was used the tritium release profile for $E_{ads} = 15, 30$ and 50 kJ/mol were again virtually identical. However, for those cases, the calculated release returns to the steady state value much faster than the experimental data. Again, this suggests

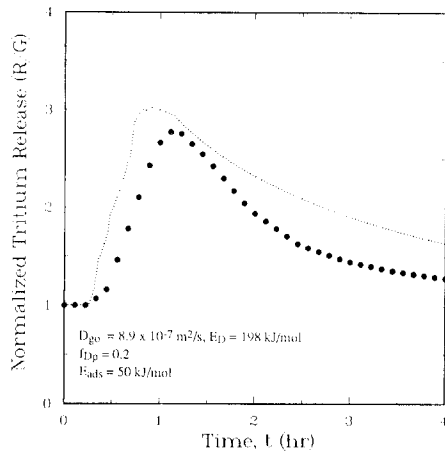


Fig. 9. Calculated tritium release history from the LiAlO_2 S2 sample for case 1.3 of the TEQUILA experiment.

that an f_{D_p} value of about 0.1 might be more appropriate for this sample.

4.5. Case 1.3

In this case, the H_2 concentration remained constant (0.1%) and the temperature increased from 510°C to 560°C. The temperature history profile was not given in the experimental data and, therefore, was taken to be similar to the one in case 1.18 but 110°C higher. For this case, the low bulk diffusion coefficient was used, together with $f_{D_p} = 0.2$ and $E_{\text{ads}} = 50$ kJ/mol, and the modeling results reasonably reproduce the experimental data, as shown in fig. 9. Independently changing f_{D_p} to 0.1 and $E_{\text{ads}} = 30$ kJ/mol did not significantly affect the model results which suggests that, for this case, bulk diffusion is the rate-limiting process.

5. Conclusion

As seen from the above results, using a high diffusion coefficient results in very poor reproductions of the experimental results for the temperature transient cases. Therefore, it seems reasonable to assume that the low diffusion coefficient is more appropriate for use under similar conditions. From the H_2 concentration transients, especially case 1.16, it seems that an

adsorption activation energy of 30 kJ/mol together with a value of f_{D_p} of 0.1–0.2 will yield tritium release histories comparable to the experimental results. Therefore, it is suggested that in order to analyze the tritium behavior in the blanket test module using LiAlO_2 similar to the TEQUILA P sample, the property data shown in table 1 be used, together with $D_{\text{go}} = 8.9 \times 10^{-7}$ m²/s, $E_D = 198$ kJ/mol, $f_{D_p} = 0.1$ –0.2, and $E_{\text{ads}} = 30$ –50 kJ/mol.

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References

- [1] G. Federici, A.R. Raffray and M.A. Abdou, MISTRAL: a comprehensive model for tritium transport in lithium-base ceramics – Parts I and II, *J. Nucl. Mater.* 173 (1990) 184–228.
- [2] M. Brieç, The TEQUILA experiment, In pile tritium extraction from LiAlO_2 , Centre d'Etudes Nucleaires de Grenoble, Grenoble (April 1990).
- [3] M. Brieç, Private communication, CEN, Grenoble (November 1990).
- [4] A.R. Raffray, Z. Gorbis and M.A. Abdou, Rate-controlling tritium transport mechanisms in solid breeder, presented at the 9th topical meeting on the technology of fusion energy, Chicago (October 1990).
- [5] A.S. Michaels, Diffusion in a pore of irregular cross section – a simplified treatment, *AIChE J.* 5(2) (1959) 270–271.
- [6] T. Kurasawa, H. Watanabe, G.W. Hollenberg, Y. Ishii, A. Nishimura, H. Yoshida, Y. Naruse, M. Aizawa, H. Ohno and S. Konishi, The time dependence of in-situ tritium release from lithium oxide and lithium aluminate (VOM-22H experiment), *J. Nucl. Mater.* 141–143 (1986) 265–270.
- [7] K. Okuno and J. Kudo, Tritium diffusivity in lithium-based ceramic breeders irradiated with neutrons, *Fusion Engrg. Des.* 8 (1989) 355–358.
- [8] A.K. Fischer and C.E. Johnson, Measurements of adsorption in the LiAlO_2 – $\text{H}_2\text{O}(\text{g})$ System, *Fusion Technol.* 15 2B (1989) 1212–1216.
- [9] A.K. Fischer, Processes for desorption from LiAlO_2 treated with H_2 as studied by temperature programmed desorption, presented at the 9th topical meeting on the technology of fusion energy, Chicago (October 1990).