

# Present Status of Liquid Blanket Chemistry Study in Japan and Proposal to Japan-US Collaboration

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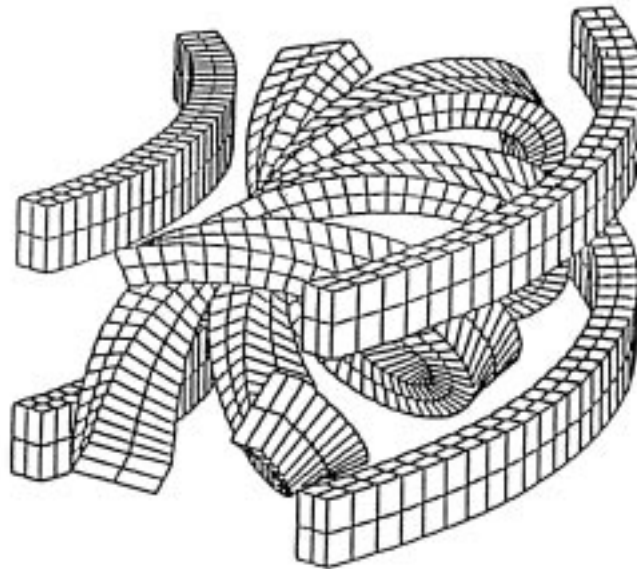
Presented by S. Toda  
(Tohoku University)

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- 1) Flibe in NIFS FFHR Design and Its Critical Issues
- 2) Compatibility of Structural Materials with Flibe
- 3) Tritium-related Studies on Flibe
- 4) Proposal to Japan-US Collaboration

# Introduction (FFHR)

## Conceptual Design of Force-Free Helical Reactor (LHD Project)



Blanket : complex shape

→ (requests) maintenance free  
self-cooling system

A mixture of  $\text{LiF-BeF}_2$  (Flibe)  
the most promising breeding material

### Advantages

- 1) High chemical stability in itself  
→ No reaction with air and water
- 2) Low electric conductivity  
→ Low MHD pressure drop

## FLIBE-RELATED TOPICS IN FFHR BLANKET R&D

- 1) Low TBR --> Utilization of Be
- 2) High melting temperature  
--> Narrow temperature window
- 3) Heat transfer, Forced convection  
--> Design of cooling system
- 4) Tritium release  
--> Tritium recovery with high efficiency  
--> Tritium permeation protection
- 5) Compatibility of structure materials  
--> Improvement of compatibility
- 6) Molten salt technology  
--> Circulation, sensor, purification

## COMPATIBILITY OF STRUCTURAL MATERIALS WITH FLIBE

- 1) Analyses of corrosion mechanism and corrosion protection are very important from the points of reliability and safety.
- 2) There are a lot of data obtained on Ni-based alloy ( in ORNL/MSRE). There are still few data on the candidate materials (JLF-1, V alloy, etc.) Flibe produces  $\text{HF-H}_2\text{O-O}_2$  by nuclear reaction with neutrons.
- 3) Compatibility test of the materials with flowing Flibe in a loop irradiation is required in the controlled condition of impurities under neutron irradiation.
- 4) Corrosion behavior in Flibe should be investigated under controlled Redox potential (with metal scavenger (Be) and  $\text{H}_2$  addition).
- 5) Improvement of compatibility should be investigated by using Redox buffer, metal scavenger, coating, etc.

## Introduction (candidate materials)

Compatibility of structural materials with molten Flibe is one of the critical issues.

Ni-based superalloys (such as Hastelloy) were sufficiently investigated as the structural material for the core container of MSRE (ORNL).

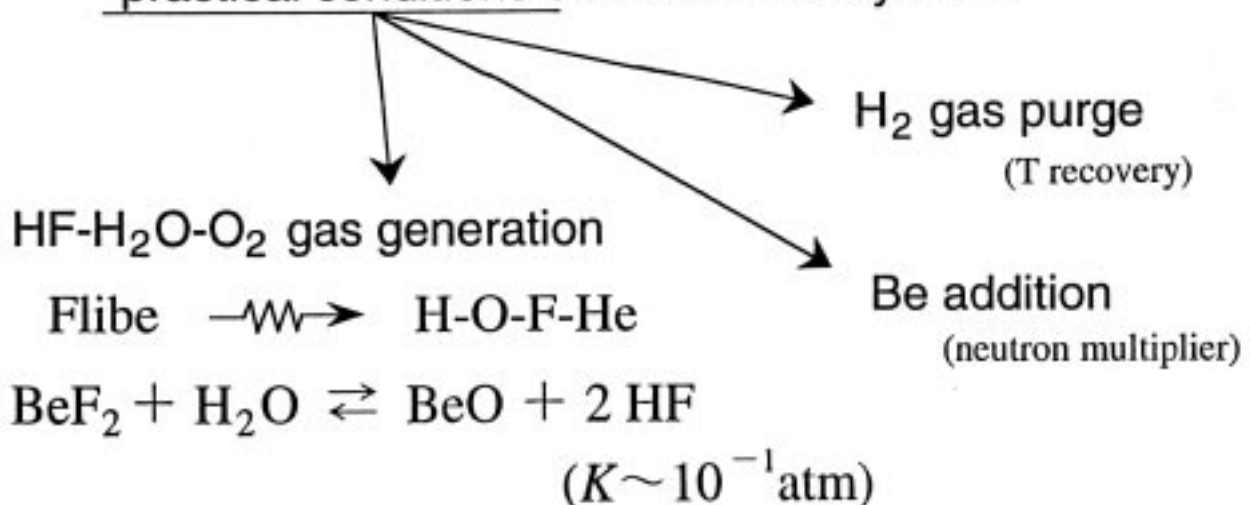


× Ni : going highly radioactive under the heavy neutron irradiation

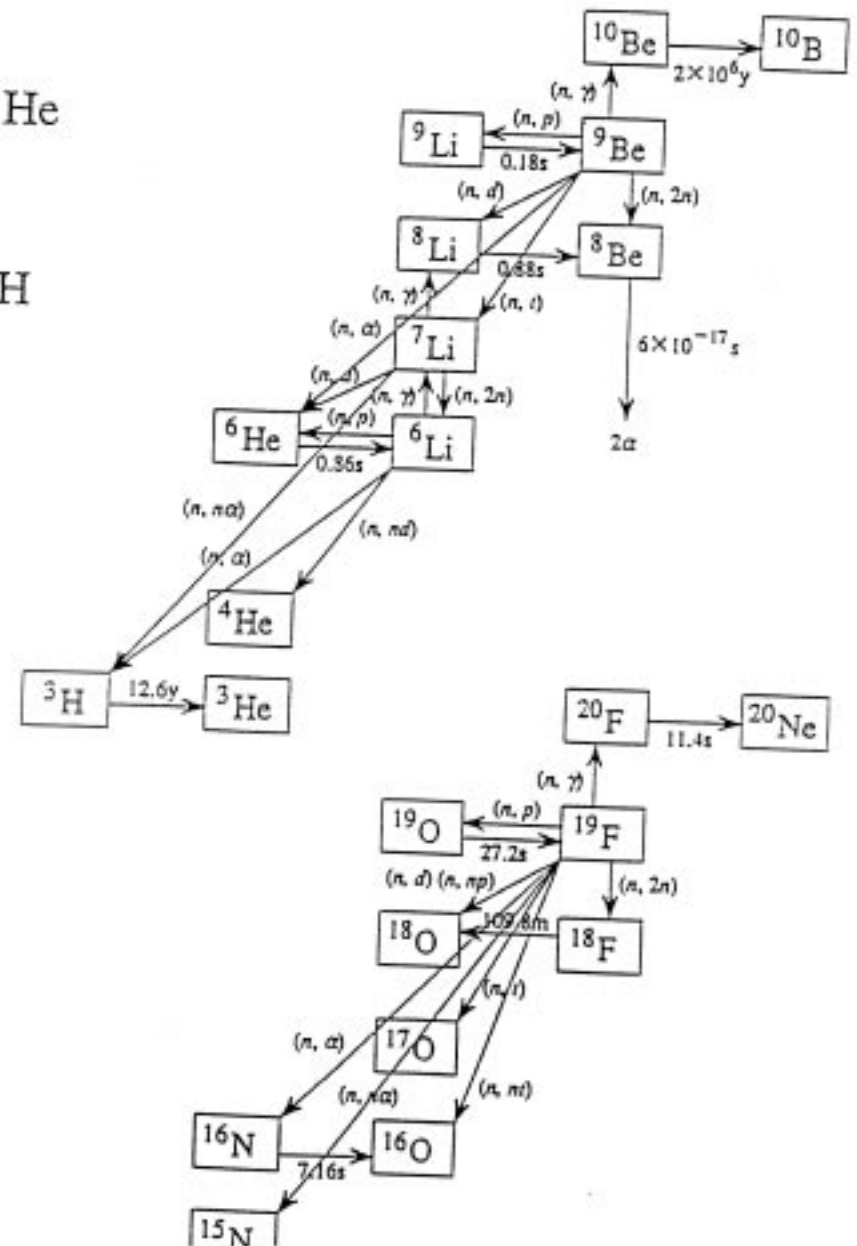
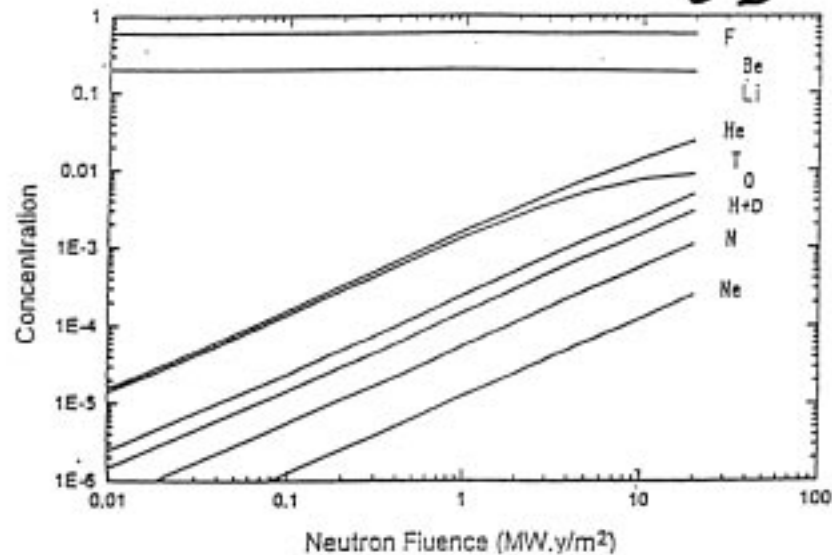
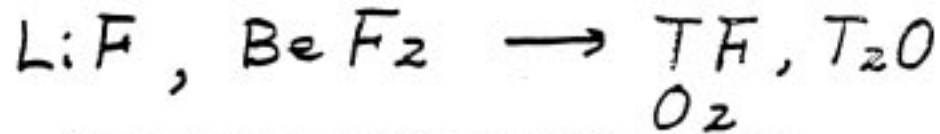
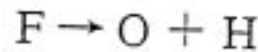
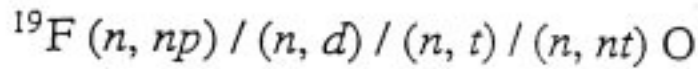
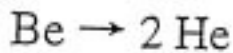
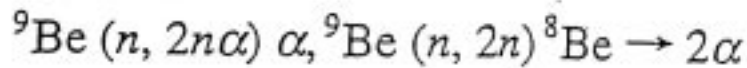
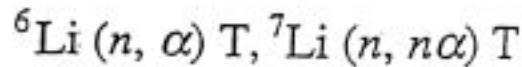
Candidate Materials

Ferritic steel (Fe-9Cr-2W, JLF-1),  
V-based alloy (V-4Cr-4Ti), etc.

As for these materials, almost NOTHING is known about corrosion-resistance against Flibe under the practical conditions of the blanket system.



Nuclear transmutation of Flibe by neutron irradiation



# **REQUIRED CONDITIONS FOR COMPATIBILITY TESTS**

## **Fusion blanket conditions**

### **Temperature**

#### **Loop Experiment**

- **Temperature distribution (gradient)**
- **Thermal cycles – cracking, etc.**
- **Magnetic field – magnetic particle deposition**
- **MHD effect – electromotive force**
- **Liquid breeder flow – mass transfer**

#### **Irradiation**

- **Radiation damages**
- **Transmutation**  
**(in structural materials, in liquid breeder)**
- **Radiation-induced phenomena**  
**(Diffusion Enhancement, Swelling,**  
**Phase segregation,**  
**Corrosion Enhancement, etc.)**

# **SCENARIO FOR COMPATIBILITY TESTS**

## **1) Thermodynamic analysis**

## **2) Kinetics**

**Static experiment**  
**No irradiation**  
**(Pot experiment)**



**Dynamic experiment**  
**No irradiation**  
**(Loop experiment)**



**Static experiment**  
**Irradiation**  
**(Capsule experiment)**



**Dynamic experiment**  
**Irradiation**  
**(Loop experiment)**

## **3) Well-characterized specimens**

- Texture, Microstructure, Porosity**
- Impurities**

## **4) Well-characterized conditions**

- Impurities**



# Research Plan

1997

thermodynamic calculations  
designing experimental system  
dipping test (preliminary)

1998

dipping test (pre. contd.)  
fabrication of apparatus  
fundamental study on  
dipping experiment (static condition)

1999

long-term dipping experiment  
(static condition)  
fundamental study on  
the chemical effects of additives  
planning dynamic experiment

2000

dipping experiment  
(dynamic condition)

# Thermodynamic Analysis

## Discussion

As is expected, HF fluorinates ferritic steel and V alloy. However, oxides ( $\text{Cr}_2\text{O}_3$ ,  $\text{TiO}$ , respectively) can coexist.

Oxidizing additives ( $\text{O}_2$ ,  $\text{H}_2\text{O}$ ) only result in gain of oxide.

	2ppm- $\text{O}_2$ + $\text{H}_2\text{O}$	2ppm- $\text{O}_2$ +HF	100ppm- $\text{O}_2$ +HF
Fe-9Cr-2W	Oxidation ( $\text{Cr}_2\text{O}_3$ / $\text{FeCr}_2\text{O}_4$ / $\text{BeWO}_4$ )	Oxidation Fluorination ( $\text{CrF}_2$ / $\text{CrF}_3$ , $\text{FeF}_2$ )	← Gain of Oxide
V-4Cr-4Ti	Oxidation ( $\text{TiO}$ / $\text{Ti}_2\text{O}_3$ / $\text{VO}$ )	Oxidation Fluorination ( $\text{TiF}_3$ / $\text{VF}_3$ )	← Gain of Oxide
Mo	Oxidation ( $\text{MoO}_2$ )	Oxidation Fluorination ( $\text{MoOF}_4$ )	← Gain of Oxide

Formation of Oxyfluorides ? ( $\text{OF}$ ), ( $\text{OF}_2$ )

These materials would have sufficient corrosion-resistance if the oxides function as a protective scale.

$\text{H}_2$  atmosphere

more moderate circumstance (Fe-9Cr-2W)

almost no effect (V-4Cr-4Ti)

Be addition

no oxidation

very effective scavenger

## Dipping

All dipping experiments were performed in the glove box under argon gas.

Molybdenum crucibles were used as containers, in which a test specimen was put with fluoride components which were weighed and sufficiently mixed in an agate mortar.

### Test Specimen

Mo (99.95%)

430 ferritic steel (Fe-18Cr)

(Mn<1%, Si<0.75%, S<0.03%, C<0.12%, P<0.04%)

550°C × 3hr

Fluoride Mixture  
2:1 of LiF-BeF<sub>2</sub>

Mo Crucible

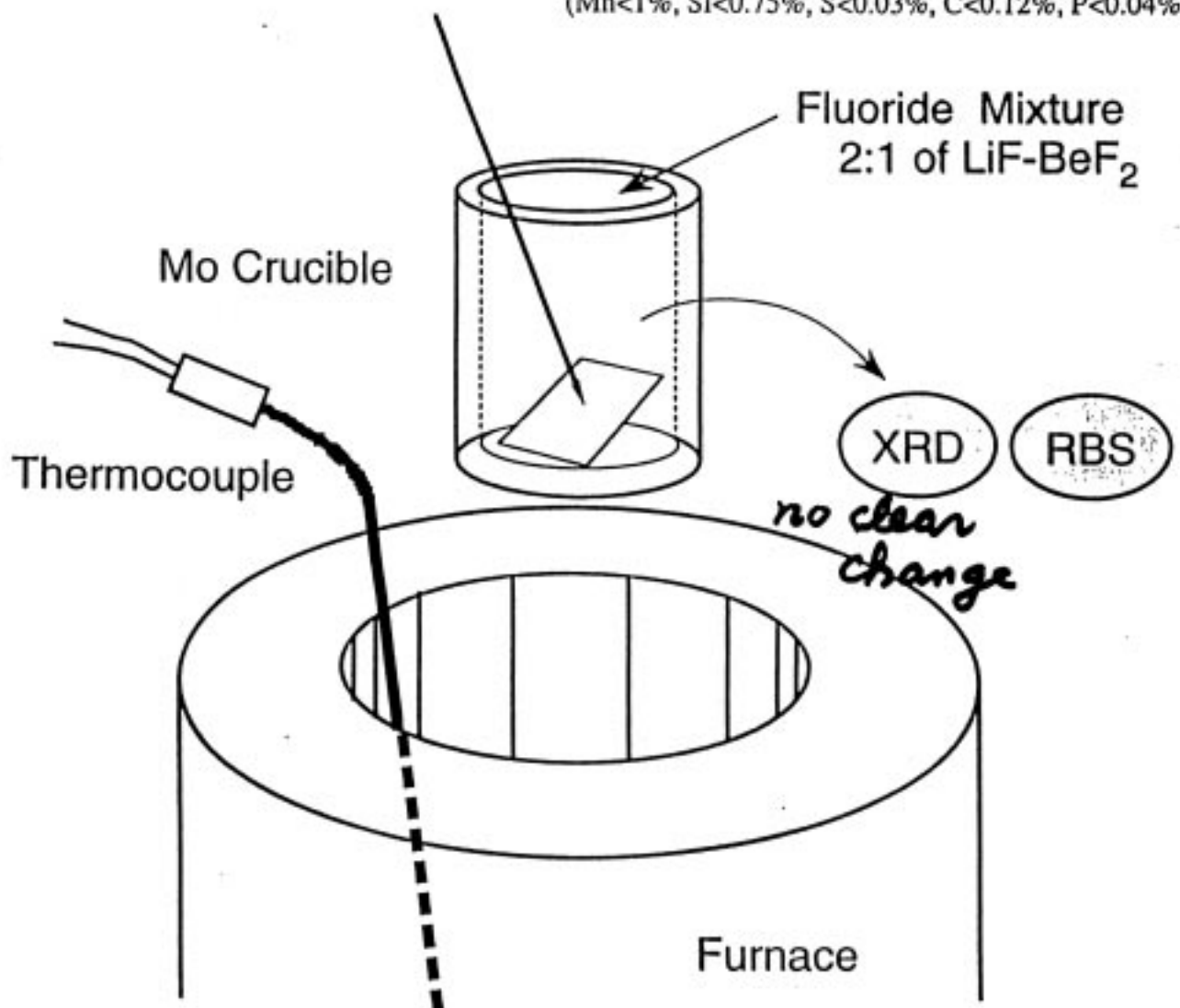
Thermocouple

XRD

RBS

*no clear  
change*

Furnace



## TRITIUM BEHAVIOR IN FLIBE

- 1) Tritium behavior (released chemical form, diffusivity, solubility, mass-transfer coefficient, surface reaction rate, tritium permeation rate through structural materials) should be elucidated for design of tritium recovery systems and estimation of tritium inventory and tritium leakage.
- 2) These data are being measured with a trace of tritium or  $H_2$  and  $D_2$ . Released tritium chemical form depends on Redox potential in the system. Tritium release rate is different between HT and TF, and they change to each other depending on the Redox condition. Hot atom effect of tritium on the kinetic parameters is also expected.
- 3) Tritium behavior should be investigated using enough amount of tritium.
- 4) Mass transfer experiment for hydrogen isotopes including tritium should be carried out in a dynamic system (e.g. using a Flibe loop).

# Apparatus for In-Pile Tritium Release Experiment

Fast neutron source :  $10^8 \sim 10^9 \text{ n/cm}^2 \text{ s}$

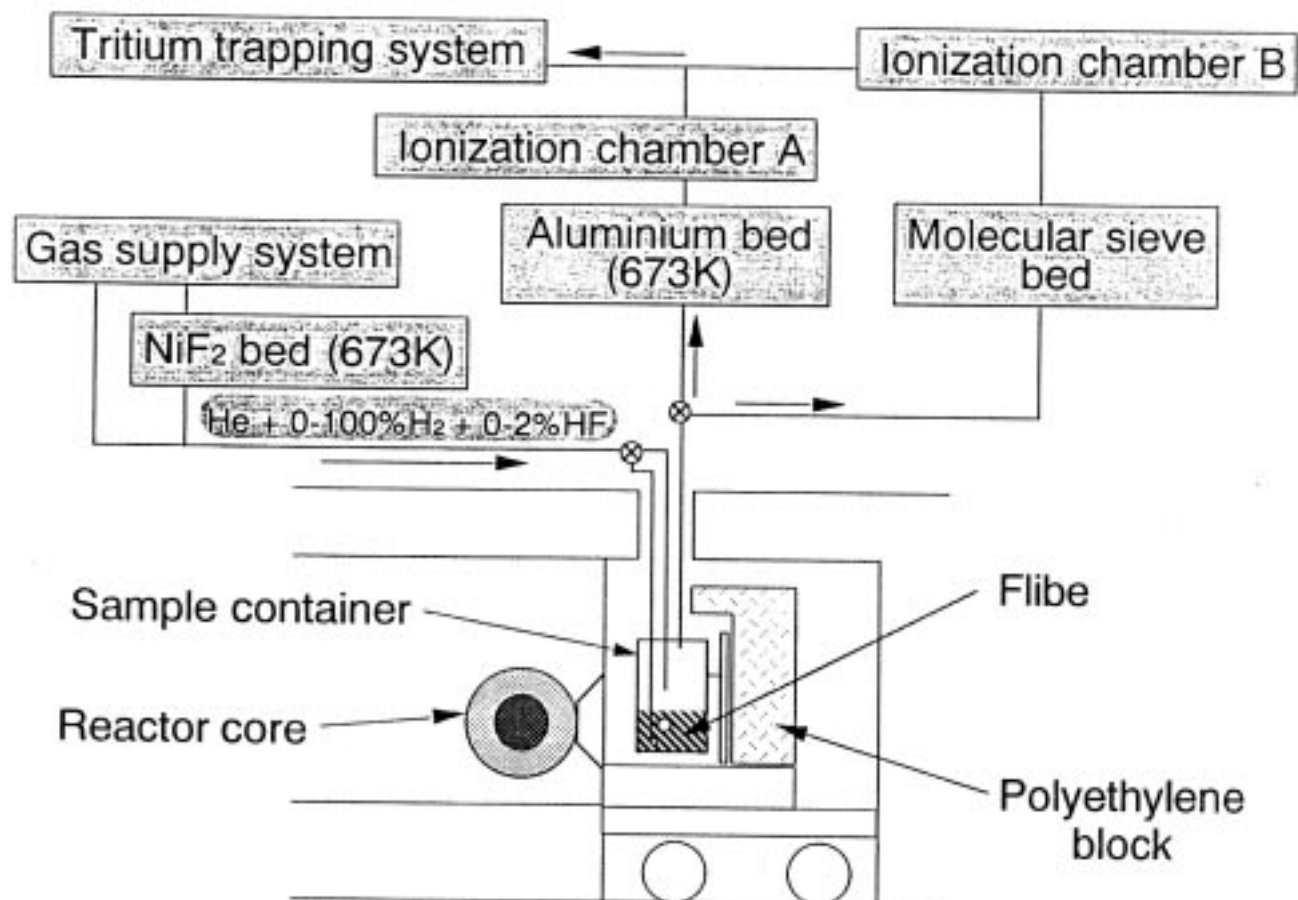
("YAYOI" of the University of Tokyo)

→ Detailed info.  
given by Suzuki

Tritium generation rate :  $\sim 40 \text{ Bq/g-Li, s}$

Purge gas : pure He, He + 0.001-10%  $\text{H}_2$ , pure  $\text{H}_2$ , He+2% HF

irradiation time : for about 150 minutes



TF is converted to HT in the aluminium bed and the concentration of all released tritium (HT and TF) is monitored by the ionization chamber A.

TF is captured in the molecular sieve bed and only the concentration of HT is monitored by the ionization chamber B.

Chemical form of T, T permeation,  
T release rate → D, K, mechanisms  
etc.

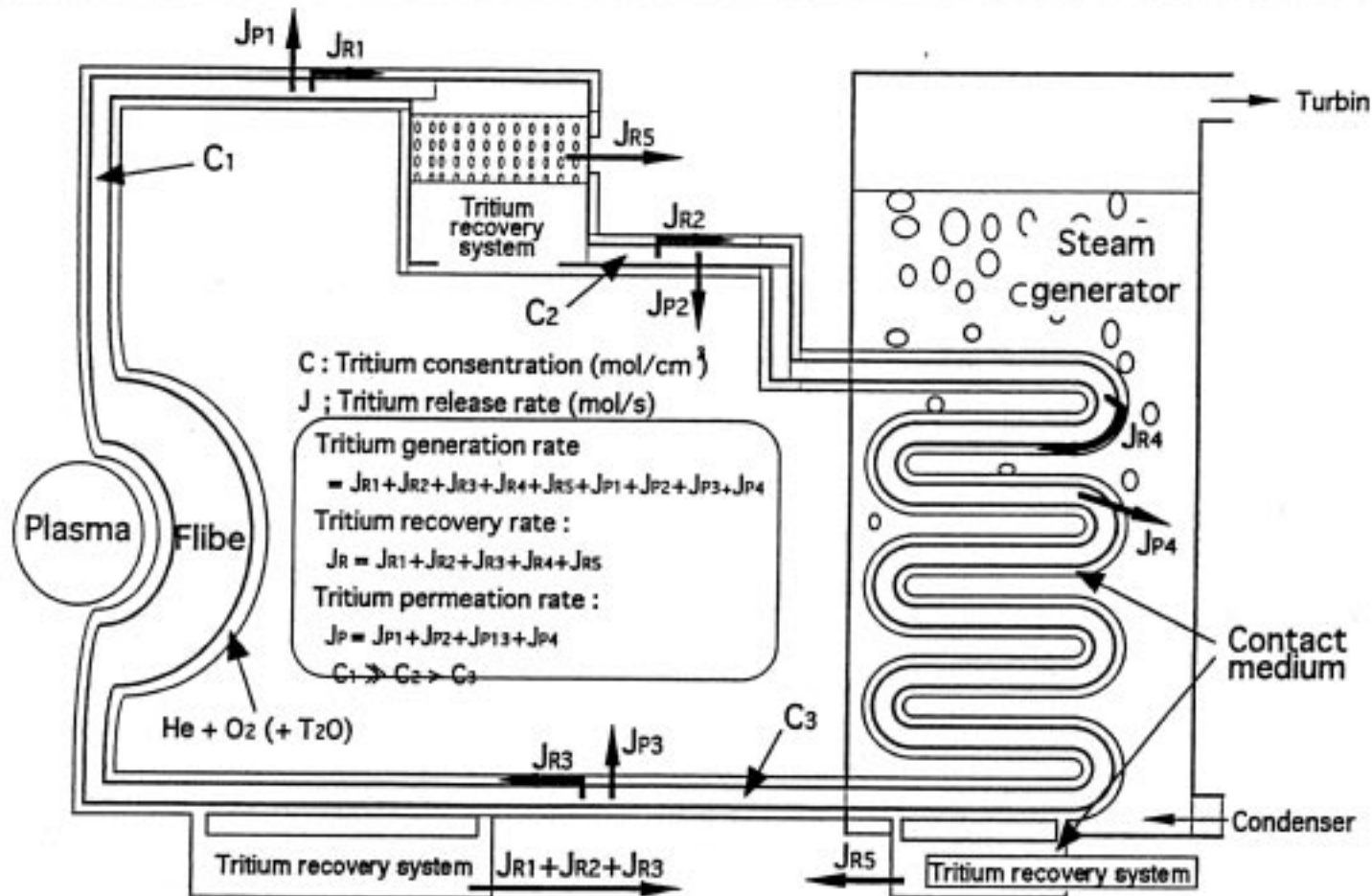
## TRITIUM TRANSFER CONTROL

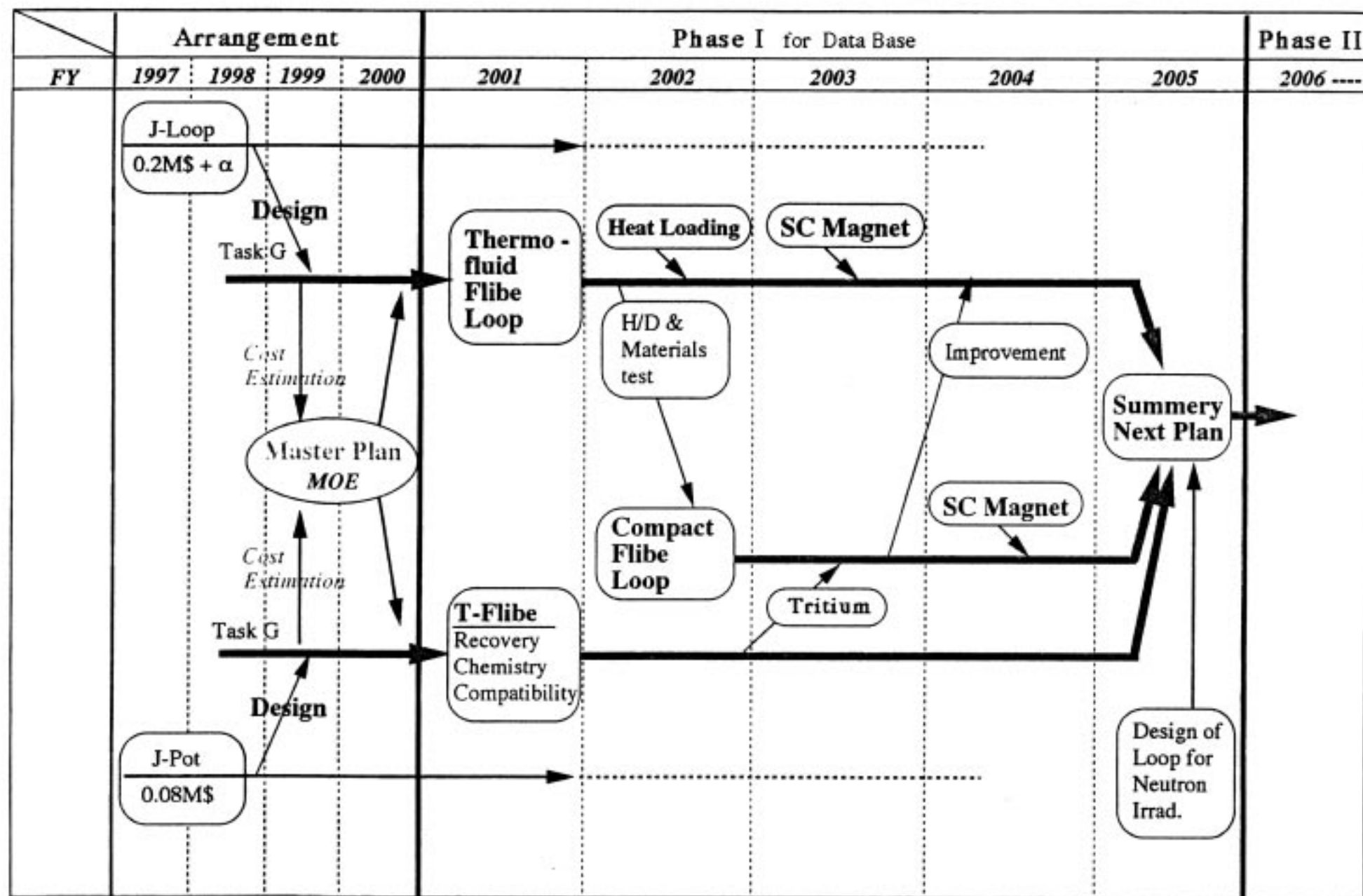
- 1) Effective tritium recovery and reduction for tritium leakage are very important for tritium economy and safety.
- 2) Spray tower and permeation window methods are considered for tritium recovery and double-wall tubing, contacting medium and tritium permeation barrier are proposed for control of tritium permeation. However, there have been few demonstration experiments.
- 3) Demonstration experiments are required using hydrogen isotopes including enough amount of tritium in a dynamic system (e.g. Flibe loop).
- 4) Tritium permeation barrier should be investigated in fabrication and properties.
- 5) Control of tritium transfer rate by the Redox potential control should be examined.



# The vacuum disengager is promising to recover > 90% of T,

resulting in T inventory < 1g in the 400 tons of Flibe in the loop, where the double walled tube is reliable to sweep out the permeated T with He, and the rate-determining step of T<sub>2</sub> release should be studied furthermore.







Proposal on Flibe Chemistry and Tritium to  
Japan-US Collaboration (1)  
Compatibility and Chemistry Control in Flibe

- 1-1) Corrosion mechanism and compatibility studies of structural candidate materials (JLF-1, V-alloys, SiC, etc.)
- 1-2) Control of Redox potential and impurities in Flibe by Redox buffer (Be) and getter materials
- 1-3) Development of in-situ monitors for Redox potential and impurities
- 1-4) Improvement of compatibility of structural materials with Flibe by coatings
- 1-5) Study on electro-magnetic effect on corrosion phenomena

Proposal on Flibe Chemistry and Tritium to  
Japan-US Collaboration (2)  
Behavior and Control of tritium in Flibe

- 2-1) Study on tritium transport mechanisms under well-characterized condition
- 2-2) Investigation and demonstration on high-efficiency tritium recovery from Flibe
- 2-3) Study on tritium permeation behavior through structural wall
- 2-4) Investigation and demonstration on tritium confinement
- 2-5) Development of tritium monitors for Flibe blanket system

<p>Proposal on Flibe Chemistry and Tritium to Japan-US Collaboration (3) Tritium System Design in Flibe Blanket</p>
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Based on the above results, design study will be carried out in comparison with another types of liquid blankets (including liquid Li and Li-Pb blankets) and solid blankets.

In particular, the study will be focused on tritium fuel cycle including blanket tritium system.

## Experimental Apparatus

### **(1) Flibe Pot for Chemistry and Tritium Experiments (for 1-1, 1-2, 2-1 and 2-2)**

Structural material: Hastelloy or SUS316

Flibe volume: < 5 liter with agitation

Tritium amount: < 10 g (pure  $T_2$  required)

### **(2) Flibe Loop for Chemistry and Tritium Experiments (for 1-1, 1-2, 1-3, 1-4, 1-5, 2-1, 2-2, 2-3, 2-4, and 2-5)**

Structural material: Hastelloy or SUS316

Flibe volume: < 50 liter with forced convection

Tritium amount: < 10 g (pure  $T_2$  and diluted T required)

