Experimental evaluation of tritium inventory in Li, Li-Pb and Flibe.

Design of tritium and heat recovery from three blankets of fusion reactors

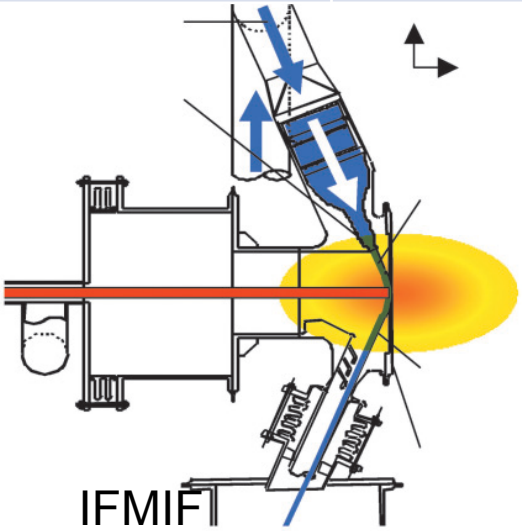
Satoshi Fukada (Kyushu University, Lab. of Energy Chemical Engineering)

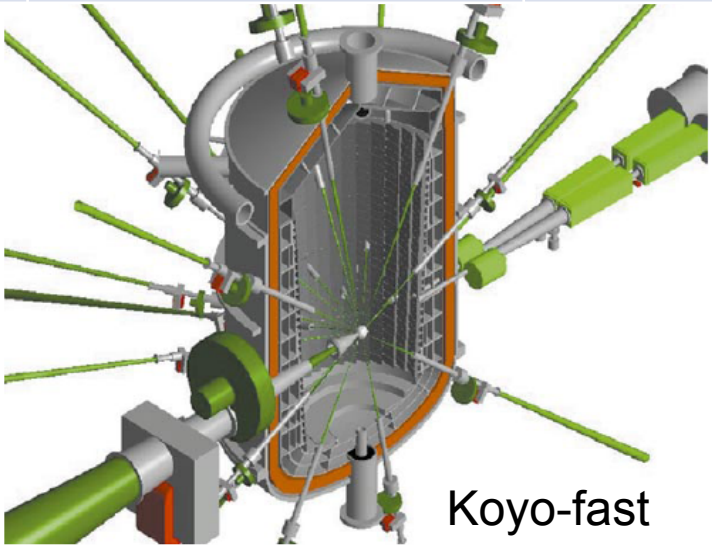
Kyushu University group

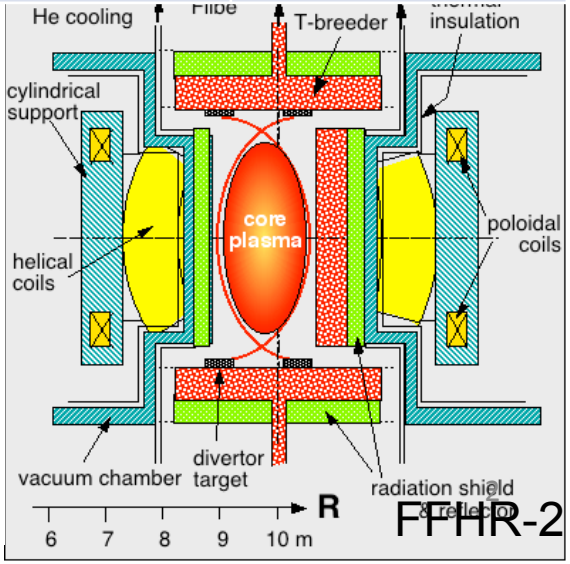
This research is performed under a framework of TITAN and Jupiter-II and is party financed by grant-in-aid for scientific research.

Research information on tritium behavior in liquid breeders

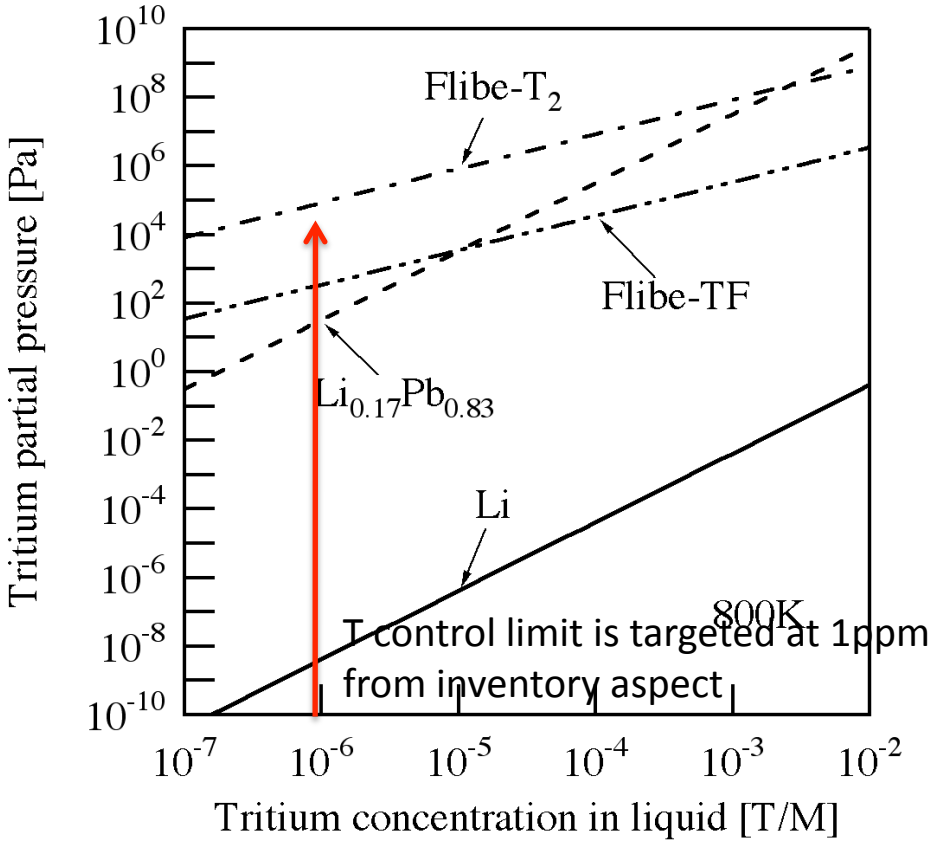
Liquid breeder Candidates	Tritium recovery	Issues to be solved on tritium	Involved Japanese research project	Reactor design activity
Li	Y hot trap	Extremely low pressure (Impurity control)	IFMIF-EVEDA (2007-2013)	Li/V blanket
$Li_{17}Pb_{83}$	He purge permeator	Data scatters and less experiments (large pumping power)	TITAN (2007-2012) ITER-TBM	DCLL or HCLL, Koyo-fast
Li_2BeF_4 (Flibe)	He purge permeator	HF generation (narrow temperature window)	JUPITER-II (2001-2996)	FFHR-2







Comparison of tritium solubility and diffusivity among Li, Li-Pb, Flibe



Tritium equilibrium pressure of Li, Li-Pb, Flibe

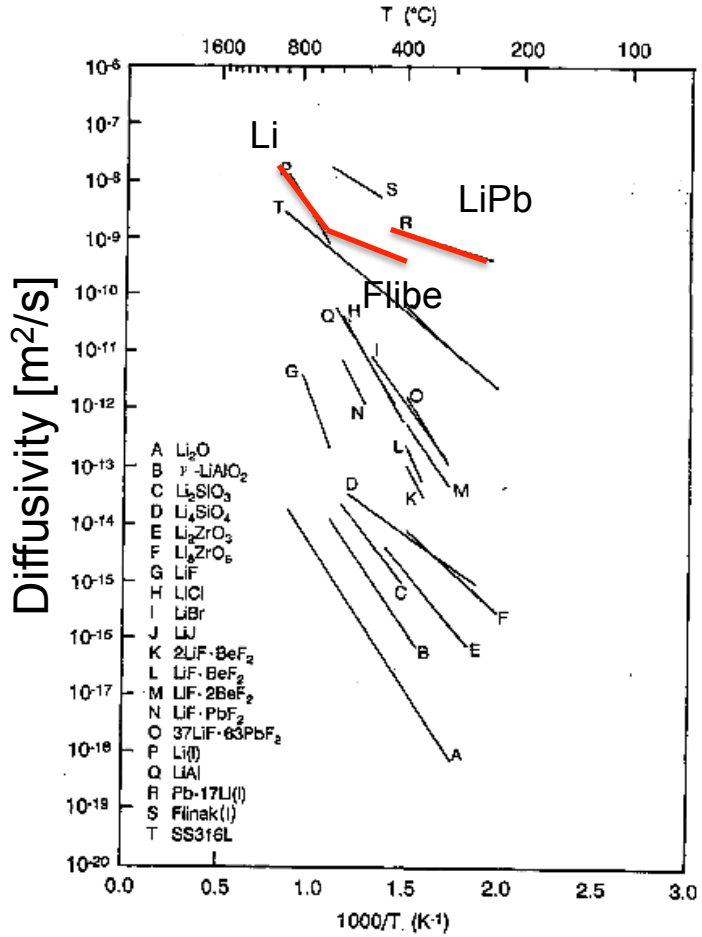


Fig. A.5 Tritium Diffusivities in Tritium Breeding Materials

	Li	$Li_{0.17}Pb_{0.83}$	Flibe
vaporn pressure(800K)	2.1Pa	0.37Pa	0.011Pa
latent heat	140kJ/mol	180kJ/mol	205kJ/mol
viscosity	3.6×10^{-5}kgs/m^2	2.0×10^{-4}kgs/m^2	1.5×10^{-3}kgs/m^2
density	0.48g/cm^3	9.5g/cm^3	2.0g/cm^3

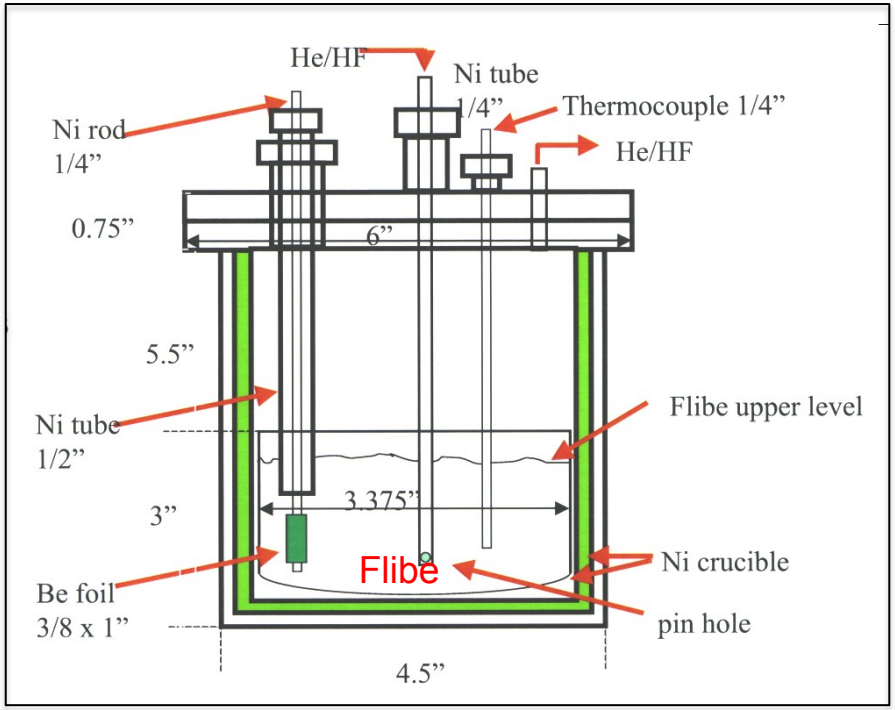
Recovery and control of tritium in Li_2BeF_4

The largest problem on recovery of tritium in Flibe is TF generation.
Two experiments are performed recently related with FFHR-2:

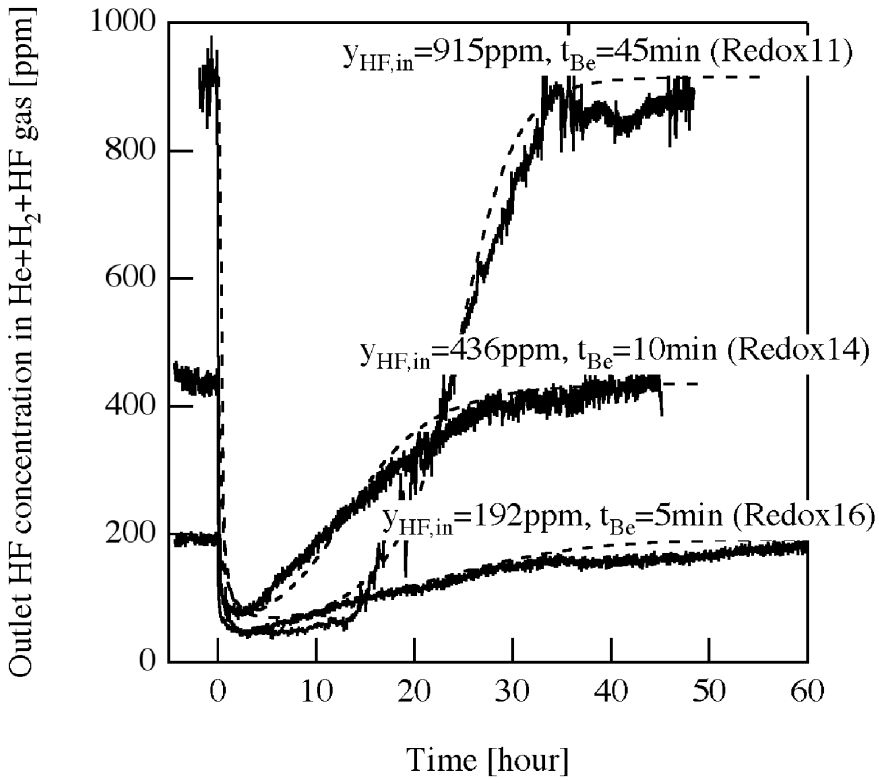
1. Redox control experiment in Flibe
   Whether the reaction 2TF + Be = BeF_2 is possible or not?
   The possibility of conversion of TF to T_2 by a Be rod inserted in fluidized Flibe is tested in JUPITER-II project.

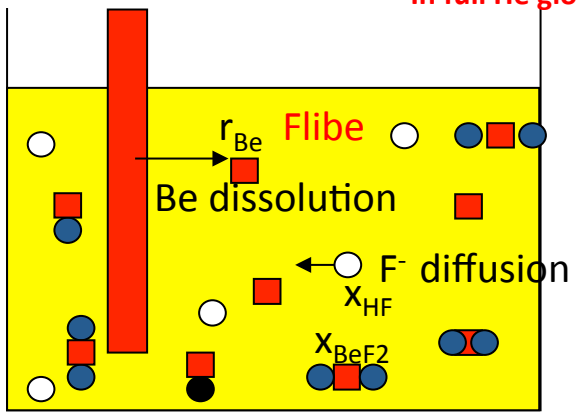
2. Recovery of TF and T_2 from Flibe is experimentally proved by He gas purge including $H_2(D_2)$.

TF reduction by Redox control of Flibe



In full He glove-box atmosphere





$2HF + Be = BeF_2 + H_2$

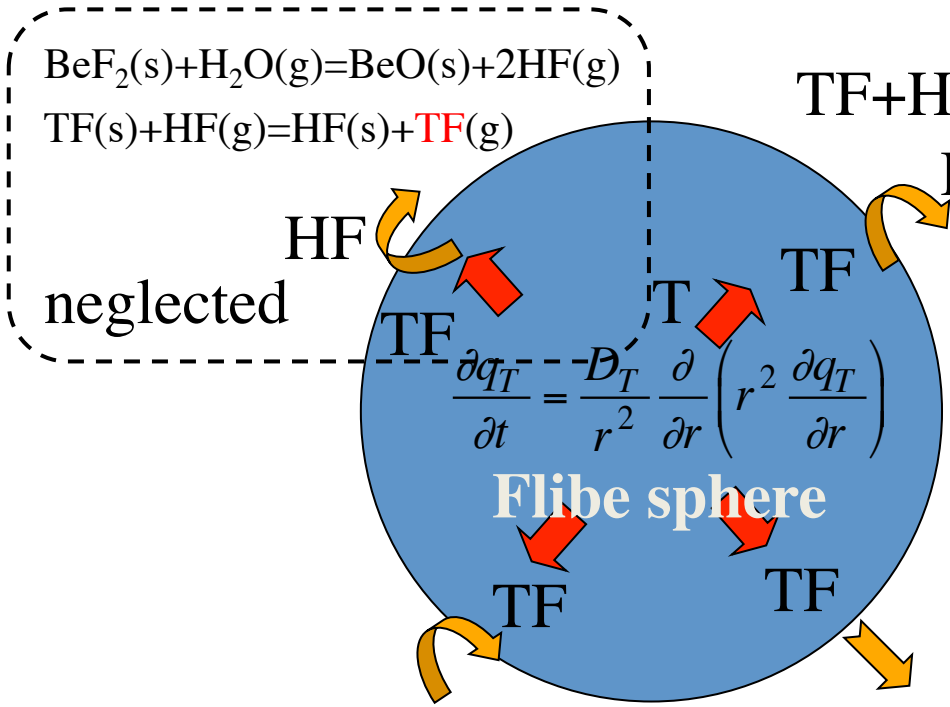
Experimental reduction of HF to H_2 is well simulated by a 1st-order reaction model (broken lines in figure)

This means generated TF in liquid blanket can be reduced Be inserted in Flibe breeder

S. Fukada et al., J. Nucl. Mater., 367 (2007) 1190.

achieved under Japan-US joint project (JUPITER-II, (2001-2006))

Tritium transfer between Flibe-Ar+H_2 or Ar gas



$$\frac{\partial q_T}{\partial t} = \frac{D_T}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial q_T}{\partial r}\right)$$

$TF+H_2=HF+\mathbf{HT}$

H_2 exchange

$$j_{HT} = -D_T \frac{\partial q_T}{\partial r} = k_{exc,H_2}\left(q_T c_{H_2} - \frac{q_H c_{HT}}{K_{H_2-HT}}\right)$$

$$j_{TF} = -D_T \frac{\partial q_T}{\partial r} = k_{des,TF}\left(q_T - \frac{c_{TF}}{K_{Henry,TF}}\right)$$

H_2O exchange

TF desorption

$TF+H_2O=\mathbf{HTO}+HF$

$$j_{HTO} = -D_T \frac{\partial q_T}{\partial r} = k_{exc,H_2O}\left(q_T c_{H_2O} - \frac{c_{HTO} q_H}{K_{H_2O-HTO}}\right)$$

- Zero-A grade Ar (99.999%)
  <2ppm O_2
  <10ppm N_2
  <0.5ppm CO
  <0.5ppm CO_2
  <0.5ppm CH_4
  <5ppm H_2O

Tritium release from Flibe under neutron irradiation

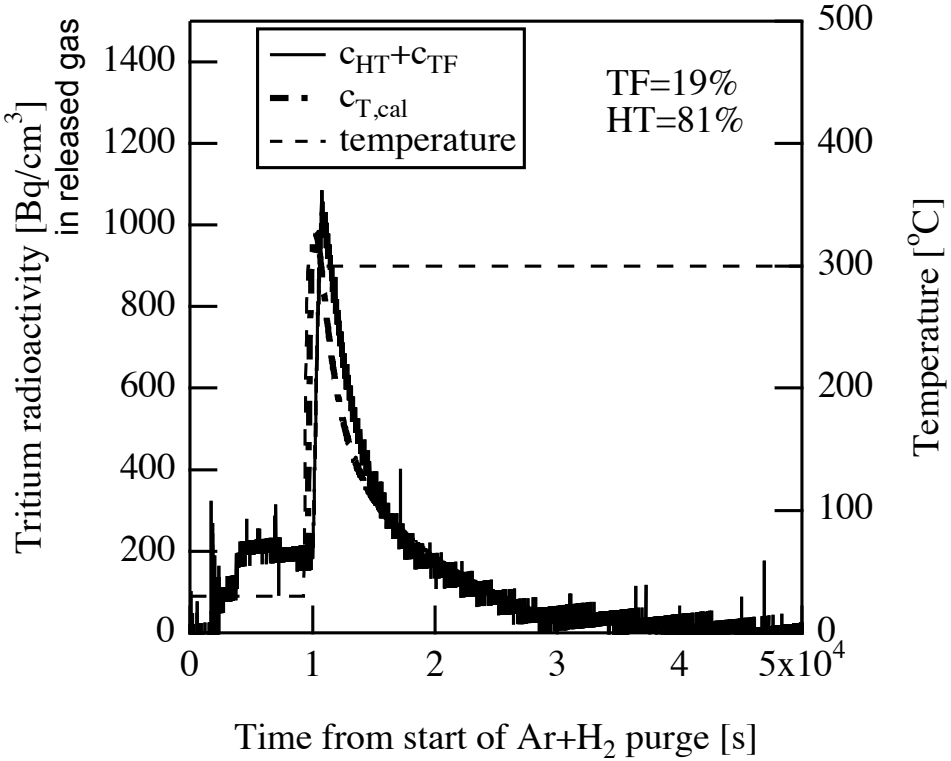
$$\frac{\partial q_T}{\partial t} = \frac{D_T}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial q_T}{\partial r}\right)$$

$$t = 0 \qquad q_T = q_{T,0}$$

$$r = 0 \qquad \frac{\partial q_T}{\partial r} = 0$$

$$r = a \qquad j_T = -D_T \frac{\partial q_T}{\partial r} = k_T\left(q_T c_{H_2} - \frac{q_H c_{HT}}{K_{T-H_2}}\right)$$

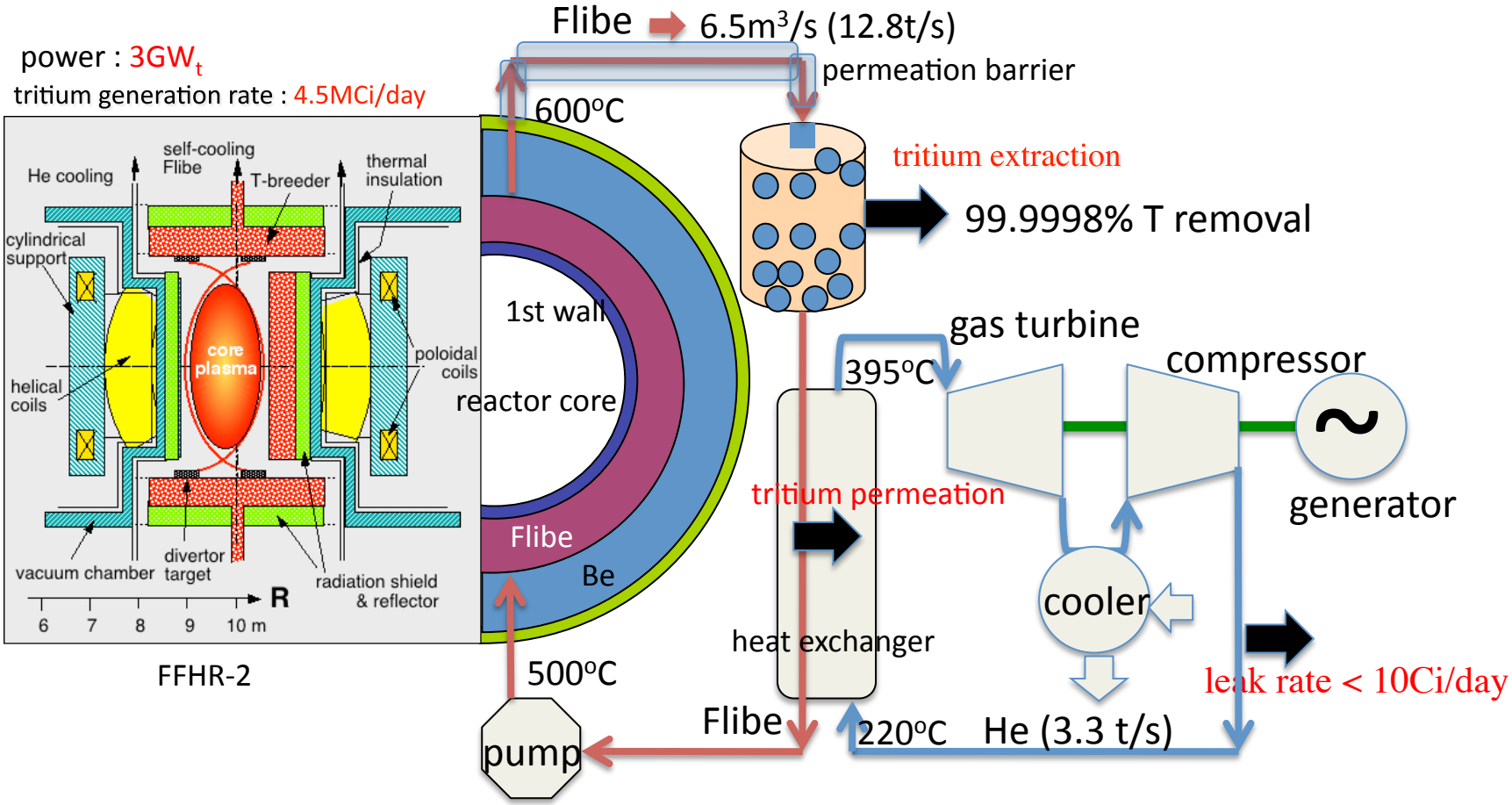
$$j_T = 2k_T' q_{T,0} \sum_{n=1}^{\infty} \frac{\exp\left(-\frac{p_n^2 D_T}{a^2} t\right)}{\frac{D_T}{k_T' a} p_n^2 + \frac{k_T' a}{D_T} - 1}$$



- Good fitting is obtained between tritium (TF+HT) release experiment (solid line) and diffusion-limiting tritium desorption rate equation (chained line).
- This means that TF or HT (T_2) generated in Flibe breeder can be recovered direct contact with He purge gas.

S. Fukada, et al., Fus. Sci. Technol., 52 (2007) 677.

Design study of Flibe/He loop for FFHR-2 self-coolant system



Primary Flibe loop and secondary He Brayton cycle for FFHR

T concentration in Flibe (partial pressure) : x_T=0.013ppm (p_T=760Pa)

T removal ratio from Flibe per once through : 1/(5x10^5)

A. Sagara, et al., Fus. Eng. Des., 83 (2008) 1690.
S. Fukada, et al., Fus. Eng. Des., 85 (2010) 1314.

8

Recovery of tritium from Li

Y absorption method was previously proposed, but no experimental proof has ever been presented, because Y is much sensitive to impurities of O and N.

We performed the following experiments and calculations:

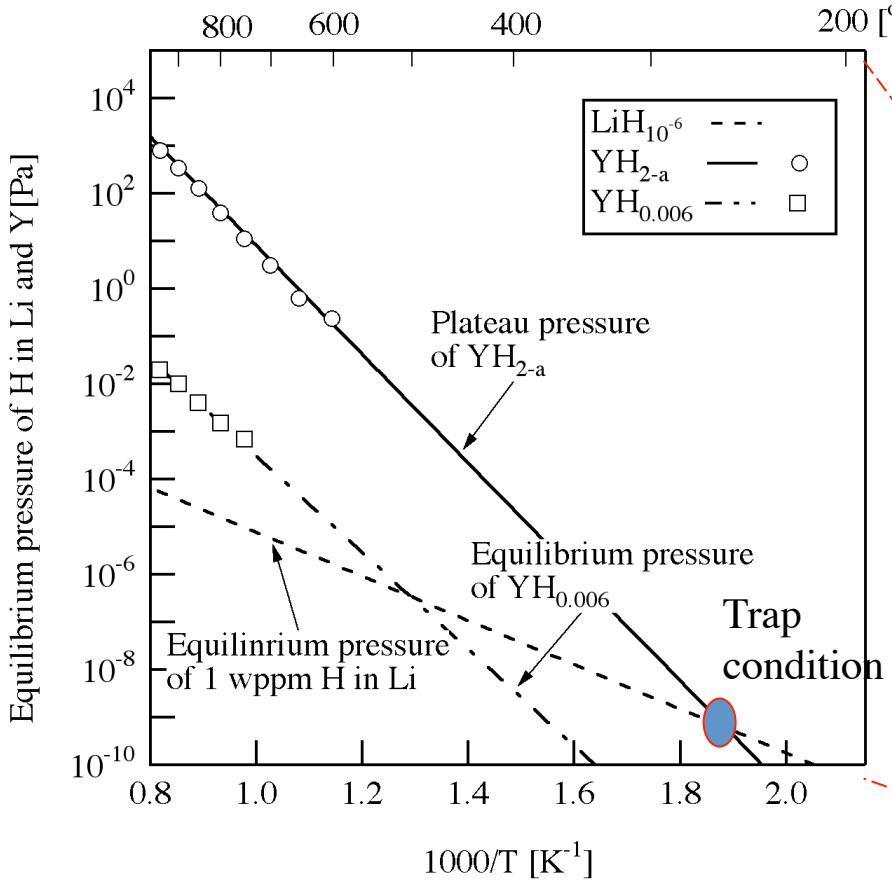
(1)Development of HF treatment technique to remove oxide formed on Y surfaces

(2) Experiment on recovery of 1ppm tritium from Li by HF-treated Y particle

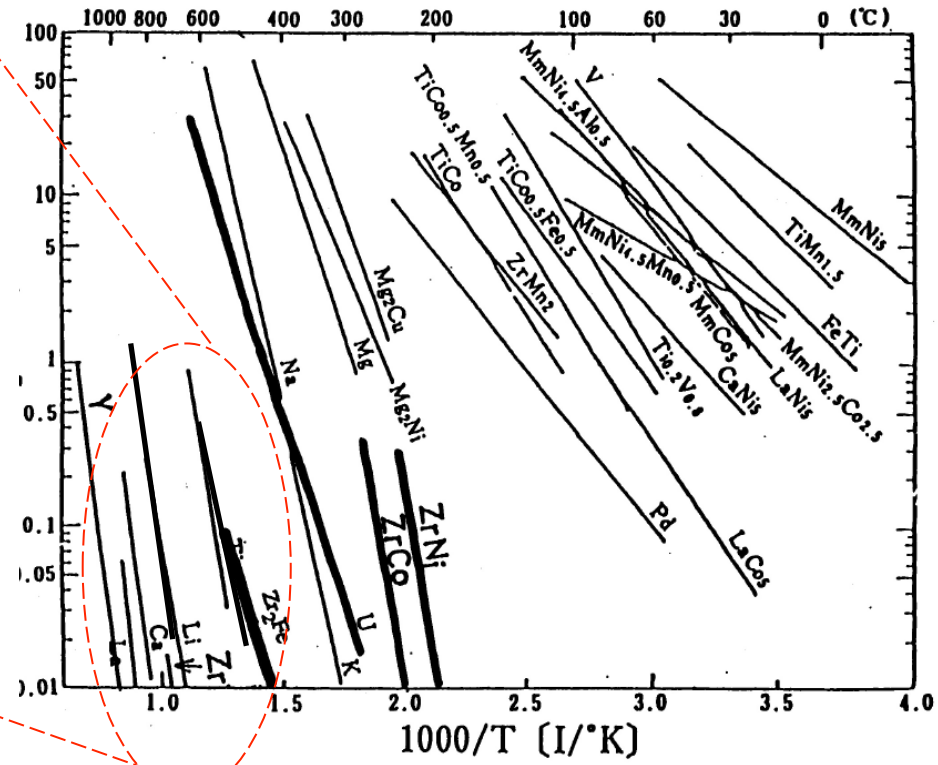
(3) Experiment on recovery of H or D from fluidized Li by HF-treated Y plate

(4)Design of Y hot trap for Li loop of IFMIF-EVEDA

Y condition to recover tritium in Li down to 1 ppm



Dissociation pressure of YH_2 and 1ppm T in Li and operation condition of **Y hot trap**



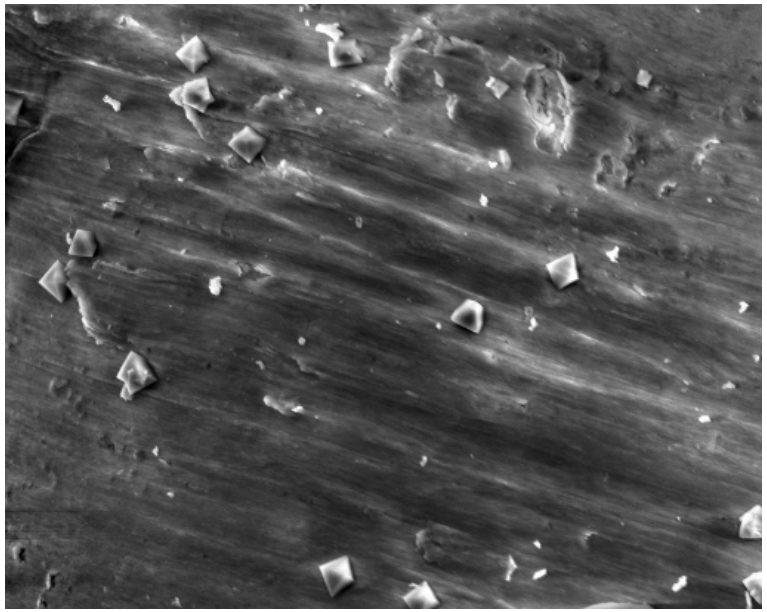
Dissociation pressure for various metal-hydride systems

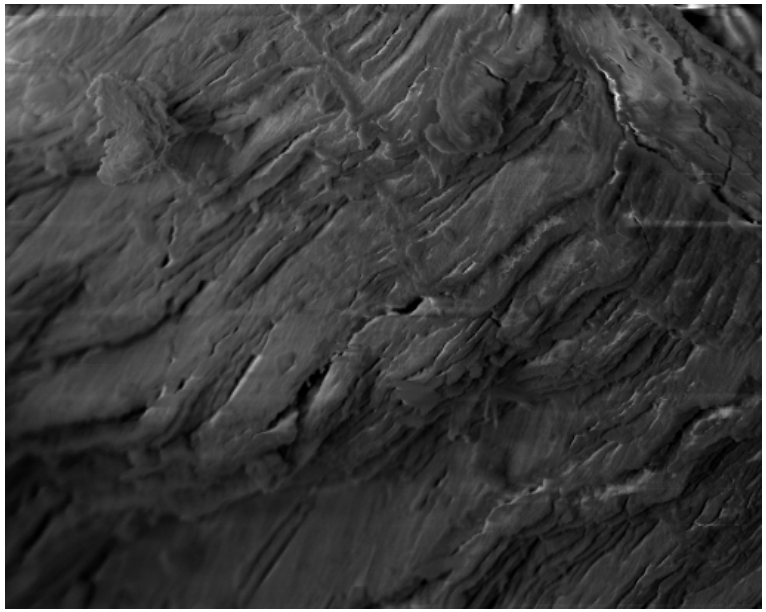
- There is no sufficient research on removal of hydrogen (tritium)<1ppm in Li.
- This is because the oxide on formed on Y inevitably interferes hydrogen (tritium) removal in Li.
- A new technique of HF treatment that we proposed in FED is tested to improve H absorption performance at the Y trap temperature (250-300°C).

HF-treated Y before H absorption

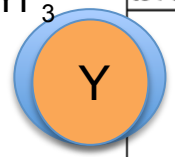
HF-treated Y after H absorption

SEM



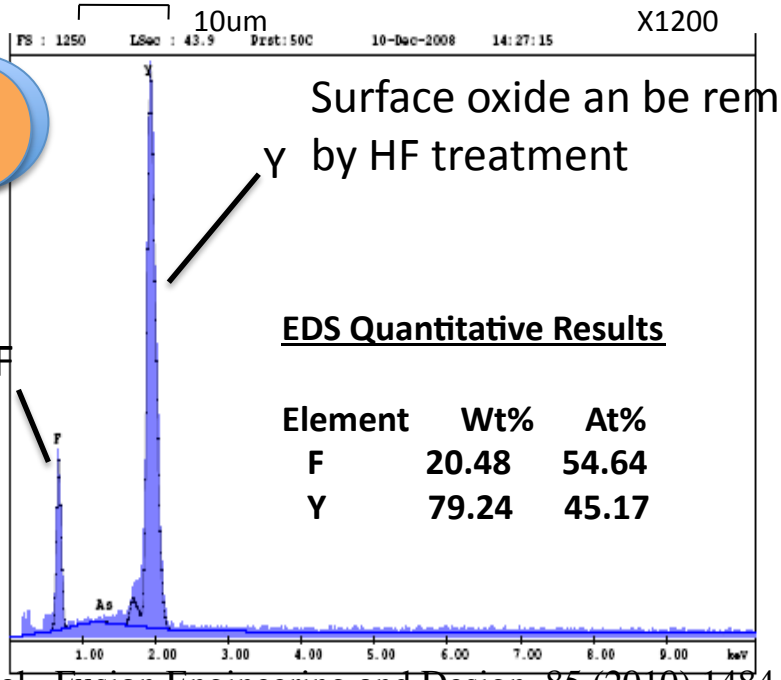


Porous YF_3



10um X1200

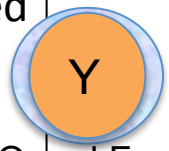
EDX



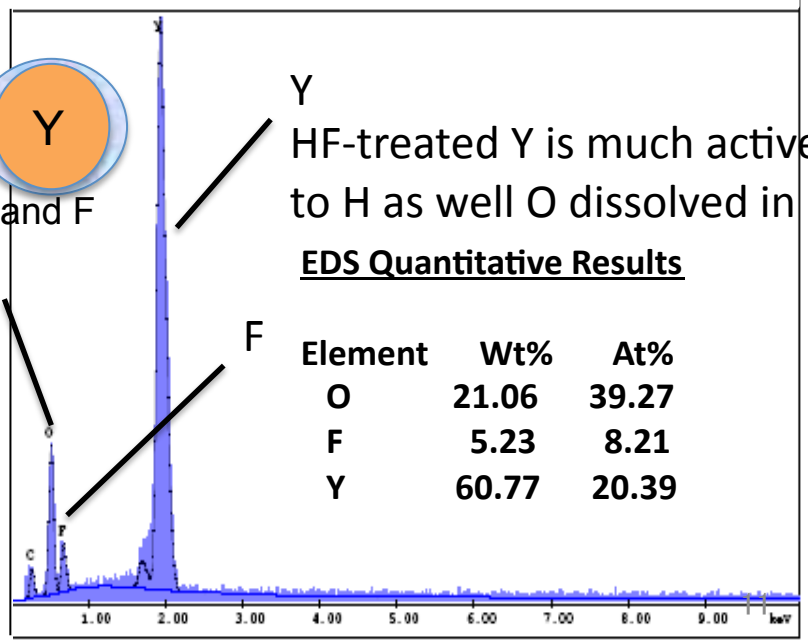
Surface oxide an be removed by HF treatment

EDS Quantitative Results

Element	Wt%	At%
F	20.48	54.64
Y	79.24	45.17



10um X1200



O and F

Y

HF-treated Y is much active to H as well O dissolved in Li.

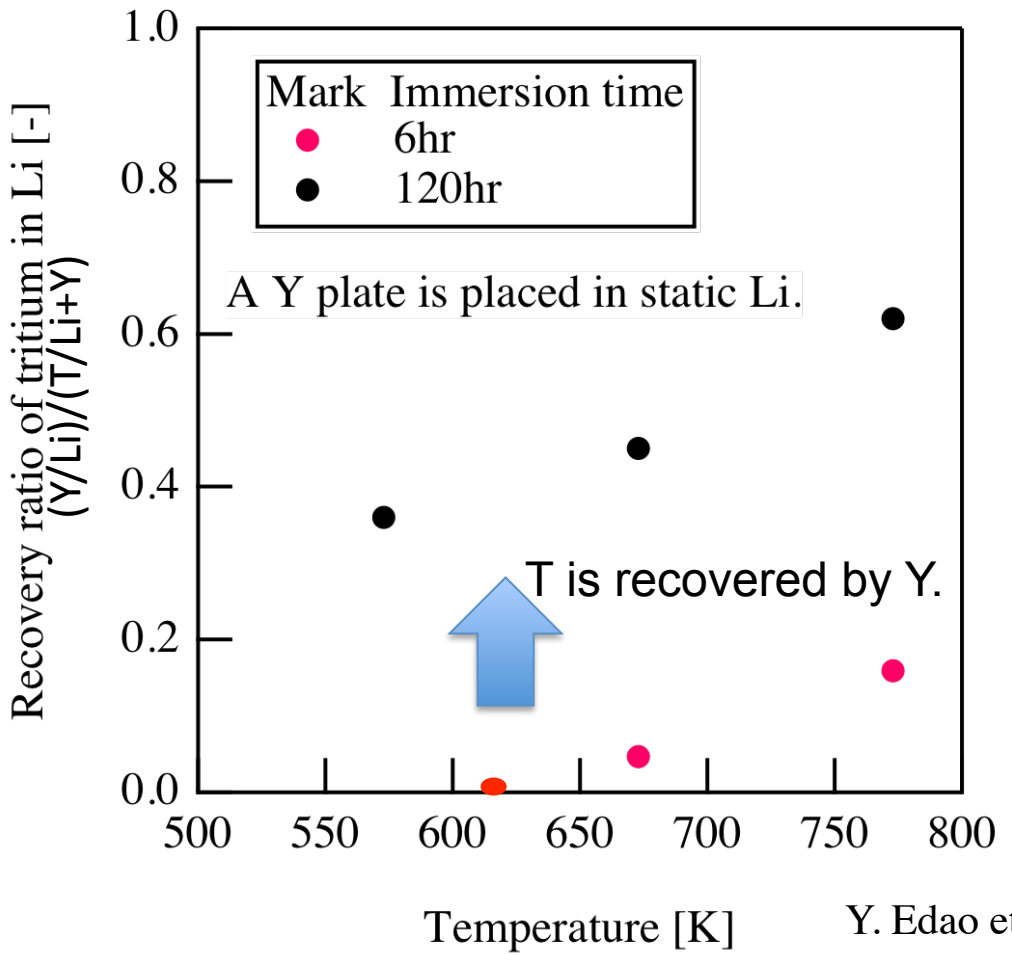
EDS Quantitative Results

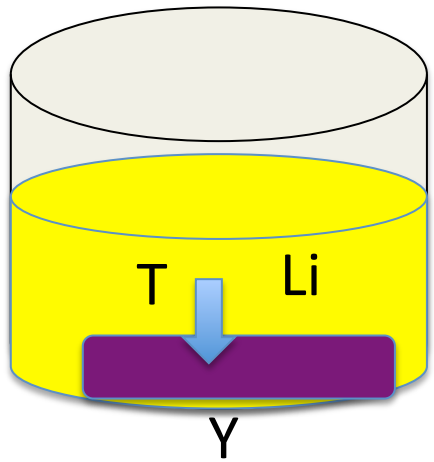
Element	Wt%	At%
O	21.06	39.27
F	5.23	8.21
Y	60.77	20.39

Y. Wu et al., Fusion Engineering and Design, 85 (2010) 1484

Experiment of T recovery by Y plate from stationary Li

•After T of 0.12ppm is generated in Li by neutron irradiation, Li contacts with a Y plate.
Then, the T amounts dissolved in Li and Y are detected by a liquid scintillation counter after H_2O and HNO_3 dissolution.





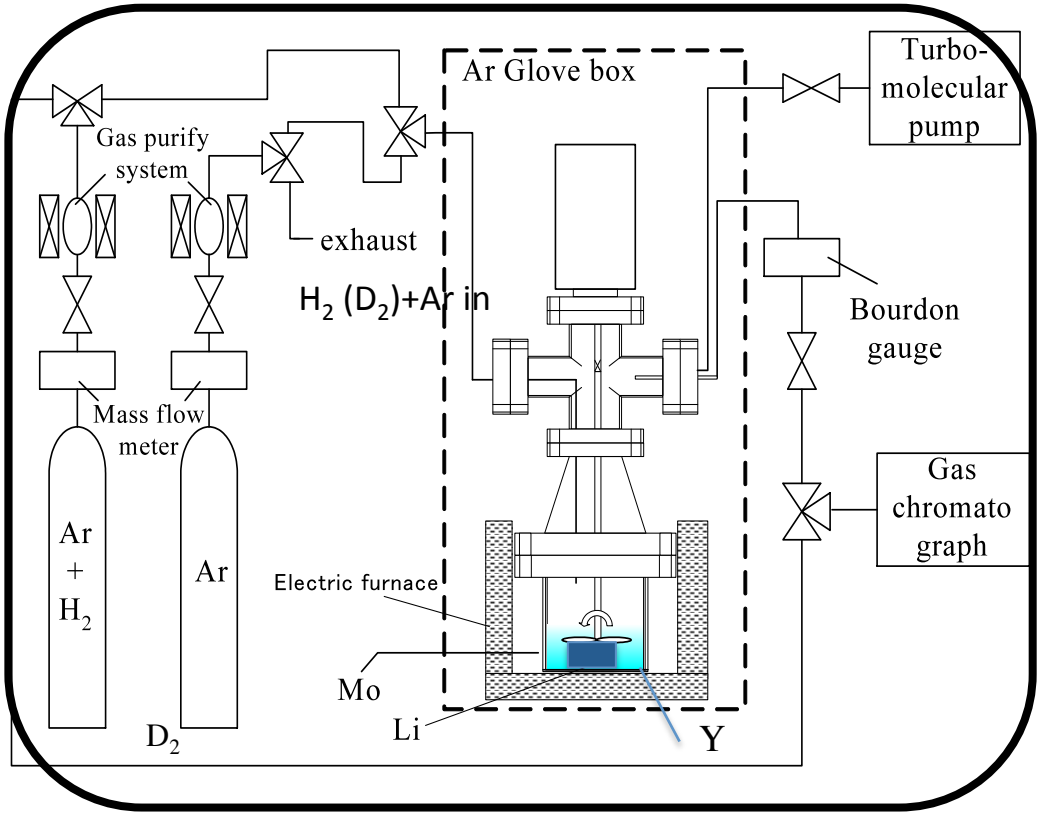
Finding:

Y. Edao et al., Fus. Eng. Des., 85 (2010) 53

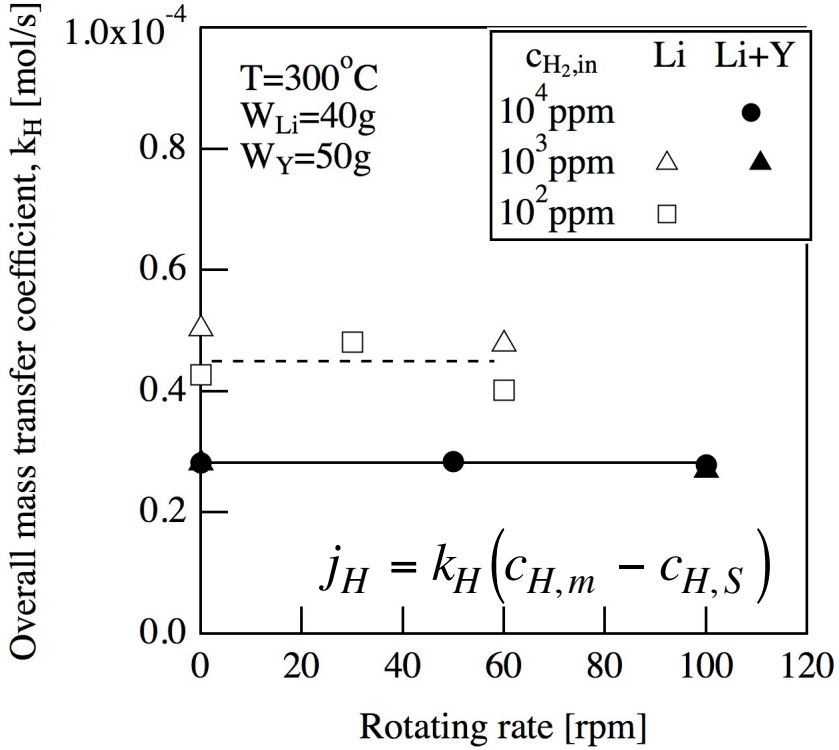
- HF-treated Y can absorb T dissolved in Li down to 0.1ppm at 300°C.
- Recovery ratio from Li to Y is determined as a function of temperature and contact time.

IFMIF-EVEDA achievement in FY 2009-2010

Experiment of H recovery by Y plate from agitated Li



Experimental apparatus to test H_2, D_2 absorption in fluidized Li using agitated vessel



H absorption rate as a function of H concentration and rotating rate

K. Katekari et al., Presented in Tritium conference, (2010)

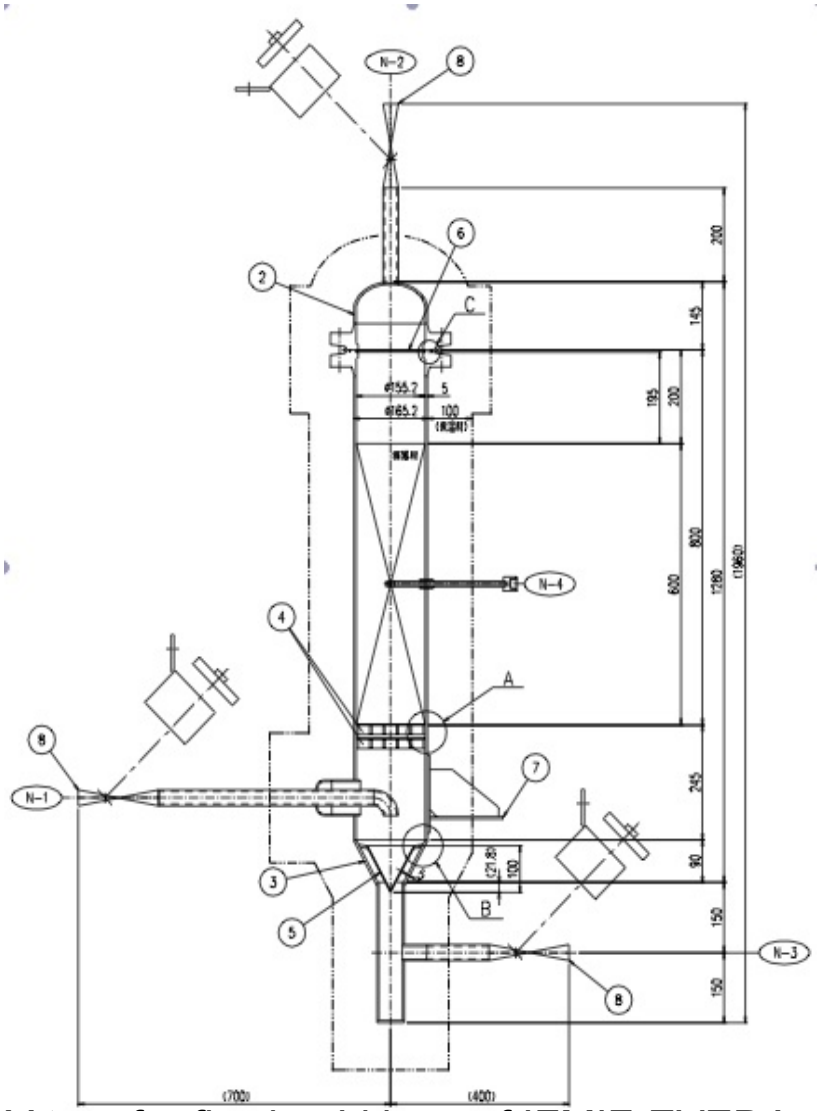
Summary of experimental results:

- Y can absorb H isotopes efficiently even at 300°C by using HF-treatment technique.
- Overall H absorption rates are independent of rotating rate.
- Absorption mass-transfer coefficient is independent of the inlet H_2 concentration.
- The above results support the idea that the surface dissociation reaction limits the overall absorption rate.

Design and construction of Y trap for IFMIF/EVEDA Li loop

Nitrogen trap is design by Terai's group

Bird-view of IFMIF-EVEDA Li loop under construction



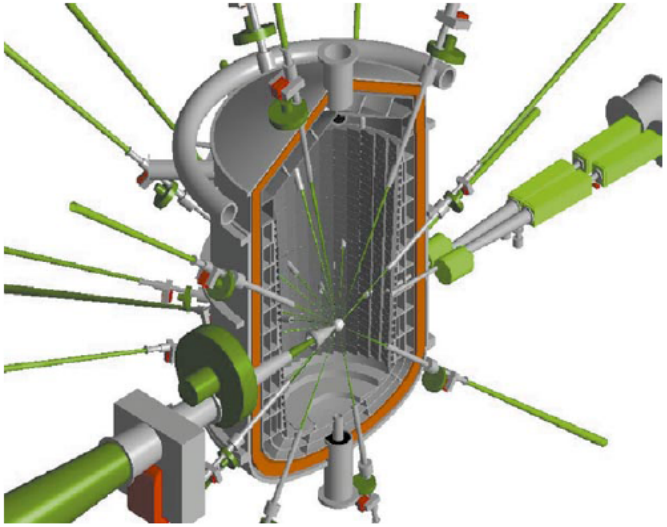
Y trap for flowing Li loop of IFMIF-EVEDA

S. Fukada et al., IFMIF-EVEDA 3rd workshop 2010, Madrid CIEMAT

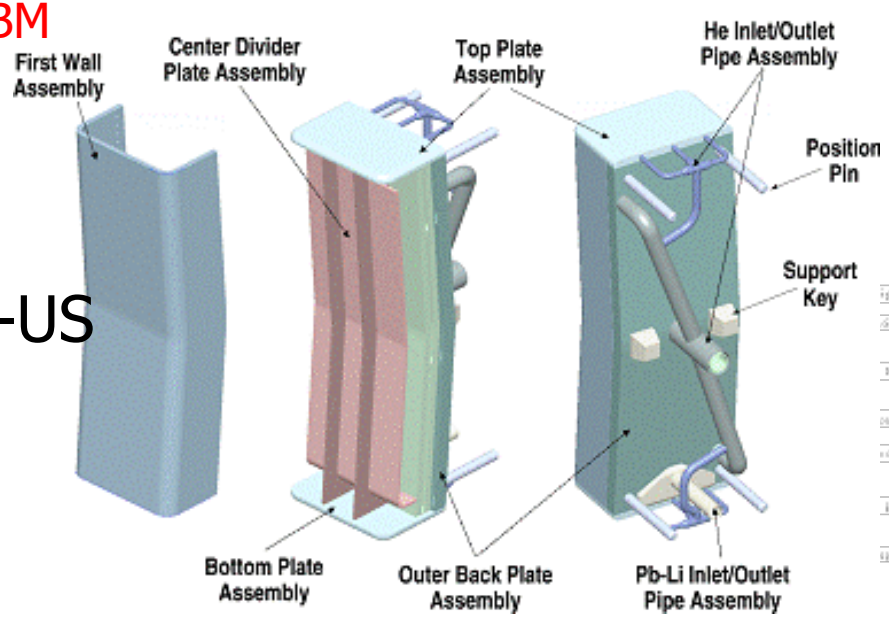
LiPb blanket designs

- **$Li_{15.8}Pb_{84.2}$ ($Li_{17}Pb_{83}$) eutectic alloy**
  - High TBR
  - Low reactivity with N, C, O
  - Simplified blanket structure (low m.p.)
- **Tritium breeding blanket**
  - Self-sufficient tritium cycle
  - Highly-efficient heat recovery

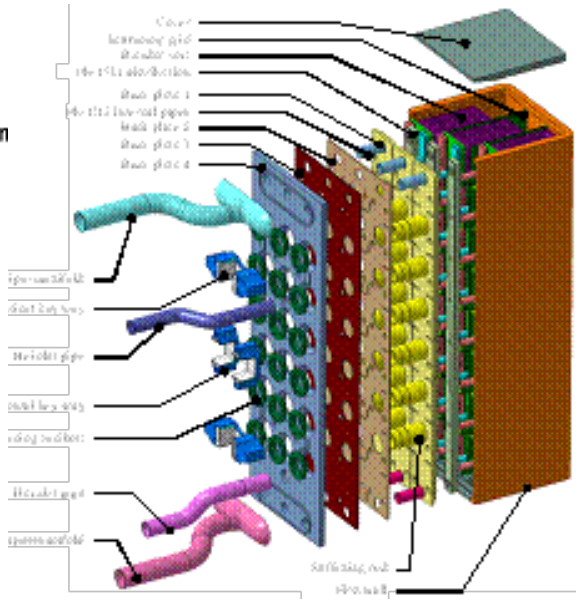
Inertial fusion reactor, KOYO-Fast



ITER-TBM



DCLL-US



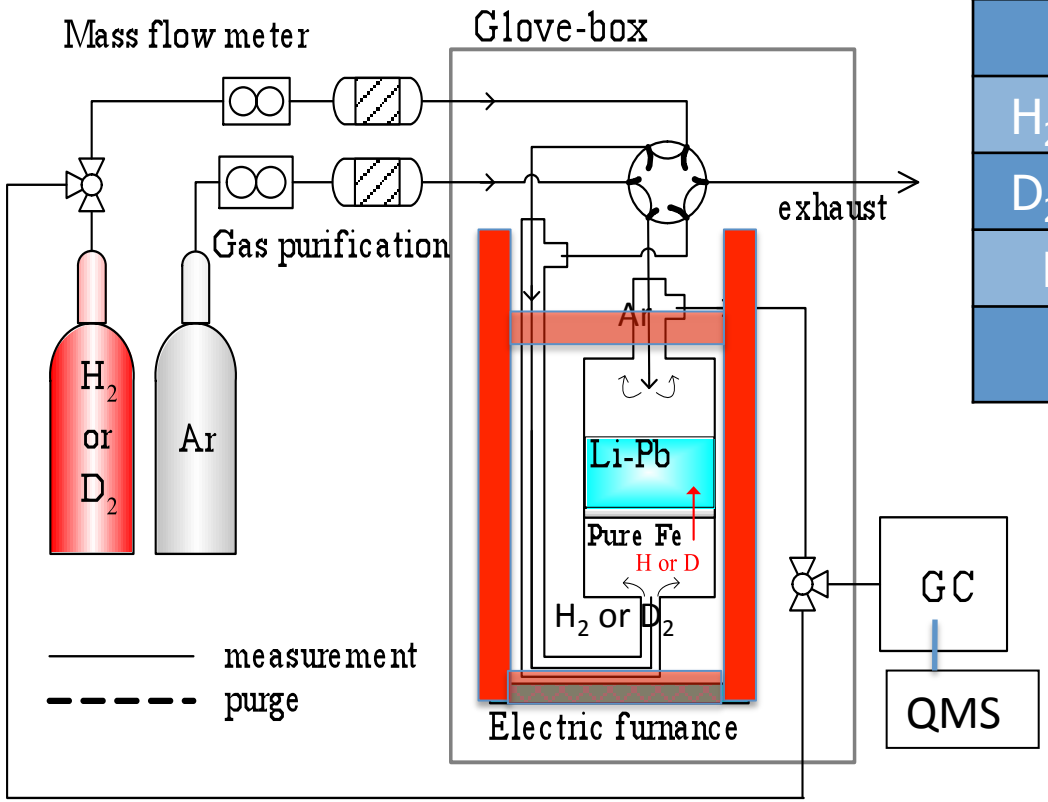
HCLL-EU

Tritium-related study of Li-Pb blankets

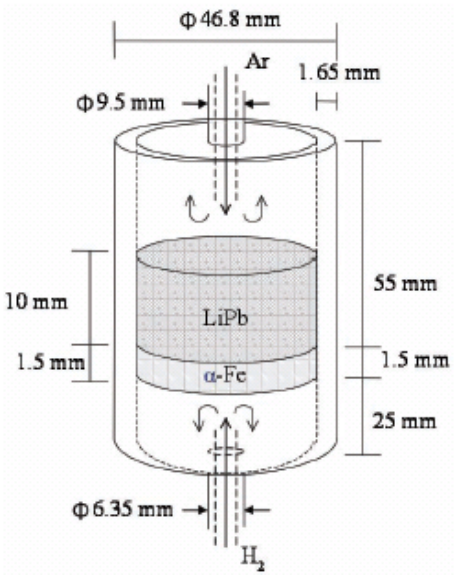
- We determined solubility and diffusivity of H, D (and T) in $Li_{17}Pb_{83}$ eutectic alloys.
- We determine chemical state and isotope effects of H isotopes dissolved in Li-Pb eutectic alloy.
- We design a system for tritium recovery from Li-Pb loop from Koyo-fast inertial fusion reactor

Permeation of single component H,D or dual component H+D through $Li_{16}Pb_{84}$ are determined by a permeation method.

Solubility, diffusivity and permeability are determined at the same time from fitting experiment and calculation.

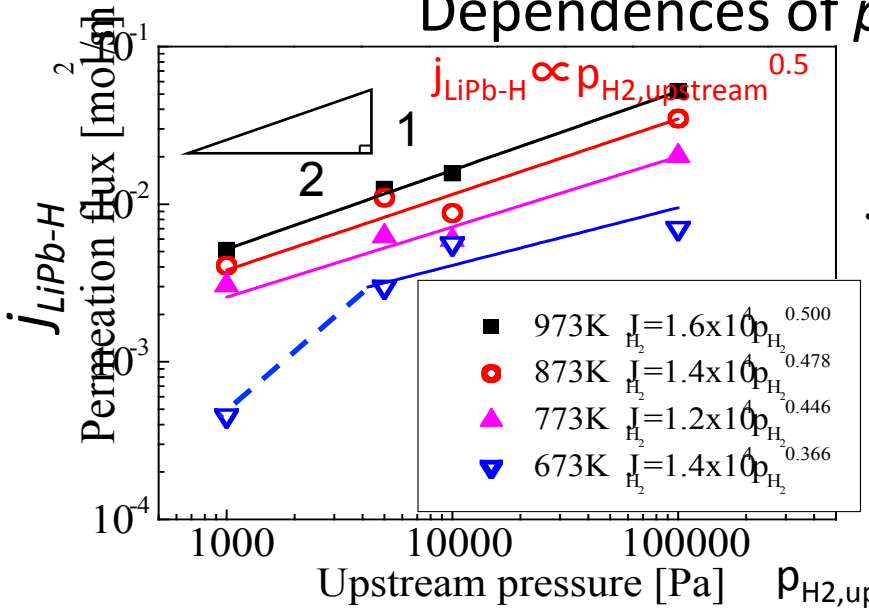


Experimental conditions	
Temperature	573-973 K
H_2 partial pressure	10^3-10^5 Pa
D_2 partial pressure	10^3-10^5 Pa
H_2, D_2 flow rate	5 cm^3/min
Ar flow rate	5 cm^3/min



A schematic diagram of the experimental apparatus

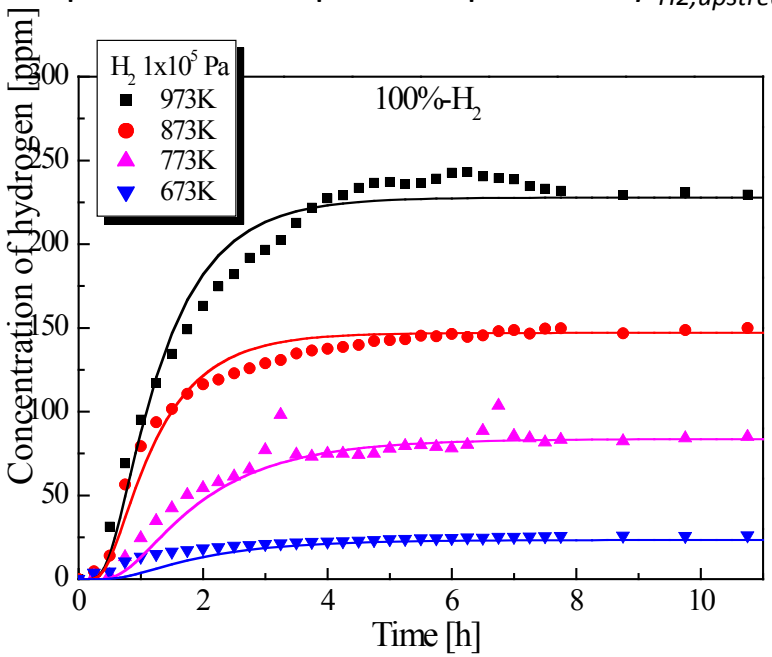
Dependences of $p_{H2,\ upstream}$ and L on $J_{LiPb\text{-}H}$



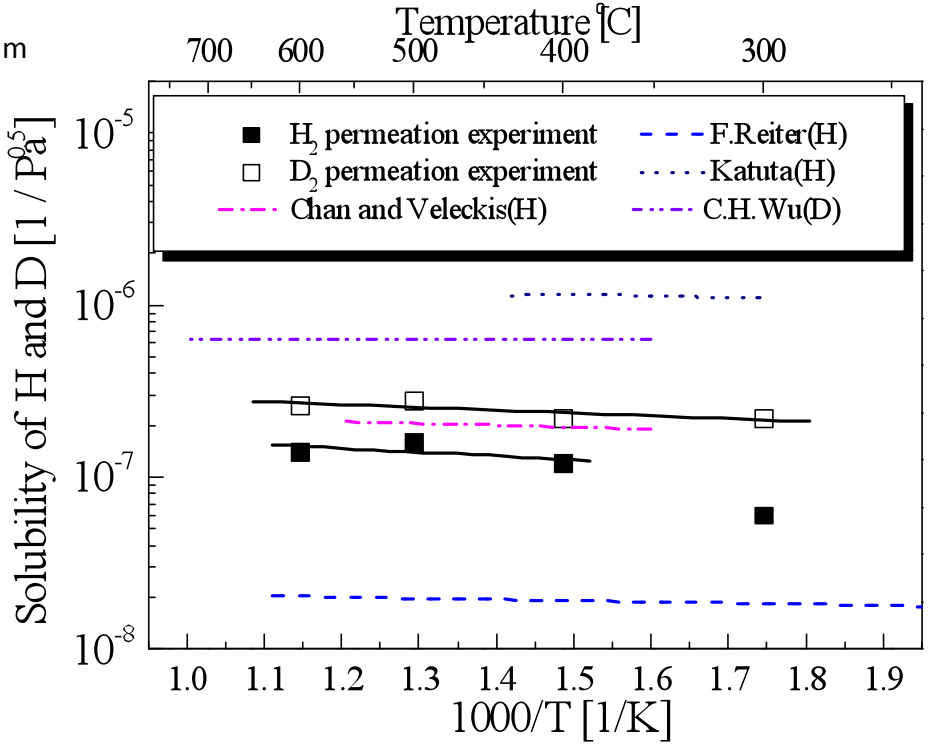
Dependence of upstream pressure, $p_{H2,upstream}$

$$j_{LiPb-H} = \frac{P_{LiPb-H}}{L}\left(\sqrt{p_{H_2,upstream}} - \sqrt{p_{H_2,downstream}}\right)$$

$P_{LiPb\text{-}H}$: H permeability [mol/msPa$^{0.5}$]

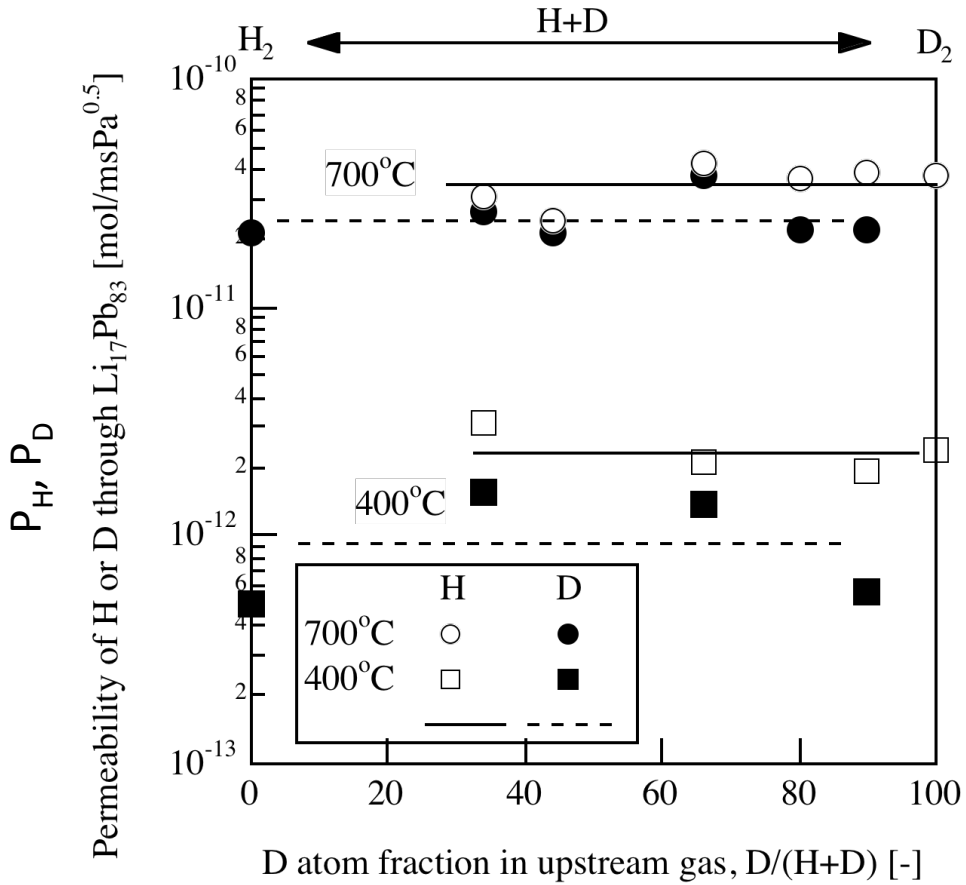


Dependence of temperature, T

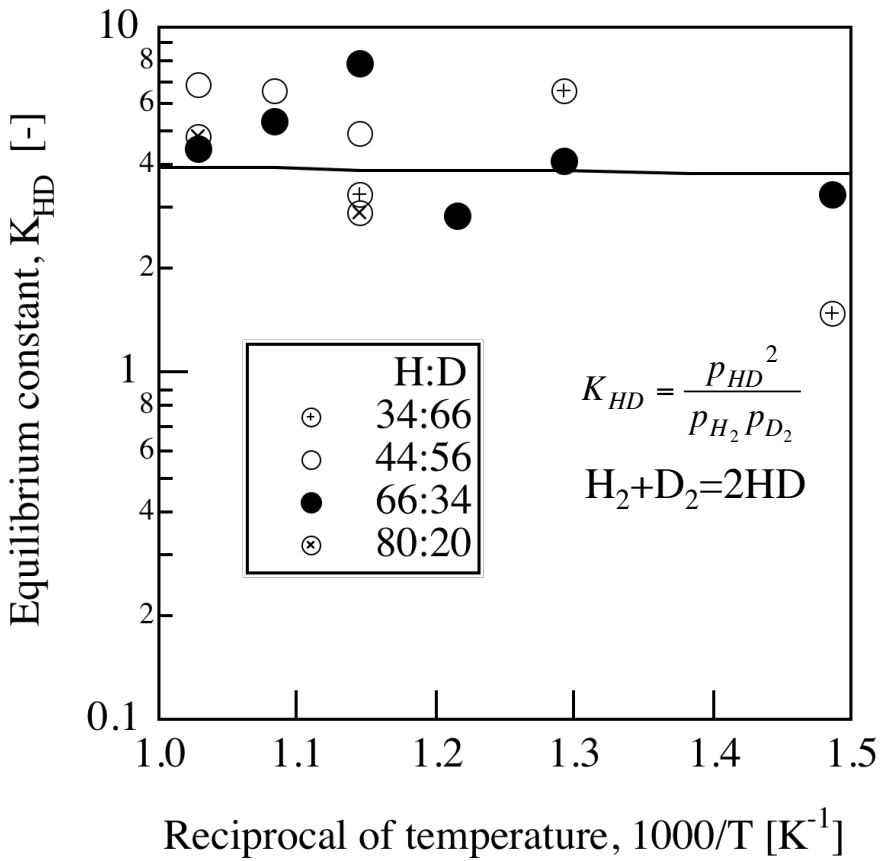


Temperature dependence of solubility

The ratio of H and D permeability through Li-Pb, P_H and P_D



Permeability of H and D through $Li_{16}Pb_{84}$



Equilibrium constant at the downstream side of $Li_{16}Pb_{84}$ layer, the line is theoretical value.

Finding:

- H permeability is around 1.4 times larger than D one as the isotope effect independent of the H:D composition ratio.
- The isotope equilibrium of $H_2+D_2=2HD$ is achieved at the downstream side.

Y. Edao, et al., Proc. tritium conference (2010)

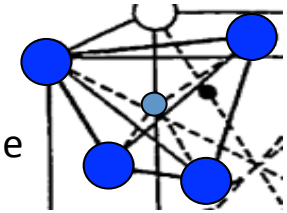
1st principle numerical simulation for diffusion of H in PbLi

D. Masuyama, et al., Chem. Phys. Let., 483 (2009) 214-218

crystal

Pb crystal⇒fcc stable at tetrahedral site

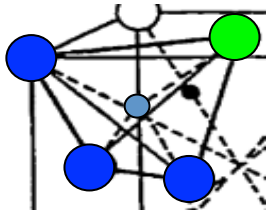
4 Pb atoms



-229.95 eV

>

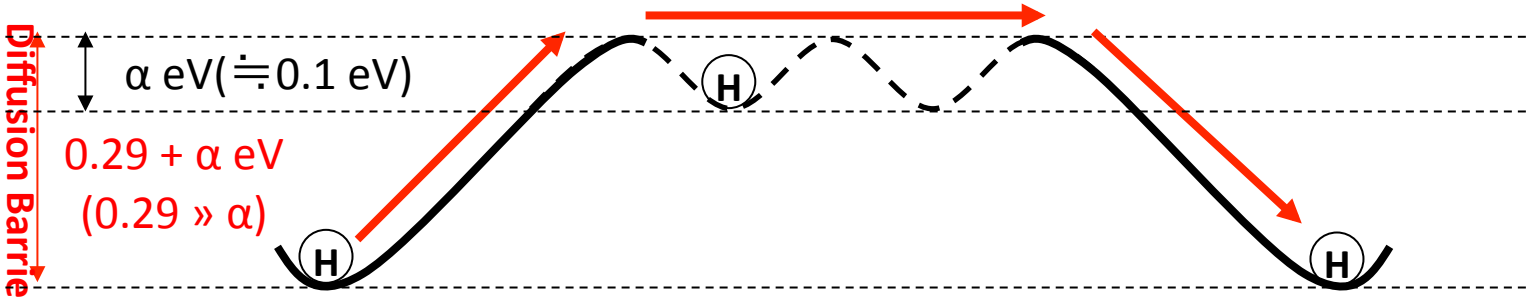
3 Pb atoms, 1Li atoms

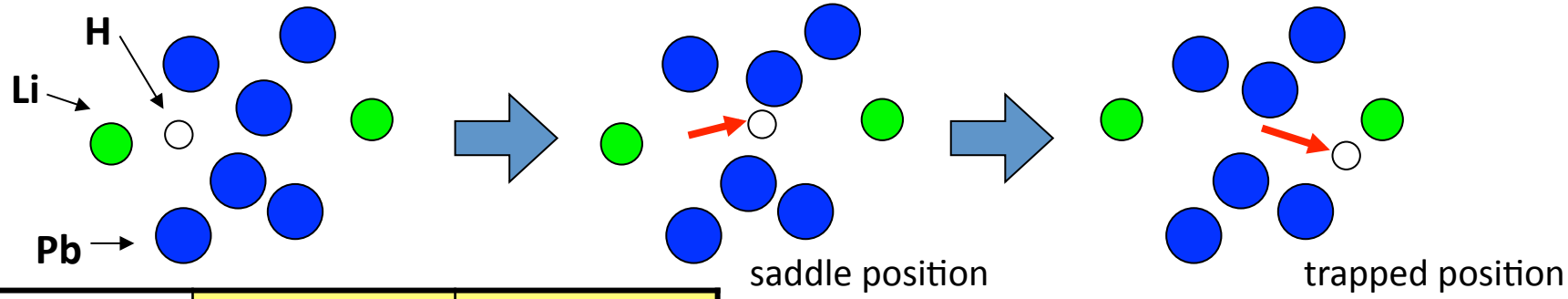


-230.24 eV

◆H atoms are present at positions near to Li than Pb.

Energy difference⇒0.29 eV



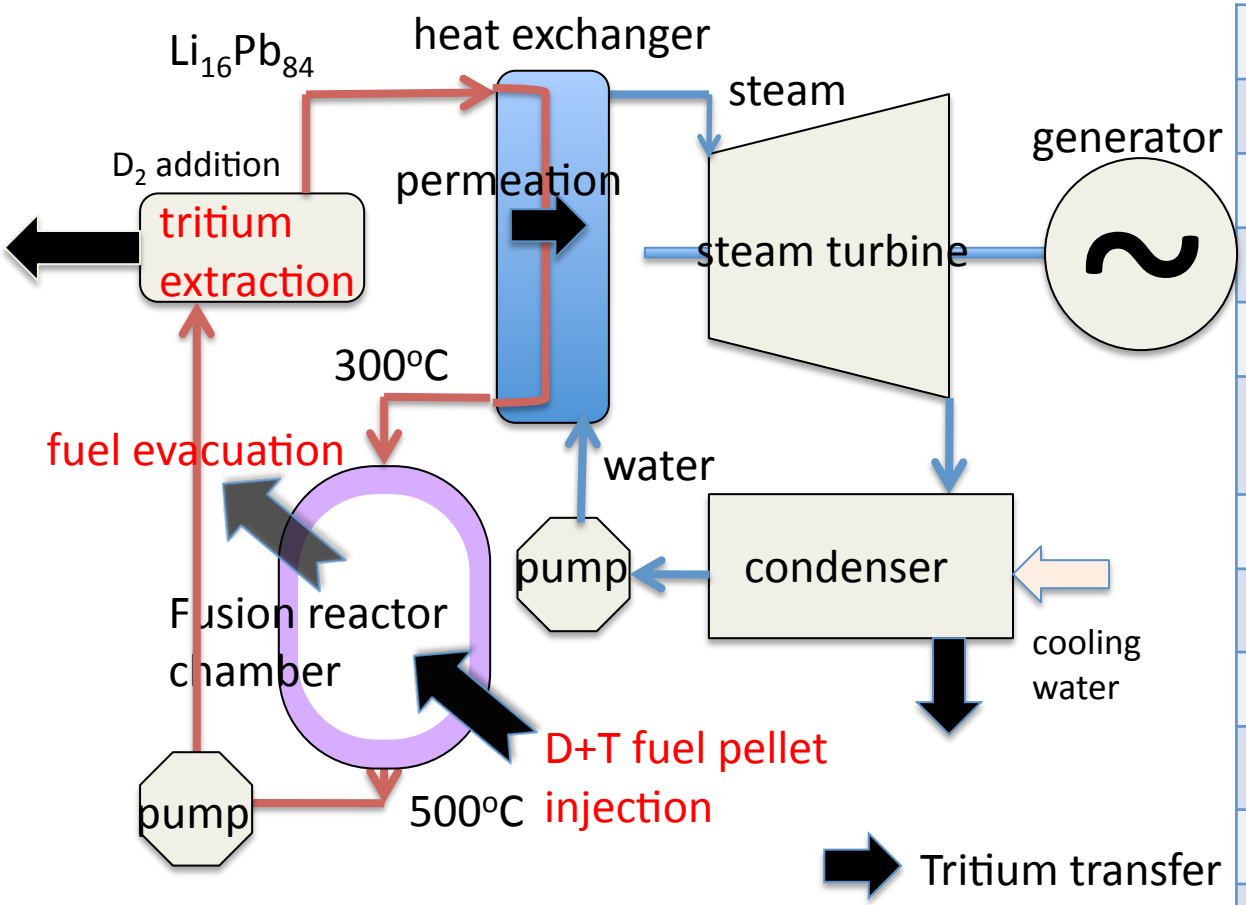


	calculation	experiment
Diffusion barrier	0.29+α eV	0.27 eV

- H behavior in $Li_{17}Pb_{83}$ can be understood by pure numerical calculation!

(5) Blanket T recovery design

Tritium extraction and Heat exchanger system for Koyo laser fusion reactor



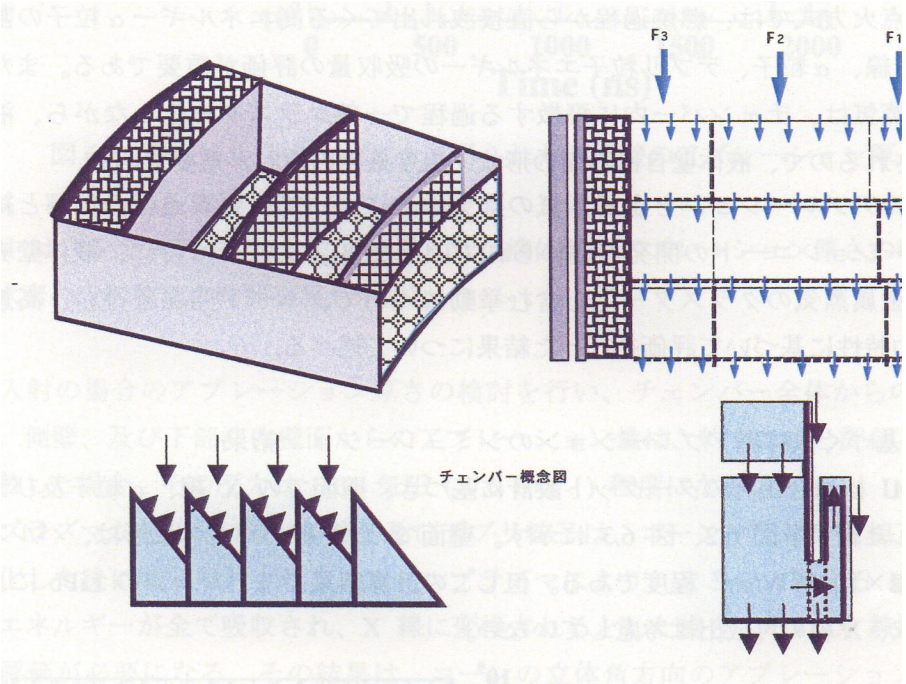
$Li_{16}Pb_{84}$ loop for Laser fusion reactor and steam Rankine cycle

Total power	1 GWt
$Li_{16}Pb_{84}$ inlet temp.	300 °C
$Li_{16}Pb_{84}$ outlet temp.	500 °C
$Li_{16}Pb_{84}$ mass flow rate	18.4 t/s
T generation rate	1.43 MCi/day
T concentration in $Li_{16}Pb_{84}$	8.6×10^{-9} $T/Li_{16}Pb_{84}$
T partial pressure in LiPb	1.8×10^{-3} Pa
Heat transfer coefficient of heat exchanger	5.0×10^{3} W/m^2K
Surface area of het exchanger	690 m^2
Logarithmic temperature difference in heat exchanger	290 °C
Estimated T leak rate	255 Ci/day
Rate-determining step	T permeation through tube wall

Integration is based on design of compositions for heat and T recovery.

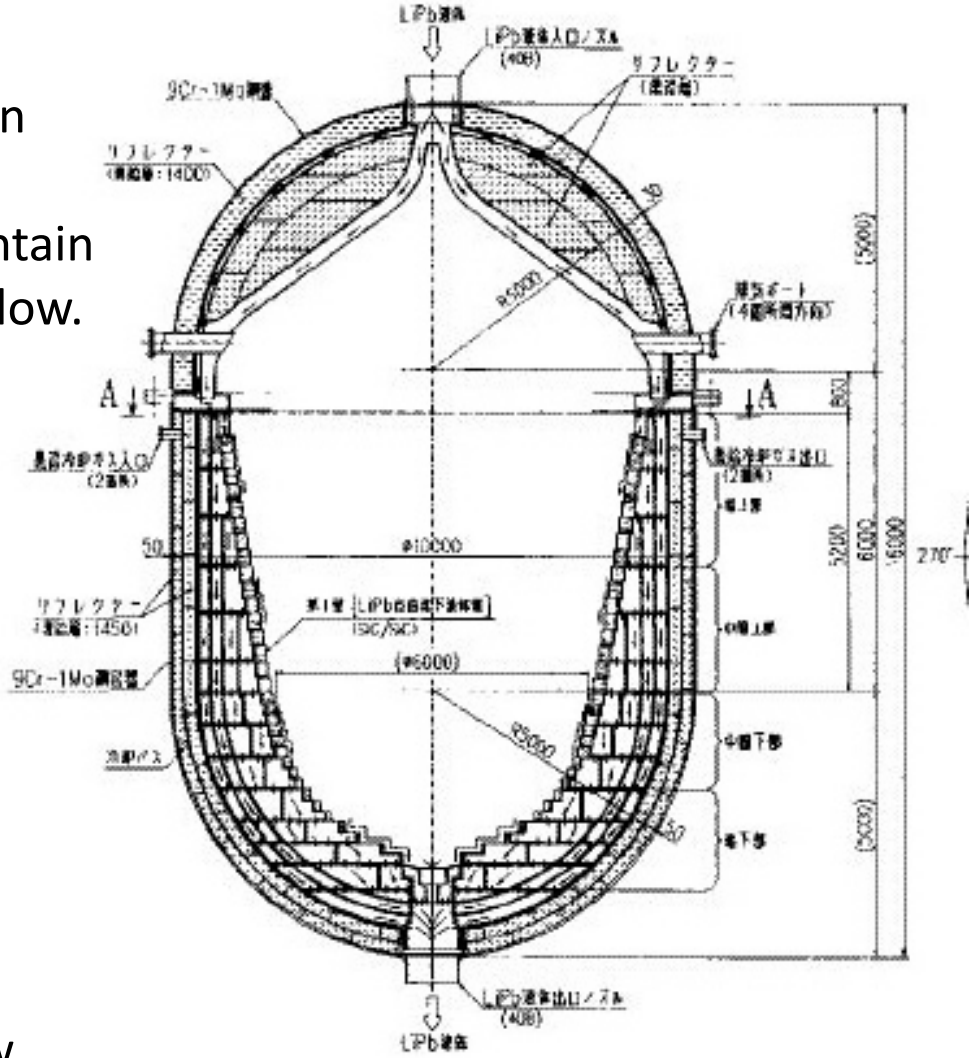
Li-Pb Liquid wall concept for inertial fusion reactor

Wet wall of continuously-flowing Li-Pb is maintained to protect it from heavy neutron irradiation during D-T burning.
Proper wall structures are designed to maintain sufficient residence time of wet wall Li-Pb flow.



Wall structure to maintain stable liquid flow
Residence time

LiPb

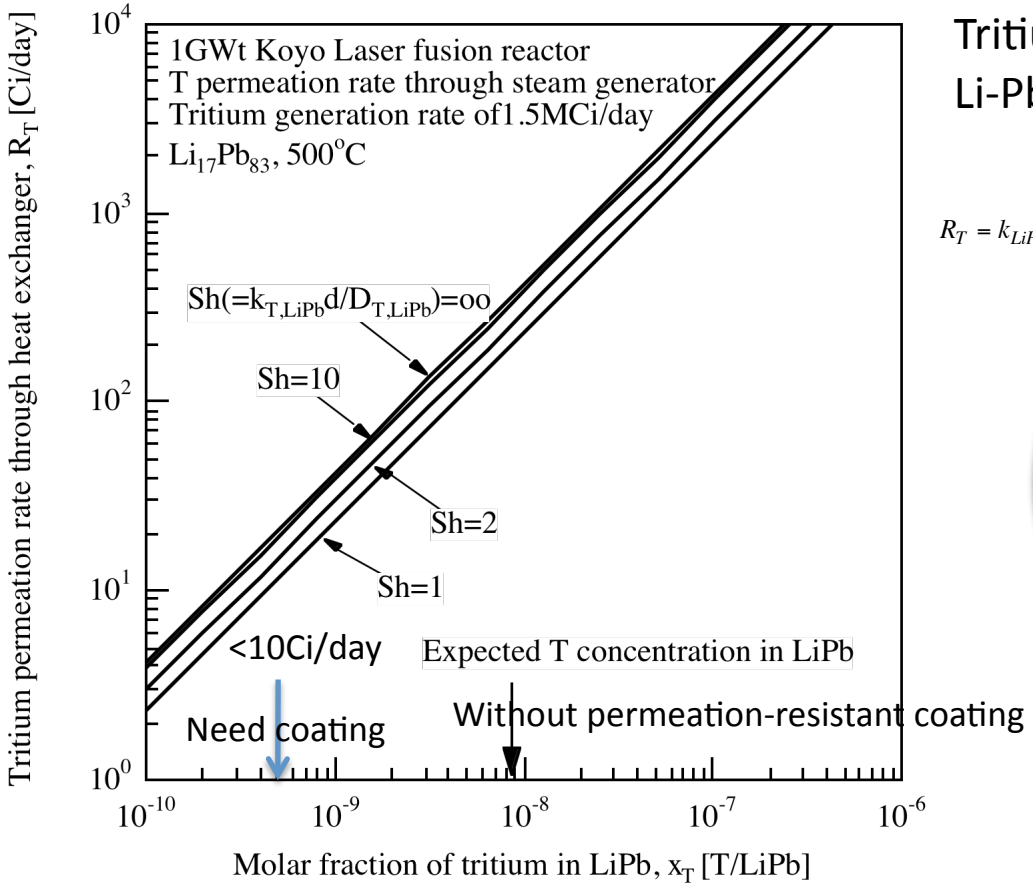


Reactor chamber of Koyo-first

Reference: “Conceptual design of Koyo-fast”

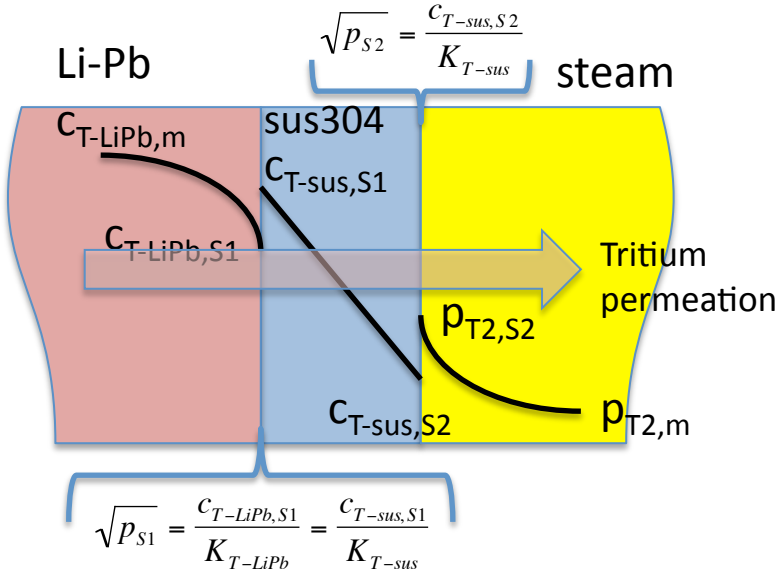
(5) Blanket T recovery design

Tritium permeation rate through steam generator of laser fusion reactor system as a function of tritium concentration in Li-Pb



Tritium is dissolved as an atomic form in Li-Pb as well as in sus 304 tube wall.

$$R_T = k_{LiPb}\left(c_{T,LiPb,m} - c_{T,LiPb,S1}\right) = \frac{D_{T,sus}}{t_s}\left(c_{T,sus,S1} - c_{T,sus,S2}\right) = k_{He}\left(\frac{p_{T_2,S2}}{R_g T_{S2}} - \frac{p_{T_2,m}}{R_g T_m}\right)$$



Calculation under the condition where $p_{T2,m}$ is negligibly small.

Conclusions on LiPb

1. Permeability, diffusivity and solubility of H and D in $Li_{16}Pb_{84}$ alloy are determined.
2. Isotope effects of solubility and diffusivity are correlated by harmonic oscillation model and vibration energy in solution site and transient site.
3. The energy determined so is consistent with 1st principle numerical simulation for H behavior in $Li_{16}Pb_{84}$ eutectic alloy.
4. When H and D mixtures are present simultaneously, their permeations are determined by the ideal solution model, and the solubility and diffusivity are determined in a similar way to the single component of H_2 or D_2.
5. Li activity and H energy in trap site for solubility in arbitral composition of Li+Pb alloys are correlated by the linear addition rule of Li and Pb atoms.
6. Hydrogen permeation through $Li_{16}Pb_{84}$ flow surrounded by solid walls is determined by the conjugated system of flow-wall-gas purge.