Hydrogen isotope retention and release in beryllium: The full picture from experiment and ab initio calculations

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Overview

1. Wall materials and particle loads
2. Retention mechanisms
3. Retention and thermal release: results
4. Lattice orientation: single vs. polycrystal
5. Outlook:
   - Neutron-induced defects
   - Multi-component materials
6. Conclusions
Materials in ITER and DEMO
ITER first wall

Fusion power: 500 MW
Plasma volume: 840 m$^3$
Plasma current: 15 MA
Typical density: $10^{20}$ m$^{-3}$
Typical temperature: 20 keV

700 m$^2$ beryllium first wall
100 m$^2$ tungsten divertor
50 m$^2$ CFC strike point
First wall loads: particle energy

ASDEX Upgrade conditions

Divertor
\( I^+ = 10^{19} \text{ cm}^{-2} \text{ s}^{-1} \)
CX: similar

Baffle
\( \text{CX: } 10^{17} \text{ cm}^{-2} \text{ s}^{-1} \)
\( I^+ = 10^{19} \text{ cm}^{-2} \text{ s}^{-1} \)

\( T_e = 40 \text{ eV} \)

CX flux (atm\(^2\) s\(^{-1}\) eV\(^{-1}\))

LEN A, Verbeek et al.)

First wall
\( \text{CX: } 10^{16} \text{ cm}^{-2} \text{ s}^{-1} \)
D retention in beryllium

Variation by 1-2 orders of magnitude!

[D, T]

Be: ~700 m²

[Anderl 1999]
Hydrogen in Be: saturation

D retention demonstrates saturation. For 1 keV D ion irradiation, the saturation is observed at a fluence of $10^{22}$ D/m$^2$.

For D is trapped in the implantation zone with negligible diffusion into the bulk.

When the irradiation temperature increases, the D retention decreases.

Strategy

Possible reasons for quantitative uncertainties:
- undefined BeO coverage
- undefined crystal structure
- unclear retention mechanisms

Need for well-defined experiments and theory!

To be resolved:
- retention in pure Be
- influence of crystal structure/orientation
- influence of surface oxide
- retention and release mechanisms
Experimental concept

- **QMS**
  - desorption rate

- **TPD**
  - Temperature Programmed Desorption

- **NRA**
  - \(^3\text{He}(d,p)^4\text{He}\)

- **Retention mechanisms**
  - \(\text{Be}_{\text{poly}}, \text{Be}(0001), \text{Be}(11-20)\)

- **Hydrogen retention**
  - D implantation (mass and energy separated)

- **bulk + surface processes**
  - Sequential release of D
  - Limited by combination of bulk + surface processes

- Energy barriers for ...:
  - Diffusion
  - Detrapping
  - Recombination
Surface morphology
Annealing

$T \rightarrow 1000 \text{ K, several hours}$:

- Formation of Be crystallites
  $\rightarrow$ Substantial material transport
- Recrystallization to low indexed facets
Annealing – sputtering cycles

Cycles of:
- Cleaning
- D Implantation
- Degassing 1000 K

- Recrystallization
- Erosion
- D-induced structural modifications
Erosion: orientation-dependent

Be$_{PC}$ + D shows crystallites with ...
... **less damage**

... **more damage**

| Red                  | = Basal plane $\perp$ surface  
|                      | FAST diffusion to surface       |
| White                | = Basal plane $\parallel$ surface  
|                      | SLOW diffusion to surface        |
| Black                | = Not indexed                    |
Retention and release mechanisms
Hydrogen isotope inventory

Main mechanisms for retention
- Implantation

and release
- Diffusion
- Desorption
Implantation

Simulation of collision cascade with Monte Carlo codes (TRIM)

- Binary collision approximation
- Energy loss: stopping
- Creation of displaced atoms and vacancies
- Projectile is trapped

Result: Depth profile

- Deuterium in polycrystalline beryllium
- Depth profile measured with 10 MeV $^{28}$Si
**Thermal release**

**Elementary steps**
- diffusion of H in the solid
- trapping and release of H from binding sites (defects)
- recombination and desorption of $H_2$ from the surface
Thermal release

Described by **Diffusion-Trapping Model**

**Local elementary reactions** (trapping / release of H)
- thermally activated processes

with:

- $n_i$: number density of each species
- $k$: reaction rate constant
- $E_a$: activation energy

$$R = n_i \cdot k \cdot \exp \left( \frac{-E_a}{k_B \cdot T} \right)$$

**Diffusion:**
- driven by concentration gradient
  (1st Fick’s law)

local concentration change:
- Diffusion described by continuity equation
  (2nd Fick’s law)

$$j_i = -D_i \cdot \text{grad} \ n_i$$

$$\frac{\partial n_i}{\partial t} = -\text{div} \ j_i$$
Particle flux at desorption

Partial differential equation:
considers both diffusion and elementary reactions

\[
\frac{\partial n_i}{\partial t} = -D_i \text{ div (grad } n_i) + \sum R^{\text{Source}} + \sum R^{\text{Sink}}
\]

Example:

\( n_i \): concentration of mobile (dissolved) \( H^{\text{mobil}} \)
\( R \): rates for trapping and release at traps \( \Box^{\text{trap}} \)

PDE describes H diffusion and the reaction:

\( H^{\text{trap}} \Leftrightarrow H^{\text{mobil}} + \Box^{\text{trap}} \)

\( \Rightarrow \) Consider arbitrary elementary reactions

Description of the thermal release by a system of coupled differential equations
Saturation of retention

- Trapping of D at ion-induced defects
- Reemission above 25 at.%

\[ (D/Be)_{\text{max}} = \text{const} \]

\[ \text{Ion range} \]

\[ \text{Be} \]

low fluence
- linear

high fluence
- saturation

Implantation: D at 1 keV into Be (1120)

Retained areal density [10^{16} D cm^{-2}]

Fluence [10^{16} D cm^{-2}]

95%
Saturation of retention

- Trapping of D at ion-induced defects
- Reemission above 25 at.%
- Retention within ion range
- Low inventory in main wall of ITER

\[ \Gamma = 10^{15} \text{ D cm}^{-2} \]

\[ \Gamma = 10^{17} \text{ D cm}^{-2} \]
Saturation of retention

- Trapping of D at ion-induced defects
- Reemission above 25 at.%
  - Retention within ion range
  - Low inventory in main wall of ITER

- Annihilation of traps at grain boundaries
- Anisotropic diffusion of interstitials (DFT)

\[ \Gamma = 10^{15} \text{ D cm}^{-2} \]

\[ \Gamma = 10^{17} \text{ D cm}^{-2} \]
Thermal release
Trapping sites and desorption stages

Temperature-programmed desorption spectra

Be poly, $E_{\text{impl}}=1$ keV

ITER main wall bake-out temperature

Fluence $[10^{16}$ cm$^{-2}]$

Desorption rate [a.u.]

Temperature [K]

Fluence $[10^{16}$ cm$^{-2}]$

Desorption rate [a.u.]
Trapping sites and desorption stages

Temperature-programmed desorption spectra

Be poly, $E_{\text{impl}} = 1$ keV

![Graph showing desorption rate vs. temperature and retention in structural modifications vs. incident fluence.](image)

- Desorption rate [a.u.]
- Temperature [K]
- Retention in the structural modifications [%]
- Incident fluence $[10^{15} \text{ D cm}^{-2}]$
Saturation: Simulation by SDTrim.SP

Supersaturation

Bulk saturation concentration:
26 at% D

Concentration build-up in a depth of 40 nm

Supersaturation Structural modifications

SDTrim.SP Calculation

Retention in structural modifications [%]

Incident fluence \(10^{15} \text{ D cm}^{-2}\)
Trapping sites and desorption stages

Temperature-programmed desorption spectra

Stable structures from density functional theory (DFT) calculations by A. Allouche

Desorption rate [a.u.] vs. Temperature [K]

Be poly, $E_{\text{impl}}=1$ keV

Fluence $[10^{16}$ cm$^{-2}]$

400 600 800 1000

11.7 13.1 19.9

4.5 2.5

Amorphous BeH$_{2-x}$
Trapping sites and desorption stages

Temperature-programmed desorption spectra

Be poly, $E_{\text{Impl}}=1 \text{ keV}$

Fluence $[10^{16} \text{ cm}^{-2}]$

Desorption rate [a.u.]

Temperature-programmed desorption spectra

Stable structures from density functional theory (DFT) calculations by A. Allouche

Amorphous BeH$_{2-x}$

Position of H inside a monovacancy

Ch. Linsmeier | ICTP-IAEA PMI in Fusion Devices | 2014-11-03
Modelling the release at low fluences

- Be (1120)
  - 2.7 * 10^{15} D cm^{-2}

**Implantation energy**
- 1 keV
- 3 keV

**Temperature [K]**
- 600
- 700
- 800

**Desorption flux \left[ 10^{13} \text{ cm}^{-2} \text{s}^{-1} \right]**
- 0
- 1
- 2
- 3
- 4

**Reaction-diffusion equation**
\[
\frac{\partial n^{\text{mob}}}{\partial t} = \frac{\partial}{\partial x} \left[ D \cdot \frac{\partial n^{\text{mob}}}{\partial x} \right] + R_{\text{source/sink}}
\]

- Solve set of coupled differential equations numerically
- Reproduce both spectra (different initial conditions) with identical set of parameters

**Notes**
- Single processes not accessible in experiments
- \( E^{\text{act}} \)
- \textbf{Density functional theory}
Modelling the release at low fluences

**Implantation energy**
- 1 keV
- 3 keV

Be \((1\bar{1}20)\)
- \(2.7 \times 10^{15} \text{ D cm}^{-2}\)

**Graph:**
- **Desorption flux** \(\left[10^{13} \text{ cm}^{-2} \text{s}^{-1}\right]\)
- **Temperature** \([\text{K}]\)

**Model 1:**
- static traps
- diffusion barrier from literature
- adapted barrier for detrapping

**Implemented processes:**
- diffusion of \(D\) \(E_{\text{act}} = 0.3 \text{ eV}\)
- trapping \(D_{\text{mob}} + \text{trap} \rightarrow D_{\text{trap}}\)
- detrapping \(D_{\text{trap}} \rightarrow D_{\text{mob}} + \text{trap}\)

- **Shift with initial depth due to effective diffusion**
- **Simulated peaks broader than experiment!**

**Assumed missing physics:** Annealing of defects

**Implement trap mobility**
Modelling the release at low fluences

Forward calculations yield

- **Shift** with initial depth profile
- **Peak width**
- **Assymmetry**

**Implantation energy**

- 1 keV
- 3 keV

**Desorption flux** $[10^{13} \text{ cm}^{-2} \text{s}^{-1}]$

- **Temperature [K]**
- **Be (1120) 2.7 * 10^{15} \text{ D cm}^{-2}**

**Model 2:**

- trapping at mobile vacancies
- accumulation of $D_{\text{mob}}$ at $D_{\text{trap}}$
- diffusion barriers from DFT
- adapted barrier for detrapping

**Implemented processes:**

- diffusion of vac $E_{\text{act}} = 0.70 \text{ eV}$
- diffusion (||) of D $E_{\text{act}} = 0.41 \text{ eV}$
- trapping $E_{\text{act}} = 0.41 \text{ eV}$
- accumulation $E_{\text{act}} = 0.41 \text{ eV}$
- detrapping $E_{\text{act}} = 1.86 \text{ eV}$

**Assumption of trapping at single vacancies** consistent with experimental desorption spectra
Lattice orientation
D diffusion in beryllium

- Beryllium has **not an “ideal” hcp structure.** Be-Be distances are closer in \( <0001> \) than perpendicular to it (e.g. \( <11-20> \))

- DFT (Density Functional Theory) calculations show anisotropy in transport processes with respect to Be basal planes
Modeling: 2D coupled rate equations

Strategy

- Solve a coupled reaction diffusion system (CRDS) consisting of an arbitrary number of diffusing species \(i=A,B,C\ldots\) in 1, 2 or 3 dimensions.
- Solve system of partial differential equations for the time dependent 2D depth profile \(\rho(x,z,t)\) [m\(^{-3}\)]

\[
\frac{\partial \rho_A(x,z,t)}{\partial t} = \frac{\partial}{\partial x} \left( D_x(T(t)) \frac{\partial \rho_A(x,z,t)}{\partial x} \right) + \frac{\partial}{\partial z} \left( D_z(T(t)) \frac{\partial \rho_A(x,z,t)}{\partial z} \right) + \\
+ \sum_i \Gamma_{i,Form}^{Form} (\rho_{A,B,C}) - \sum_i \Gamma_{i,Annihilation}^{Annihilation} (\rho_{A,B,C}) + \Gamma_{i,Source}^{Source} (x,z,t)
\]

\(A + B \rightarrow C\)

\(C \rightarrow A + B\)

\[
\Gamma_1(\rho_A, \rho_B, t) = k_1 \rho_A \rho_B \exp \left( -\frac{\Delta E_1}{k_B T(t)} \right) \quad \Gamma_2(\rho_C, t) = k_2 \rho_C \exp \left( -\frac{\Delta E_2}{k_B T(t)} \right)
\]
TPD of D implanted in Be single crystals

TPD spectra and 2D-CRDS simulations after implantation of D at 1 keV/D and 3 keV/D in Be(0001) and Be(11-20)

Only one type of trap!

1. Desorption temperature shift for different implantation energies
2. Desorption temperature shift for Be(0001) and Be(11-20)
3. Less D retention in Be(0001) than in Be(11-20)

1. Deeper implantation → longer diffusion path to the surface → higher TPD peak temperature
2. Anisotropy of Be lattice → 2D anisotropic modelling required to implement results from DFT calculations
3. Dynamics during D implantation (MV+SI annihilation and trapping in MV) determines retention

Simulation phases

The diagram illustrates the simulation phases with respect to time and temperature.

- **Implantation**
- **Relaxation**
- **Heating**

The x-axis represents time in seconds, ranging from 0 to 2000. The y-axis represents temperature in Kelvin, ranging from 200 to 1000.

The implantation phase is marked at the start of the simulation, the relaxation phase occurs at a constant temperature, followed by the heating phase that shows a linear increase in temperature over time.
Simulation phases

- self interstitials during implantation
- mono vacancies stable after implantation, thermally instable

- self interstitials during implantation
- mono vacancies vanish quickly
TPD from Be polycrystal

Identical parameters also applied for polycrystalline Be

- Shift for Be\textsubscript{poly} reproduced with no retrapping: fast grain boundary diffusion
- heating ramp variation reproduced: no (self)trapping during heating

SEM (EBSD)

- Be(11-20)
- Be(0001)

Symbols: Experiment

Lines: 2D CRDS Model

- [11-20] With re-trapping
- [0001] With re-trapping
- [11-20] No re-trapping
- [0001] No re-trapping

Parameters for D release and diffusion

Experimentally and DFT determined parameters for full description

<table>
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<tr>
<th></th>
<th>( \nu )</th>
<th>( \Delta E_{\text{act}} ) [eV]</th>
<th>( \Delta E_{\text{act}} ) [eV]</th>
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<tr>
<td></td>
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<td>CRDS</td>
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<td><strong>Basal Plane</strong></td>
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<td><strong>Diffusivity II</strong></td>
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<td>Mobile Hydrogen ( H_{\text{mob}} )</td>
<td>3.11E-06</td>
<td>&lt;0.4*</td>
<td>0.2</td>
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<td>Mono vacancy MV</td>
<td>3.11E-06</td>
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<td>0.7</td>
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<tr>
<td>Self interstitial SI</td>
<td>3.11E-06</td>
<td>0.4</td>
<td>0.4</td>
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<tr>
<td>Trapped Hydrogen ( H_{\text{trap}} )</td>
<td>-</td>
<td>-</td>
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<tr>
<td><strong>Basal Plane</strong></td>
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<tr>
<td><strong>Diffusivity I</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>( H_{\text{mob}} )</td>
<td>7.68E-06</td>
<td>&lt;0.4*</td>
<td>0.4</td>
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<tr>
<td>MV</td>
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<tr>
<td>SI</td>
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<td>0.004</td>
<td>0.004</td>
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<tr>
<td>( H_{\text{trap}} )</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td><strong>Trapping</strong></td>
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<tr>
<td>( H_{\text{mob}} + MV \rightarrow H_{\text{trap}} )</td>
<td>1.00E+13</td>
<td>0.4</td>
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<td><strong>Detrapping</strong></td>
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<td>( H_{\text{trap}} \rightarrow H_{\text{mob}} + MV )</td>
<td>1.00E+11*</td>
<td>1.75</td>
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<td><strong>Annihilation</strong></td>
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<tr>
<td>( MV + SI \rightarrow - )</td>
<td>1.00E+13</td>
<td>0.004</td>
<td>0.004</td>
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<tr>
<td><strong>Self trapping</strong></td>
<td></td>
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<tr>
<td>( H_{\text{mob}} + 1 H_{\text{trap}} \rightarrow 2 H_{\text{trap}} + SI )</td>
<td>1.00E+13</td>
<td>0.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Anisotropy in diffusion of self-interstitials crucial for modeling!
Surface oxide
Be with oxide layer

Composition of first atomic layer: Ion scattering spectroscopy!

LEIS (45°, 500 eV He+)

Be +
3 ML BeO
(closed surface layer)

Be terminated surface +
3 ML BeO (covered)

Segregation of Be at the surface
- Annealing (1000 K):
  Be-terminated surface
  (desorption via pure Be surface)
- No annealing:
  TPD via BeO covered surface
TPD: Influence of BeO-coverage

No change of $E_A$ of release from binding states

No recombination limit $\leftrightarrow$ Trapping in the bulk

Formation of BeO:D at the surface
Implantation at elevated temperatures

- New trapping sites appear (deuteride, surface oxide)
- \( \text{BeD}_2 \) formation (decomposition >570 K)
- Retention at 530 K: 90%, instead of expected 70%

\[
1 \text{ keV D} \rightarrow \text{Be} \\
2 \times 10^{21} \text{ D m}^{-2}
\]

Implantation of D within BeO layer changes D release:

- small amount of low-T trapping
- D release over wide temperature range
- only 75% of total D released until 850 K
- only small fraction of total D released until 513 K (ITER wall bake-out)

Similar total retained D amounts

M. Oberkofler et al., J. Nucl. Mater. 415 (2011) S724
Influence of neutron damage
Neutron-induced trap formation: Tungsten

Damage simulation
Example: Trapping in heavy-ion damage at rear surface

- Deuterium depth profiles measured on the front and rear side of W samples
- Damaged either by 20 MeV W ions
- The front side was exposed to D plasma to a fluence of \(3 \times 10^{26} \text{ D m}^{-2}\) at 550 K
- D retention decorates damage profiles, but also demonstrates long range damaging beyond ion range

Neutron-induced trap filling in ITER

Modelling of ITER wall conditions

- Damage evolution:
  - $10^{-7}$ dpa/s (from ITER Org.)
  - Saturation trap density 1%

\begin{align*}
\text{Filling of } 1 \text{ mm W armour in about 3 years steady state operation} \\
\text{Relevant to DEMO rather than ITER}
\end{align*}

Graphs showing
- Trap density, at. %
- D concentration (at. %)
- Fluence (D/m$^2$)
- Depth (µm)

Multi-component materials
DEMO first wall: W alloy

Power plant conceptual study

- Accidental loss of coolant: peak temperatures of first wall up to 1200 °C due to nuclear afterheat
- Additional air ingress: formation of highly volatile WO$_3$ (Re, Os)
- Evaporation rate: order of 10 -100 kg/h at >1000°C in a reactor (1000 m$^2$ surface)
  → large fraction of radioactive WO$_3$ may leave hot vessel

Development of self-passivating tungsten alloys

Temperature profile in PPCS Model A, 10 days after accident with a total loss of all coolant.

DEMO first wall: W alloy

W-Cr-Ti self-passivating alloy

- Optimum Cr concentration
- Ti active element: reduce oxidation rate at high T
- Ti: hydrogen retention?

Chromium concentration [wt-%]

Rate $[\mu m^2/s]$ vs. Chromium concentration [wt-%]

- 1273 K W-Cr binary
- + ~0.5% Ti, TGA 1273 K
W-Cr-Ti: D retention

D depth profiles
- room temp. loading
- 100 V bias
- $^3$He NRA depth profiles
- almost homogeneous D distribution

D content vs. Ti fraction
- linear dependence
- 2 at-% „threshold“
- TiH$_2$? Replace Ti by non-hydride former!
Summary

Hydrogen retention and release from beryllium

- Retention and release mechanisms identified and quantified
- ITER: Tritium retention in metallic Be only within ion range (small inventory)
- Release < 500 K: BeD_{2-x} “supersaturated Be-D”, D fraction \( \sim 0.25 \)
- Release > 500 K: vacancies, ion-induced traps
- Essential mechanisms:
  - effective diffusion
  - mobility of vacancies
  - accumulation of D in vacancies

BeO

- Thin (several ML) oxide: not rate-limiting for release
- Different mechanisms than for Be
- Only 75% D released <850 K
Outlook

DEMO first wall: neutrons and alloys

- Neutron wall loads: additional traps, deeper than for ion-induced defects

- DEMO PFM: most probably not a pure metal, but alloy
- New diffusion, retention and release mechanisms
- DFT data missing! Improve ability to deal with large unit cells