Tritium Adsorption/Release Behavior of Advanced EU Breeder Pebbles

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Tritium Adsorption/Release Behavior of Advanced EU Breeder Pebbles

Matthias H.H. Kolb*, Rolf Rolli, Regina Knitter

Institute for Applied Materials, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany
*Corresponding author: matthias.kolb@kit.edu

Abstract
The tritium loading of current grades of advanced ceramic breeder pebbles with three different lithium orthosilicate (LOS) / lithium metatitanate (LMT) compositions (20-30 mol% LMT in LOS) and pebbles of EU reference material, lithium orthosilicate with an excess of silica, was performed in a consistent way. The controlled, temperature dependent release of the introduced tritium was subsequently investigated by temperature programmed desorption (TPD) experiments to gain insight into the desorption characteristics. As the pebble size can be an influential parameter on the measurements, this factor was addressed by using monosized spheres. The obtained TPD data was decomposed into individual release mechanisms according to well-established desorption kinetics.

The analysis showed that neither the pebble diameter nor the pebble composition of the tested samples severely change the release behaviour. Yet, an increased content of lithium metatitanate leads to the observation of additional desorption peaks at medium temperatures. The majority of tritium is released by high temperature release mechanisms of chemisorbed tritium, while the release of physisorbed tritium is marginal in comparison. The results allow valuable projections for the tritium release behaviour in a fusion blanket.

1 Introduction
Advanced ceramic breeder pebbles composed of a mixture of $\text{Li}_2\text{SiO}_4$ (LOS) and $\text{Li}_2\text{TiO}_3$ (LMT) are fabricated and developed at KIT by a special melt-based process named KALOS [1–3]. The development of these pebbles is carried out in view of a future DEMO reactor. The produced pebbles are easily characterized for their non-nuclear properties. For instance, the increased strength of the material with increased LMT content has been documented by Knitter et al. [4]. In recent publications, the mechanical strength of the pebbles is mostly pictured as the most important property of breeder pebbles. Although this view legitimate when constant operation and safety are concerned, the main task of a tritium breeder material is the generation and release of tritium. Therefore, it is crucial that these characteristics are investigated during the development as well.

As neutron irradiation experiments are expensive and require several years of planning, preparation and post irradiation examination (PIE) in addition to several years of irradiation, the comparably rapid development of the breeder pebbles cannot be supported by classical neutron irradiation experiments. Therefore the out-of-pile loading of the pebbles with tritium is used instead as it can be conducted much more easily and frequently. But it has to be kept in mind that the results of such loading procedures are not entirely comparable with neutron irradiation experiments as the generation of tritium within the bulk material is missing. While the Reference OSI material was included in past
neutron irradiation experiments and the tritium release investigated out-of-pile as well as in-pile [5–9], such information is not yet available for the advanced ceramic breeder pebbles.

In the presented work, the loading of current grades of advanced ceramic breeder pebbles with different LOS/LMT compositions as well as pebbles of a current reference lithium orthosilicate batch, produced by Schott AG, Mainz [10], is described. Subsequently, the controlled, temperature dependent release of the introduced tritium is detailed to gain insight into the desorption characteristics. As the pebble size can be an influential parameter on the measurements, this factor is addressed by focusing on monosized pebbles. Temperature programmed desorption (TPD) experiments are an often used way to characterize materials and surfaces, for instance catalysts [11–13]. But also in studies of reference grade tritium breeder ceramics, TPD experiments are widely used to gain insight into the release behaviour of tritium [6,8,9,14–16]. In most cases, these TPD experiments were performed as part of PIE.

In this study, novel advanced ceramic breeder pebbles fabricated by the KALOS process were examined together with one batch of reference OSi pebbles fabricated at Schott AG, Mainz. The obtained experimental data was decomposed into individual release mechanisms according to well-established desorption kinetics by a simulated annealing fitting procedure. Such an attempt was rarely made in the past, as acquired TPD curves were mostly discussed in a qualitative way.

2 Experimental

The KALOS pebbles feature three different nominal compositions of LOS/LMT, i.e. 20 mol% LMT, 25 mol% LMT and 30 mol% LMT. The Reference material consists of 90 mol% LOS and 10 mol% of lithium metasilicate (LMS). To eliminate potential effects of the surface area of the samples, the samples were screened and two pebble sizes, i.e. 560 µm and 630 µm, were selected for the experiments. In total eight individual samples were thus available for the experiments (see Table 1).

Table 1: Compilation of the used samples.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Nominal composition</th>
<th>Pebble diameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>KALOS 20 LMT</td>
<td>80 mol% LOS + 20 mol% LMT</td>
<td>560 µm</td>
</tr>
<tr>
<td>(K20)</td>
<td></td>
<td>630 µm</td>
</tr>
<tr>
<td>KALOS 25 LMT</td>
<td>75 mol% LOS + 25 mol% LMT</td>
<td>560 µm</td>
</tr>
<tr>
<td>(K25)</td>
<td></td>
<td>630 µm</td>
</tr>
<tr>
<td>KALOS 30 LMT</td>
<td>70 mol% LOS + 30 mol% LMT</td>
<td>560 µm</td>
</tr>
<tr>
<td>(K30)</td>
<td></td>
<td>630 µm</td>
</tr>
<tr>
<td>Reference OSi</td>
<td>90 mol% LOS + 10 mol% LMS</td>
<td>560 µm</td>
</tr>
<tr>
<td>(OSi)</td>
<td></td>
<td>630 µm</td>
</tr>
</tbody>
</table>

As neutron irradiated pebbles are not available, the pebbles were loaded with tritium. The loading process was performed individually on each sample right before the TPD experiment. Special care was taken to keep the timespans between all experimental steps low and constant. Each pebble sample was dried for 1 hour in inert gas atmosphere at 300 °C in the first step of the loading process. Then the actual loading was performed for 6 hours in a sealed containment which was flooded with hydrogen gas containing 500 ppm tritium and heated to 850 °C. As a result, a maximum pressure of 4 bar was achieved.

There are many ways to perform TPD experiments. Yet, the use of a temperature ramp during desorption is the most convenient way to carry out such experiments. For the TPD experiments, the loaded samples were placed in a tube furnace which is purged by a constant stream (25 ml/min) of reference purge gas (helium with 0.1% hydrogen). The purge gas stream is led through a proportional...
counter to detect the desorbed tritium as a function of time (see Figure 1). When the gas passed the proportional counter, it is led through water bubblers to catch all released tritium. A precise analysis of the activity of the bubbler water after the completion of a TPD experiment makes it possible to normalize the obtained values of the proportional counter in retrospect. For this analysis a scintillation counter is used. Once the samples are in place, the furnace is ramped from room temperature to 1080 °C at a rate of 7.1 K/min, while the temperature as well as the released activity are constantly monitored.

Figure 1: Schematic of the experimental setup that is used to conduct the TPD measurements.

Once the maximum temperature is reached, it is kept for 2.5 hours to ensure that the tritium leaves the pebbles completely. Before each measurement run, an empty run is performed to be able to remove any background from the apparatus in a later step from the recorded data.

The analysis of the obtained data is performed by applying Bruker-AXS TOPAS v5, which is by design a Rietveld analysis software for X-ray diffraction data. Yet, it is possible to modify the routines of the software in a way that any data in x-y-format is processable and thus its highly efficient least-squares minimization routines are available for the analysis of TPD data. TOPAS also provides the possibility to use custom fitting functions by its own script programming language. For the analysis just the tritium release during the ramp up of the temperature is considered. A maximum of 10 peak functions (see section 3) with independent parameters were considered to model the experiment at first. These functions are convoluted to form the envelope shape of the experimental data. Yet, only the necessary minimum of functions for modelling the experimental data was used in the later stages of the refinement. To ensure that the minimizations reach the global minimum, the refined parameters of the last refinement were randomized after convergence and used as starting parameters for another refinement cycle. After converging the refined parameters were randomized again and so on, while the best solution is saved. This refinement process, which is also referred to as “simulated annealing”, was carried out for at least 10000 iterations to ensure sufficiently precise refined parameters at the global minimum. The quality of a refinement is estimated by the parameter $R_{wp}$, which is automatically calculated by TOPAS. The higher the quality of the fit, the lower $R_{wp}$ will be. An excellent fit is obtained for values of about 1, while reasonable fits may show values of about 10.

3 Theoretical Treatment

Desorption of a gaseous species $A$ from a substrate can usually be described by a simple kinetic term if the removal of the desorbed species is sufficiently fast, which is assumed for all considerations in this report. As described in equation 1, the desorption rate is proportional to the adsorbed concentration...
of the species A raised to the power of \( x \), which is the reaction order. The proportionality factor \( k \) is generally temperature dependent and can be assumed as an Arrhenius term with a pre-exponential factor \( k_0 \) and the desorption energy \( \Delta E_{\text{des}} \) (see equation 2). However, no other dependence of the desorption kinetics is considered in this approach.

\[
- \frac{d[A]}{dt} = k[A]^x \quad (1)
\]

\[
k = k_0 e^{-\frac{\Delta E_{\text{des}}}{RT}} \quad (2)
\]

For a temperature ramp TPD experiment, the derivative of time can be converted into a derivative of temperature by using the identity of equation 3, with the heating rate \( \beta \) and the starting temperature \( T_0 \). The combination of the equations 1, 2 and 3 yields the so-called Wigner-Polanyi equation 4 [17]. In equation 4, the generic factor \( k_0 \) has been replaced by a vibrational factor \( \nu_x \) since its unit is \( s^{-1} \) for first order desorption kinetics.

\[
T(t) = T_0 + \beta t = T_0 + \frac{dT}{dt} t \quad (3)
\]

\[
- \frac{d[A]}{dT} = \frac{[A]^{x} \nu_x}{\beta} e^{-\frac{\Delta E_{\text{des}}}{RT}} \quad (4)
\]

It should be noted, that the Wigner-Polanyi equation consists of two parts. The pre-exponential part represents the available supply or coverage of adsorbed species, which declines as species are desorbed. The exponential term represents the energetic part of desorption, which increases rapidly with increasing temperature. It is only because of the declining supply of adsorbed species and an increasing energetic activation, that a peak in the desorption rate is observed. The shape of the peak depends significantly on the reaction order. While a first order kinetic generates a TPD peak with strong asymmetry with a shoulder towards lower temperatures, a second order kinetic leads to an almost symmetric peak shape. The peak temperature for a first order kinetic is independent of the concentration of adsorbed species, whereas the peak temperature decreases with increasing surface coverage.

Generally, diffusion is not addressed by standard TPD analysis. Yet, the diffusion of species from within the pebble to the surface can be viewed as a replenishment of the surface coverage. Then equation 1 can be written as follows, where \( J \) represents the diffusion flux to the surface by grain boundary and/or bulk diffusion.

\[
- \frac{d[A]}{dt} = k([A] + J)^x \quad (5)
\]

Given the fact that desorption as well as diffusion are thermally activated processes and with the assumption that a maximum coverage of the pebble surface with the species A exists, which is the case for chemisorption, either desorption or diffusion will strongly dominate the release behaviour. Therefore two extreme cases can be discussed. If the diffusion flux is low compared to the rate of desorption of A, diffusion does not play a significant role for the release rate and the peak shape. Otherwise, if the diffusion flux is much larger than the desorption rate of A, no TPD peak will be measured, but rather an exponential increase in the release rate. In this case, a peak will only appear in the signal if the supply of A solved in the pebble runs out. As all performed measurements (see section 4) do not show this behaviour and the release temperatures suggest chemisorption, diffusion as
expressed in equation 5 is not discussed. Yet, an interaction of diffusion and desorption in these experiments is not principally excluded.

In order to use the Wigner-Polanyi equation as a fitting function, an explicit form of it is mandatory. For the case of simple tritium desorption a mechanism according to equation 6 is assumed.

\[ T_{ads} + T_{ads} \xrightarrow{\Delta} T_{2,ads} \rightarrow T_{2,g} \]  

(6)

The integration of the Wigner-Polanyi equation for this case leads to equation 7a, which introduces the initial concentration at the surface \([A]_0\). An analytical solution of the exponential integral is not known. However, the integral can be approximated by an asymptotic series and a remainder integral according to Biegen and Czanderna [26] (see equations 7b, 7c and 7d).

\[
\frac{1}{[A]} - \frac{1}{[A]_0} = \int_{T_0}^T e^{-\frac{\Delta E_{des}}{RT}} dT 
\]

(7a)

\[
\int_{T_0}^T e^{-\frac{\Delta E_{des}}{RT}} dT = \frac{\Delta E_{des}\nu_2}{\beta R} I(\alpha) 
\]

(7b)

\[
\alpha = \frac{\Delta E_{des}}{RT}
\]

(7c)

\[
I(\alpha) = \frac{e^{-\alpha}}{\alpha^2} \sum_{n=1}^{\infty} \left( \frac{-1}{\alpha} \right)^{n-1} n! + \int_{-\infty}^{\alpha} \left( n+1 \right)! \cdot e^{-r} dr 
\]

(7d)

By combining the equations 4 and 7a-d, while neglecting the remainder integral, the desired explicit form of the Wigner-Polanyi equation for second order kinetics is established (see equation 8).

\[
- \frac{d[A]}{dt} = \nu_2 \left( \frac{1}{[A]_0} + \frac{\Delta E_{des}\nu_2}{\beta R} \frac{e^{-\frac{\Delta E_{des}}{RT}}}{\Delta E_{des}} \sum_{n=1}^{\infty} \left( \frac{-\frac{RT}{\Delta E_{des}}}{n!} \right) \cdot e^{-\frac{\Delta E_{des}}{RT}} \right)^{-2} \cdot \frac{\Delta E_{des}}{RT}
\]

(8)

Yet, hydrogen is added to the purge gas to promote exchange reactions, as detailed in equation (9). Therefore a second desorption kinetic is expected to be present. It is reasonable to assume that the concentration of hydrogen in the purge gas is constant. As a result, the reaction kinetic is of first order.

\[ H_{2,g} + T_{ads} \xrightarrow{\Delta} HT_g + H_{ads} \]

(9)

For a first order kinetic, the integration of the Wigner-Polanyi equation leads to equation 10 and its explicit form is then given by equation 11.

\[
\ln \left( \frac{[A]}{[A]_0} \right) = \int_{T_0}^T e^{-\frac{\Delta E_{des}}{RT}} dT 
\]

(10)

\[
- \frac{d[A]}{dt} = \nu_1 \frac{[A]_0 e^{-\frac{\Delta E_{des}}{RT}}}{\beta} \left( \frac{\Delta E_{des}}{\beta R} \right) \sum_{n=1}^{\infty} \left( \frac{-\frac{RT}{\Delta E_{des}}}{n!} \right) \cdot e^{-\frac{\Delta E_{des}}{RT}}
\]

(11)

As Biegen and Czanderna [18] pointed out, using 15 terms for the approximation of the exponential integral, e.g. \( n = 15 \), provides a sufficiently low error which can be decreased even further by just adding half of the last term as Chen [19] suggested. In the evaluation of the obtained TPD data both considerations were implemented. Effectively, equations 8 and 11 only show three independent
parameters which have to be refined, the desorption energy $\Delta E_{\text{des}}$, the vibrational factor $\nu_x$ and the initial concentration at the surface $[A]_0$.

The simultaneous use of two or more functions as given by equations 8 and 11 for modelling the release behaviour implies that there is no interaction between the adsorbed species on the surface and that there is no “parasitic” release from one adsorption centre by two kinetic mechanisms. This may not be fully true in general or for the given case. Yet taking such effects into account would raise the complexity of these investigations enormously.

4 Results and Discussion

The experimentally obtained data significantly differ between pebbles of different composition, but there are also visible differences between pebbles of identical composition and different pebble size. Especially the Reference OSI samples’ TPD curves are clearly different from each other (see Figure 2). The approximate peak temperatures of the TPD curves, given in Table 2, also illustrate this point. In tendency the LMT containing pebbles seem to show higher tritium release temperatures. To analyse the different TPD curves in more detail, the obtained data was decomposed into a number of peaks using the theoretical framework of section 3 and the techniques explained in section 2. By that, underlying similarities between the samples of identical composition as well as between samples of different compositions may be found.

Table 2: Approximate temperatures of maximum tritium release rate for all samples.

<table>
<thead>
<tr>
<th>Sample/pebble size</th>
<th>Reference OSI</th>
<th>KALOS 20 LMT</th>
<th>KALOS 25 LMT</th>
<th>KALOS 30 LMT</th>
</tr>
</thead>
<tbody>
<tr>
<td>560 µm</td>
<td>915 K</td>
<td>1115 K</td>
<td>1060 K</td>
<td>1105 K</td>
</tr>
<tr>
<td>630 µm</td>
<td>840 K</td>
<td>1100 K</td>
<td>1120 K</td>
<td>1105 K</td>
</tr>
</tbody>
</table>

The fitting of the experimental data required the use of a maximum of six peak functions. Of these six functions not more than two were of first order. Although up to six functions have to be employed to reproduce the experiments, only three or four functions are necessary to represent the major part of the tritium release. The other functions model the initial tritium release at low temperatures which is not relevant in terms of blanket conditions and, of course, not as well established as for higher temperatures. For all eight TPD experiments excellent fits were obtained with $R_{wp}$ values of less than 1.2. Therefore an excellent representation of the experimental data of all samples is achieved. The resultant peak functions and the experimental data are shown in Figure 2.

From Figure 2, it is obvious, that for a given composition, the tritium desorption can be modelled with the same number of functions, with the exception of the KALOS 25 LMT, 630 µm and KALOS 30 LMT, 560 µm samples where one additional function is necessary for a satisfying model. Yet, these functions are of minor importance as they are only relevant for the low temperature desorption when low release rates are determined as Figure 2 shows. Not only is the number of functions identical to model the TPD curves for a certain composition, but also are the determined desorption energies. The deviations between very similar desorption functions, i.e. within 20 pairs of corresponding functions of 560 µm and 630 µm pebbles of a total of 42 fitted functions, are $5.5\pm3.2\%$ in mean.
Figure 2: TPD results of all samples. The determined first order and second order peaks are illustrated in the graphs.
The determined vibrational factors also do not deviate greatly from each other for the major peak functions. In general the values of the vibrational factors lie in the range of $10^3$ to $10^5$ (Bq/g)$^{-1}$s$^{-1}$ for second order functions which is very low and hints at low mobility of the adsorbed tritium, which in return would suggest chemisorption as low mobility means stronger bonds. The determined values for the first order functions are in tendency higher, but as no stable value is established, they are considered to be similar. The implication that the tritium is mainly bound to the surface by chemisorption is also supported by the comparably high desorption energies which are usually less than about 50 kJ/mol for physisorption [20]. According to this classification, about half of the obtained peak functions can be linked to a physisorption process with low release rates and temperatures. However, pure chemisorption and pure physisorption are to be regarded as extreme cases. It is usually more appropriate to assume a mixed state with one more or less dominant sorption mechanism.

The observed differences in the experimental TPD curve between samples of the same composition are therefore mainly a matter of the intensity, i.e. the initial concentration or coverage, of these release peaks. The peak release temperature of a given second order kinetics function, in contrast to a first order kinetic, not only depends on the desorption energy, but also heavily on the initial coverage. This is not surprising when considering the basic reaction equation (6). As a result, differences in the coverage lead to a more pronounced difference in the overall TPD curve, while the principal release behaviour is very similar.

In the following, desorption energies are assigned to desorption mechanisms while not specifying them. The assignment should be approximately correct, but more evidence is necessary to remove any ambiguity. Comparing the desorption energies between the four compositions of the samples also shows that there are clear similarities between them. The analysis of all TPD curves showed that second order kinetic desorption mechanisms with about 91.0±5.3 kJ/mol and 112.0±5.3 kJ/mol contribute significantly to the release of tritium for all samples (see Table 3). Yamaki and Jitsukawa [15] also used activation energies for tritium release of 117 kJ/mol and 121 kJ/mol for modelling the tritium release from lithium metatitanate, which are in reasonable agreement with the obtained results. Yet, the desorption mechanisms with an activation energy of about 91 kJ/mol and 112 kJ/mol appear for all samples, whether they contain lithium metatitanate or not.

Table 3: Subsumption of the peak functions according to their desorption energy. “●” indicates that a desorption peak with the respective desorption energy exists for the given sample.

<table>
<thead>
<tr>
<th>Mean $\Delta E_{\text{des}}$ [kJ/mol]</th>
<th>22.2</th>
<th>26.5</th>
<th>34.3</th>
<th>42.7</th>
<th>51.7</th>
<th>60.3</th>
<th>69.1</th>
<th>76.0</th>
<th>91.0</th>
<th>112.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average absolute deviation [kJ/mol]</td>
<td>0.5</td>
<td>1.4</td>
<td>2.2</td>
<td>1.0</td>
<td>0.2</td>
<td>2.1</td>
<td>0.2</td>
<td>2.2</td>
<td>5.3</td>
<td>5.3</td>
</tr>
<tr>
<td>OSi, 560 µm</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OSi, 630 µm</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td></td>
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<tr>
<td>K20, 560 µm</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
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<tr>
<td>K20, 630 µm</td>
<td>●</td>
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<tr>
<td>K25, 560 µm</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td></td>
<td></td>
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<tr>
<td>K25, 630 µm</td>
<td>●</td>
<td>●</td>
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<tr>
<td>K30, 560 µm</td>
<td>●</td>
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<td>●</td>
<td>●</td>
<td>●</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K30, 630 µm</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The samples with a higher LOS concentration, i.e. KALOS 20 LMT and Reference OSi, show almost identical tritium release behaviour in terms of the determined desorption energies. Apart from the two common release mechanisms substantial tritium release takes place by a second order kinetic with a desorption energy of 60.3±2.1 kJ/mol. All other desorption energies that appear for both sets of samples are comparably insignificant. Also both pebble grades show a first order kinetic release with a desorption energy of 34.3±2.2 kJ/mol, which is however also insignificant compared to the stronger release mechanisms.

In general, the low second phase concentration of these two pebble grades seems to lead to largely identical tritium release behaviour. The only difference between both grades is an additional second order kinetic release mechanism ($\Delta E_{\text{des}}$: 26.5±1.4 kJ/mol). As the second phase concentration is increased, fewer similarities are observed. The low temperature first order tritium release mechanism, which all KALOS 20 LMT and Reference OSi pebbles show in their TPD experiment, is only observable for the KALOS 25 LMT, 630 µm sample. Similarly, desorption with an energy of 42.7±1.0 kJ/mol is only observed for the KALOS 30 LMT, 560 µm sample and for both samples of KALOS 20 and Reference OSi. Presumably, these release mechanisms exist for all samples, but are barely active and thus not detectable in the performed experiments. For pure lithium orthosilicate Wang et al. [21] also observed desorption energies of about 40 kJ/mol. This is in good agreement with the findings for the samples that show the highest lithium orthosilicate contents of the investigated samples (i.e. KALOS 20 and Reference OSi).

Also the unique release mechanism of KALOS 25 LMT with a desorption energy of 51.7±0.2 kJ/mol can possibly be related to the samples with higher LOS content, as it may be viewed as an intermediate, blurred mechanism between the 42.7 kJ/mol and 60.3 kJ/mol mechanisms. Though, a similar conclusion is hard to make for the other release mechanisms. Whereas the other samples show multiple common release mechanisms, the KALOS 25 LMT and KALOS 30 LMT samples show just one common release mechanism with a desorption energy of 76.0±2.2 kJ/mol.

Generally, there seems to be a tendency towards less release mechanisms with a medium desorption energy with increased second phase content as evident from Table 3, although the predominant phase of all pebbles is LOS. It is also evident, that with increasing LMT content, release mechanisms with desorption energies at about 70 kJ/mol evolve. Without further evidence these release mechanisms are attributed to the LMT phase, but for a precise determination of the surface reactions additional fundamental research must be carried out. The same is true for all other determined desorption energies, which presumably originate from reactions with LOS, however, also impurity phases as lithium carbonate may be present at the pebble surface to a, for these experiments, significant amount [22].

For similar samples fabricated by the KALOS process, González et al. [14] investigated the thermally induced desorption of deuterium. The shape of the release curves of these experiments were significantly different compared to the present study and more importantly, a significant release of deuterium is observed at much lower temperatures. Yet, the measurement of the release was carried out in vacuum and the adsorption of deuterium was carried out at room temperature. The authors also determined activation energies for desorption which lie in the range of 16.4 kJ/mol to 19.3 kJ/mol. Such low desorption energies were not observed in this study. However, these energies suggest the desorption of physisorbed deuterium, whereas the results of the present study show a relatively low amount of physisorbed species. As the loading of the pebbles at room temperature may not lead to a
high degree of chemisorption, it is assumed that the observed differences of both studies may originate from the different loading processes.

In contrast to the adsorption of tritium or deuterium on the pebbles, neutron irradiation generates tritium within the whole volume of the material. For the reference OSI pebbles, some TPD curves were acquired by Munakata et al [8] after irradiating the sample with neutrons for a few minutes. Also these TPD curves suggest a slightly lower peak temperature of the tritium desorption. Yet, the release of tritium vanishes at higher temperatures, which was not observed within this work or within the work of González et al. [14]. Also longer irradiation campaigns like EXOTIC 8 [5,6] seem to lead to a similar behaviour as Munakata et al. [8] observed. It is not yet clear, why these differences appear, and more investigations are necessary to deduce the transferability of sorption/desorption experiments to tritium release in neutron irradiation experiments. However, the decomposition of otherwise seemingly incomparable tritium release curves into individual release mechanisms proved to be an appropriate approach that should be used in future TPD analysis of irradiated breeder ceramics.

5 Conclusions
In conclusion, the tritium release from advanced breeder ceramics can be modelled and fitted by a number of first and second order explicit Wigner-Polanyi equations, with the developed software tools. First order kinetics are expected for exchange reactions with hydrogen additions of the purge gas, while second order kinetics involve the reaction of two adsorbed species.

The so-modelled experimental data shows that the release of tritium from the tested pebbles is relatively similar, although this is not suggested by the temperatures of maximum tritium release rate. Especially the release of chemisorbed tritium at high temperatures is nearly identical for all samples, whereas there is some ambiguity for the presumably physisorbed tritium at low release temperatures. As the LMT content of the pebbles is increased, release mechanisms with medium desorption energies become less important and release mechanisms with higher desorption energies evolve. Yet, these mechanisms show still lower desorption energies than the mechanisms which are shared by all samples. On the basis of the present data, it is impossible to assign any observed desorption energy to a specific desorption reaction. All observed major release mechanisms show a second order kinetic, which apparently means that first order kinetics play a subordinate role in the used test environment. Potentially, a higher hydrogen content in the purge gas could promote exchange reactions and thus the significance of first order kinetic reactions. Anyway, two-phase pebbles of lithium orthosilicate and lithium metatitanate seem to show an appropriate tritium release behaviour for use within a DEMO or ITER blanket, because of the high similarity with the current reference material (i.e. reference OSI).

All in all, the experimentally obtained TPD curves depend significantly on the surface concentrations of tritium and it is seemingly difficult to reproduce these concentrations, although extraordinary care was taken during tritium loading, the measurements and between both steps.

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6 References


