Analysis of BEATRIX-II tritium release results using MISTRAL

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Abstract

The MISTRAL code was used to analyze the BEATRIX-II experimental results of Li_2O ring samples. The analysis included the change in inventory due to different temperature transients, the end-of-life inventory of the Phase I ring sample, and the analysis of the transient tritium release history of both Phase I and Phase II ring samples. The change in inventory results were used in order to obtain a set of input data that will reproduce these results. Using the same input data, MISTRAL was able to predict the end-of-life inventory of the sample. In all the cases, the calculations indicated that most of the tritium was present in the bulk, leading to the assumption that LiOT formation inside the grains is the key mechanism in controlling the tritium inventory in these cases.

1. Introduction

The most recent data available on the tritium release from Li_2O comes from the BEATRIX-II experiment (see Slagle et al. [1]), in which the in-situ tritium release from Li_2O samples was measured under different conditions.

The experimental results were analyzed using the updated version of MISTRAL described by Badawi et al. [2]. The code includes the following processes [2]:

1. Diffusion of atomic tritium in the grain to the solid/gas interface.
2. Trapping and detrapping of tritium in the bulk assumed to be due to the formation and dissociation of LiOT.
3. Four surface mechanisms: bulk-to-surface flux, desorption to the pore, adsorption from the pore and dissolution to the bulk.
4. Diffusion of the gaseous species through the pore to the purge gas.

The analysis plan was to match the changes in inventory from BEATRIX-II (obtained by integrating the tritium release history) with the calculated values, by changing the input parameters within the acceptable ranges. After matching the inventory changes, the experimental end-of-life inventory was compared to the calculated values based on a consistent set of input data. The tritium release profiles were then calculated and compared to the experimental results from BEAT-RIX-II.

The results of the ring specimen in Phase I were used for the change-in-inventory and end-of-life calculations. For the transient calculations, both the results of the Phase I and II ring specimens were used. Both samples had the same dimensions: 8.9 cm length, 1.84 cm outer diameter, and 1.514 cm inner diameter. However, the Phase I sample was small grained (5.5 μm size) with medium density (20.7% porosity) whereas the Phase II sample was large grained (44 μm size) with high density (12.7% porosity). The specific surface area was 60 m^2/kg.

Due to the huge uncertainties in the experimental data in the cases of the purge gas composition [2], it was impossible to analyze such cases in order to reproduce the experimental data under a change in purge gas composition.

2. Change-in-inventory calculations

Due to the fact that there are many property data missing for Li_2O, parametric studies have to be made

Table 1
Reference values of parameters used in the analysis of experimental data

Grain diffusion coefficient	
Preexponential, D_0	4.033×10^{-6} m^2 [6]
Activation energy, E_{diff}	95.1 kJ/mol [6]
Reference values of activation energies	
Adsorption activation energy	30 kJ/mol
Desorption activation energy	140 (kJ/mol) [8]
Heat of adsorption	110 kJ/mol
Activation energy of solution	20 kJ/mol
Bulk-to-surface activation energy	$E_\beta = E_{diff} + E_{ads}$
Dissolution activation energy	$E_{diss} = E_s + E_\beta + E_{des} - E_{ads}$
Pore diffusion factor, f_{Dp}	0.1
Equilibrium constant for LiOT reaction, K_{equi}	[4,5]

in order to obtain the set of input data that would best reproduce the experimental results.

Based on the analysis by Badawi and Raffray [3] and on examination of the model parameters, the parameters that will affect the tritium inventory in Li$_2$O are: the activation energy of adsorption, E_{ads}, the activation energy of solution, E_s, the heat of adsorption, Q, and the bulk-to-surface-flux activation energy, E_β, the pore diffusion, the preexponentials of the surface fluxes, the bulk diffusion coefficient, and the equi-

librium constant, K_{equi}, for LiOT formation from the reaction

$$Li_2O + H_2O \rightleftarrows 2LiOH. \tag{1}$$

Both the equilibrium constant [4,5] and the bulk diffusion coefficient [6] are well characterized from experiments and therefore their values were left constant. Because of the lack of data, E_{des} was assumed to be independent of the surface coverage. E_{ads} is not known for Li$_2$O. However, it is known to be small for

Table 2
MISTRAL predictions for the change in inventory with and without bulk trapping, using different values of the parameters in Table 1, for a purge gas composition of He + 0.1% H$_2$ and temperatures of 550–650°C. The experimental value of inventory reduction in this case was about −50 mCi

Parameter	Value	ΔI with trapping (mCi)	ΔI without trapping (mCi)
Activation energy of solution, E_s (kJ/mol)	min. = 10	−456	–
	ref. = 20	−95	−0.304
	max. = 30	−21	−0.602
Heat of adsorption, Q (kJ/mol)	min. = 90	−95	–
	ref. = 110	−95	−0.304
	max. = 130	−96	−1.059
Pore diffusion factor, f_{Dp}	min. = 0.001	−647	−2.890
	ref. = 0.1	−95	−0.304
	max. = 1	−88	−0.295
Adsorption flux factor, f_{ads}	min. = 0.1	−31	–
	ref. = 1	−95	−0.304
	max. = 10	−298	–
Desorption and dissolution flux factor, f_{des}	min. = 0.1	−31	–
	ref. = 1	−95	−0.304
	max. = 10	−297	–
Bulk-to-surface flux factor, f_β	min. = 0.1	−935	−3.05
	ref. = 1	−95	−0.304
	max. = 10	−11	−0.03

LiAlO$_2$. Since the value of E_{ads} will not affect the tritium inventory except at high values, as shown from the parametric study presented in Ref. [3], it was assumed to be 30 kJ/mol in the present analysis. A reference value of 0.1 of the calculated pore diffusion coefficient was used in order to allow for the effect of non-uniform pore size distribution (see Federici et al. [7]). Table 1 shows the reference values of parameters used in the analysis of experimental data.

The range in which the parameters in Table 1 were changed was chosen according to the uncertainties associated with each parameter. Therefore, E_s was changed between 10–30 kJ/mol based on experiments by Katsuta [9] and O'hira [10] that estimates its value between 16–25 kJ/mol. The range for changing the heat of adsorption was based on the surface coverage. Any value of Q that produced a surface coverage of more than 0.6 was excluded from the results, since such a high value was improbable. Since the values of the pre-exponentials of the surface fluxes were based on the vibration frequency (see Trapnell [11]), an uncertainty of about one order of magnitude seemed reasonable. Finally, the pore diffusion coefficient were changed between 1, which corresponds to the calculated value that neglects any effect of pore size distribution, to 0.001, which is extremely improbable.

The first case considered in the analysis was the case of a change in temperature between 550 and 650°C. The experimental change of inventory, ΔI, associated with this temperature change was about -50 ± 10 mCi. When the reference parameters in Table 1 were used without including trapping in the bulk, the tritium inventory changed from 2.7 mCi at 550°C to 2.4 mCi at 650°C, giving a change in inventory of -0.3 mCi, which is off by a factor of more than 150. When trapping was included, the inventory changed from 160 mCi at 550°C to 65 at 650°C, giving a ΔI of -95 mCi.

In order to obtain a better estimate of ΔI, each of the reference values in Table 1 was changed within a reasonable range and the corresponding effect on the inventory change was calculated. A detailed description of the results is given by Badawi [2] for 0.1% H$_2$ and temperature change of 550–650°C. Here, the re-

sults are summarized in Table 2 where the calculated changes in inventory with and without bulk trapping are shown for the minimum, reference, and maximum values of each parameter.

It is evident from the results in Table 2 that bulk trapping of tritium, assumed to be due to LiOT formation at the local temperature and moisture partial pressure, is a key factor in determining the tritium inventory. The results suggest that the parameters that can reproduce the experimental change in inventory in this case are:

1. Using an activation energy of solution of about 23 kJ/mol.
2. Using a desorption flux preexponential lower than the reference value by a factor of 0.2.
3. Using an adsorption flux preexponential lower than the reference value by a factor of 0.2.
4. Using a bulk-to-surface preexponential higher than the reference value by a factor of 2.

It seems more reasonable to change the activation energy of solution to $E_s = 23$ kJ/mol, which is within the range of values experimentally determined by O'hira [10]. By using $E_s = 23$ kJ/mol, the calculated change in inventory was found to be about -60 mCi, which is within the range of uncertainties in the experimental data.

In order to further explore the adequacy of MISTRAL in estimating the change in inventory in BEATRIX-II, another set of data from Phase I concerning a series of temperature changes was examined. The inventory changes were calculated based on the reference parameters listed in Table 1 and with $E_s = 23$ kJ/mol. The calculated values were found to be within the experimental uncertainties when compared to the experimental data.

A summary of all the cases studied in the change of inventory analysis is shown in Table 3.

3. End-of-life calculations

The reactor shutdown in BEATRIX-II Phase 1 occurred at 640°C while the sample was purged with He + 0.1% H$_2$ for about half a day after shutdown then changed to pure helium. The temperature decreased from 640 to 335°C in 20 min then stayed at 335°C for about 8 h before decreasing again to 300°C. The measured tritium inventory at the end-of-life was 50 mCi [12].

The data shown in Table 1 were used together with E_s of 23 kJ/mol. The inventory was found to be ~ 46 mCi, with most of it in the bulk. If bulk trapping is neglected, the calculated tritium inventory is only about 1 mCi, with the majority on the surface.

Table 3
MISTRAL predictions of the change of inventory of the BEATRIX-II Phase I ring sample

Temperature (°C)	Purge gase composition	ΔI model (mCi)	ΔI experiment (mCi)
550 → 650	He + 0.1%H$_2$	-60	-48 ± 10
650 → 550	He + 0.1%H$_2$	$+60$	$+50 \pm 10$
638 → 600	He + 0.1%H$_2$	$+17$	$+28 \pm 54$
600 → 550	He + 0.1%H$_2$	$+38$	$+36 \pm 27$
550 → 597	He + 0.1%H$_2$	-36	-24 ± 19

4. Transient analysis

The first transient case considered in the analysis was a transient from Phase I in which the temperature decreased from 642 to 557°C then increased back to 642°C. The sample was purged with He + 0.1% H_2.

The data in Table 1 were used with $E_s = 23$ kJ/mol. The effective LiOT decomposition rate was obtained from Kudo [13] for irradiated Li_2O as

$$k_{dsn} = 1.6 \times 10^3 \exp(-7.86 \times 10^4/RT). \qquad (2)$$

This value was different from the value he obtained when using unirradiated samples of LiOH [14]. He found k_{dsn} to be slower in irradiated samples than in unirradiated samples by about two orders of magnitude at 650°C, which is the temperature at which BEAT-RIX-II was operating. This indicates that LiOH decomposition is dependent on the sample characteristics and operating conditions. The BEATRIX-II case is closer to the irradiated Li_2O case but with a fluence of 3.8×10^{22} n/cm² [1], which is six orders of magnitude higher than in the experiment by Kudo [13].

Based on the above discussion, it was decided to use Eq. (2) as the reference value for the rate of LiOT decomposition and to carry out a parametric analysis to observe the effect on the tritium release of varying k_{dsn} between 1 and 0.01 times the reference value of Eq. (2). The rate of formation of LiOT, k_{for}, in each case would also be changed so that the equilibrium constant, K_{equi}, for reaction (1) remains constant. Fig. 1 shows the results for the case of temperature change from 642 to 557°C and He + 0.1% H_2 purge gas. The figure shows that decreasing the rate constant de-

Fig. 2. Normalized tritium release history for the Phase I Li_2O ring sample during the temperature change sequence of 642–557–642°C in a He + 0.1% H_2 purge gas.

creases the drop in the tritium release and increases the time required to reach steady state after a transient. For $k_{dsn} = 0.01$ of the reference value, the drop was equal to 0.809 (normalized) which is close to the experimental value of 0.884 (normalized). Note that the area under the curve in all the cases are the same, since changing the LiOT formation and decomposition rate constants by the same factor does not change the steady-state inventories.

A similar behavior was found in the case of temperature increase from 557 to 642°C. Decreasing k_{dsn} lead to a smaller peak and a longer time to reach steady state.

Based on the above analysis, the values that reproduce both the inventory change and tritium release results of BEATRIX-II are those in Table 1, together with an activation energy of solution of 23 kJ/mol and an LiOT rate constant for decomposition of 0.01 that in Eq. (2). Using this data, the calculated tritium release history for the temperature transient series is shown in Fig. 2. The shifts that is found in the peaks from the experimental values could be explained by the fact that it takes 15 min for the tritium to reach the monitors from the samples [1]. The difference between the calculated and measured tritium release over the time following the transient peak is within the uncertainty in the determination of the release baseline.

In order to further validate the modeling results, a case of temperature transient from the BEATRIX-II Phase II experiment was analyzed. In this case the purge gas contained 0.01% H_2 instead of 0.1% as in the previous case. The temperature changed from 640 to 600 to 550 then back to 640°C. Fig. 3 shows the calculated and measured tritium concentration profiles
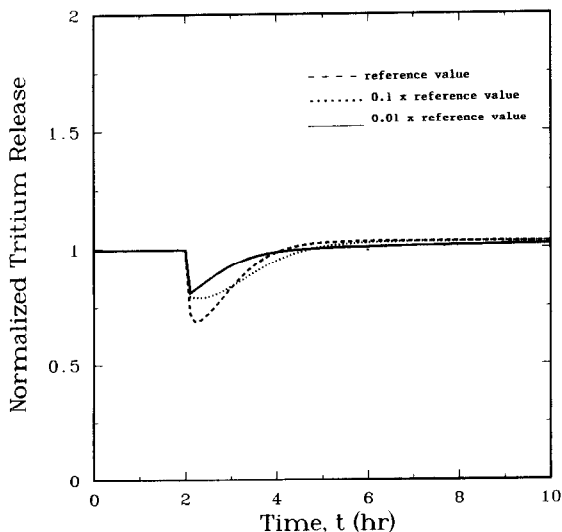

Fig. 1. The effect of the LiOT decomposition rate constant on the tritium release profile for the case of Phase I temperature change from 642 to 557°C and He + 0.1% H_2 purge gas.
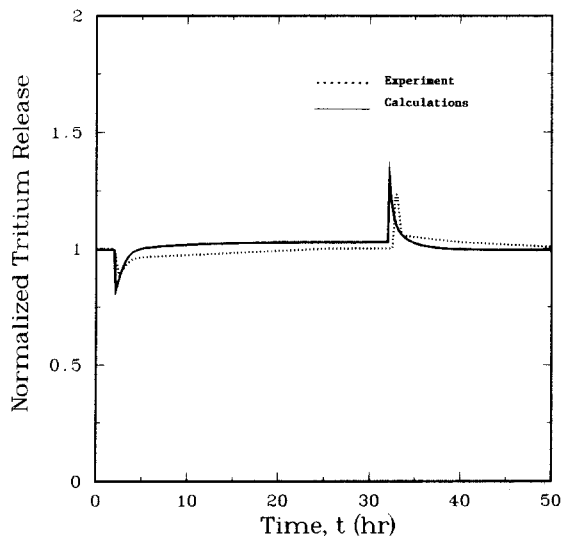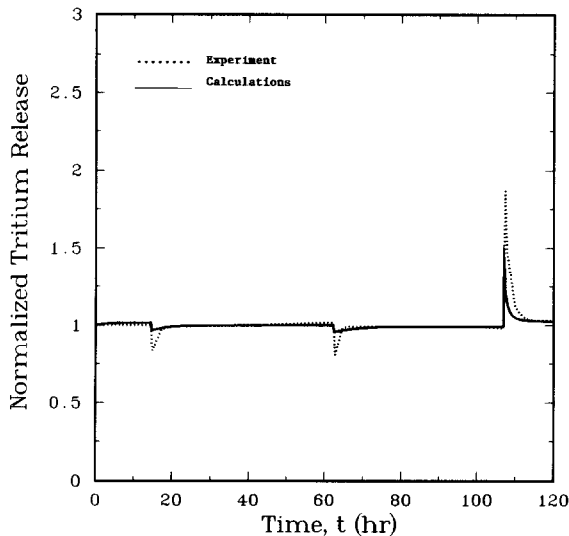
Fig. 3 Normalized tritium release history for the Phase II Li_2O ring sample during the temperature change sequence of 640–600–550–640°C in a He + 0.01% H_2 purge gas.

for the temperature change sequence. The change in the tritium concentration following each transient seem to be in reasonable agreement with the experimental results.

5. Summary and conclusions

MISTRAL was used to analyze the tritium release results from the BEATRIX-II experiment. The analysis focused on the results from the ring specimens of Phases I and II of the experiment. From the analysis, the following conclusions can be made:

- Although Li_2O has a fast diffusion coefficient, most of the tritium inventory is present in the bulk, assumed to be due to the formation of LiOT inside the grains.
- The tritium inventory is strongly dependent on the activation energy of solution.
- The tritium inventory for the cases analyzed was not dependent on the heat of adsorption, the value of which is not known for Li_2O. This indicates that there is a possibility of predicting the inventory even without the accurate knowledge of some of the basic data.
- MISTRAL was able to predict well within the experimental uncertainties the changes in inventory due to temperature transients as well as the end-of-life inventory of the sample.
- For transient cases, the code results showed reasonably good agreement with the experimental data on the tritium release history in temperature transient

cases, based on an assumed LiOT decomposition rate constant.

- Based on past experimental results, the effective LiOT decomposition rate constant seems to vary significantly depending on the material characteristics and operating conditions. The required decomposition rate constant to reproduce the BEATRIX-II temperature transient results is about 100 times lower than that obtained from irradiated Li_2O from Kudo. Further analysis is required to better understand the LiOT formation and decomposition processes and to determine the adequacy of the assumption that the transitions from mobile to trapped tritium and from trapped to mobile tritium in the bulk can be represented by LiOT formation and decomposition respectively.

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