Determination of hydrogen isotopes solubility in the eutectic PbLi alloy (LLE)

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for the **Fusion Safety Program**

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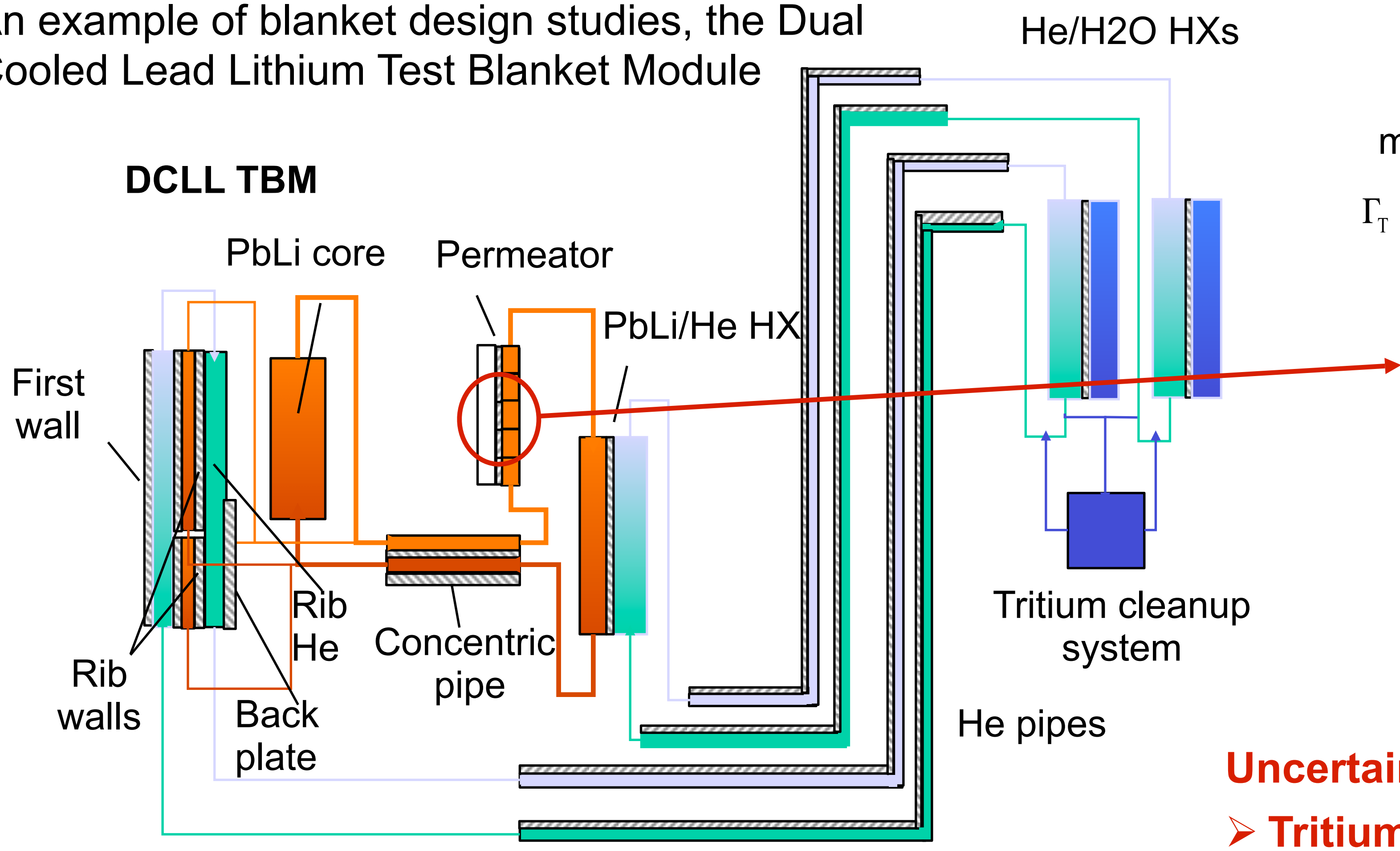
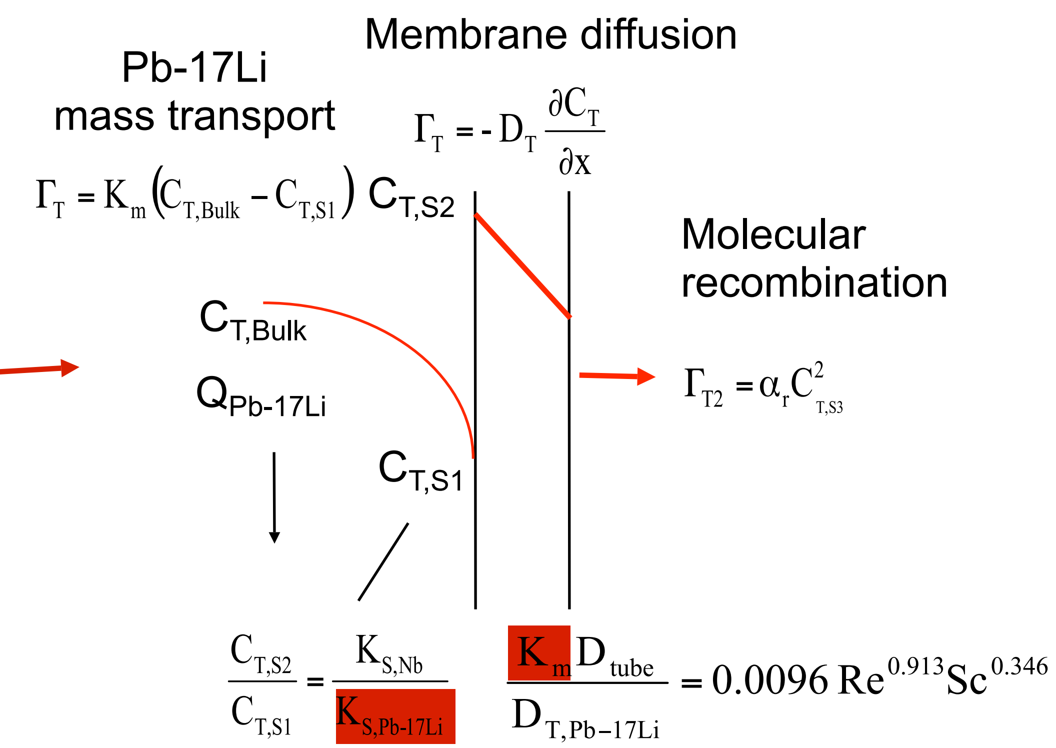
Scientific motivation

Tritium transport properties in liquid breeder and coolant materials are fundamental for the design and analysis of blanket concepts for fusion energy systems

An example of blanket design studies, the Dual Cooled Lead Lithium Test Blanket Module



Permeator T_2 transport model



Uncertainties to be resolved by experiments:

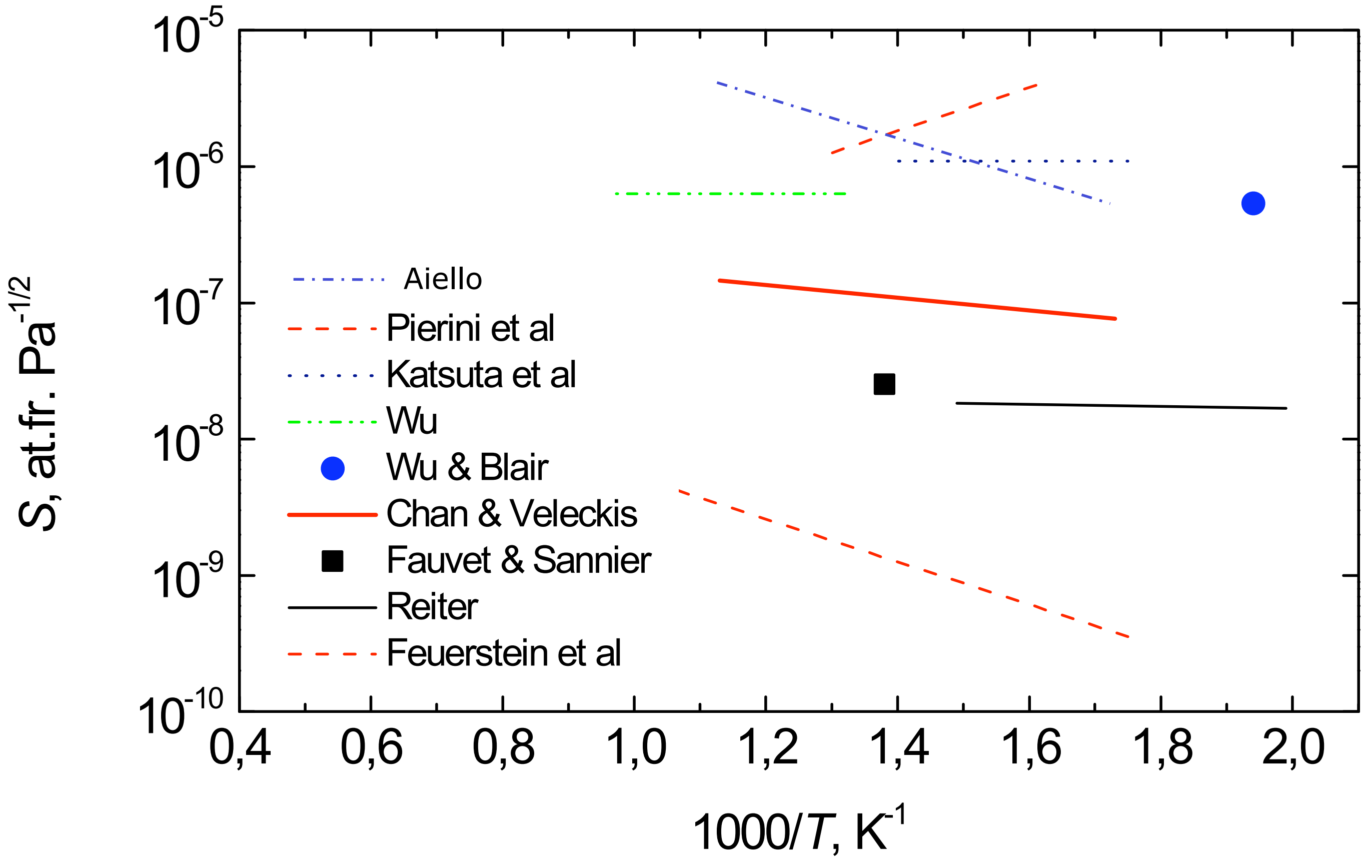
- **Tritium solubility and the mass transport correlation in flowing PbLi**
- **Tritium behavior at PbLi/FS interface**

Scientific motivation

The knowledge of the function linking the tritium concentration dissolved in liquid materials with the tritium partial pressure at a liquid/gas interface in equilibrium, $C_T=f(P_T)$, is of basic importance because it directly impacts all functional properties of a blanket determining:

- **tritium inventory**
- **tritium permeation rate**
- **tritium extraction efficiency**

State of the art database of hydrogen solubility in LLE



- Solubility database is inadequate for design
- Scatter reflects experimental approaches and measurement techniques applied
- Knowledge of dynamic transport properties (diffusion, mass transfer, interface processes) is much more limited
- Critical evaluation of database is ongoing within IEA collaboration

Programmatic framework

Japan-US Joint Project TITAN 2007-2012

TITAN Task 1-2: Tritium Behavior in Blanket Systems

Proposed Research Project Areas

- Solubility of T in Pb-Li at Blanket Conditions
  - Low pressure region of hydrogen isotopes using tritium
  - Confirmation of Sieverts' Law, Phase diagram of Pb-Li and T system
- Concentration Effects of T Permeation in Structural Materials and TPB Coating
  - Wide T pressure range covering several kinds of liquid breeders
  - Performance test on SM as well as TPB coating (to be developed in Japan)
- Tritium Extraction from Pb-Li and Other Liquid Breeders at Blanket Conditions
  - Mass transfer kinetics
  - Permeation window, gas engager, etc.
  - Performance test on a loop which is constructed inside or outside the budget
- Modeling and System Design for Tritium Behavior at Blanket Conditions

Experimental activities carried out at the INL Safety and Tritium Applied Research facility (operation is part of Fusion Safety Program activities funded by DoE OFES)

Analysis and modeling activities in direct support of US Test Blanket Module workgroup

Technical issues

Lead Lithium Eutectic, LLE

15.7 at %, 235 C mp

What is the eutectic Pb-Li alloy?

P. Hubberstey, Journal of Nuclear Materials 191- 194 (1992) 283-287

The lead-rich eutectic of the Li - Pb system has been shown to lie not at 17 at % Li, but at 15.7(2) at % Li. In a reassessment of the phase boundaries (0 < xL, (a t %) < 22.1) using equilibrium resistance-temperature data for a total of 52 compositions, the hypoeutectic liquidus was shown to decrease smoothly from the melting point of pure lead to the eutectic point (15.7(2) a t % Li, 235(l)°C.

Title, homogeneity and impurity content are general issues for nuclear applications, but directly affect Li activity and therefore hydrogen isotopes solubility

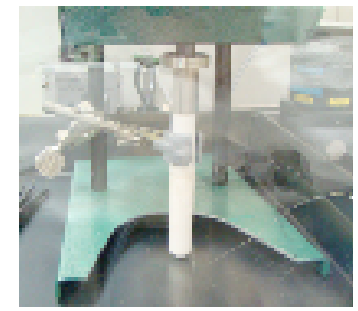
Determined by:

- raw materials
  - main concerns are neutron activated elements (Bi) and seeded precipitation of higher Li content phases
- production and purification process
  - main concern is uniformity and formation of hard melting phases Li_5Pb_2, LiPb, Li_3Pb
- handling
  - main concern is reactivity with oxygen bearing gases (air, H_20, CO, CO_2) forming Li_2O

INL is working through IEA Implementing Agreement on Nuclear Technology for Fusion Reactors (Liquid Breeder Blankets Subtask) to define reference specifications for LLE used in FNT programs

Technical issues

INL experiments are performed with material supplied in the US by Atlantic Metals but production location, methodology and composition data are not disclosed



	Atlantic Metals material								material
	LLE B1 S1-4		LLE B1 S1-3		LLE B1 S2		ORNL analysis		
Elements	LLE conc [wt%]	LLE conc [at%]	LLE conc [wt%]	LLE conc [at%]	LLE conc [wt%]	LLE conc [at%]	LLE conc [wt%]	LLE conc [at%]	LLE conc [at%]
Pb	99.37	85.78	99.33	86.16	99.33	85.37	99.38	85.06	
Li	0.54	14.01	0.52	13.34	0.56	14.29	0.56	14.31	15.80

Results from inductively coupled plasma mass spectroscopy (ICP-MS) and optical emission spectroscopy (ICP-OES) analysis by sample dissolution in nitric acid, performed at INL analytical laboratories

Impurities concentration in PbLi eutectic		Ag	Al	As	Bi	Cr	Fe	Mn	Ni	Si	Sn	Ti	V	Zn	Zr
B1S3	ppm w	16.17	✔	62.87	✔	✔	46.71	✔	✔	82.63	113.17	✔	✔	✔	✔
B1S4.1	ppm w	34.39	✔	160.51	✔	✔	76.43	✔	✔	126.11	✔	✔	✔	✔	✔
B1S4.2	ppm w		✔	6.46	22.11	✔	2.26	4.36	✔	7.75	35.03	✔	✔	5.33	✔
B1S4.3	ppm w	1.43	✔	3.73	24.69	7.02	2.41	5.38	✔	4.61	37.31	✔	✔	28.53	425.06

Fe, Si, Ag traces present in DI water blank

Bi, Sn, Zn impurities in lead ore - Bi of particular concern for activation

Cr, Mn from metallic crucibles

High conc Zr in one sample only maybe due to handling

Technical issues

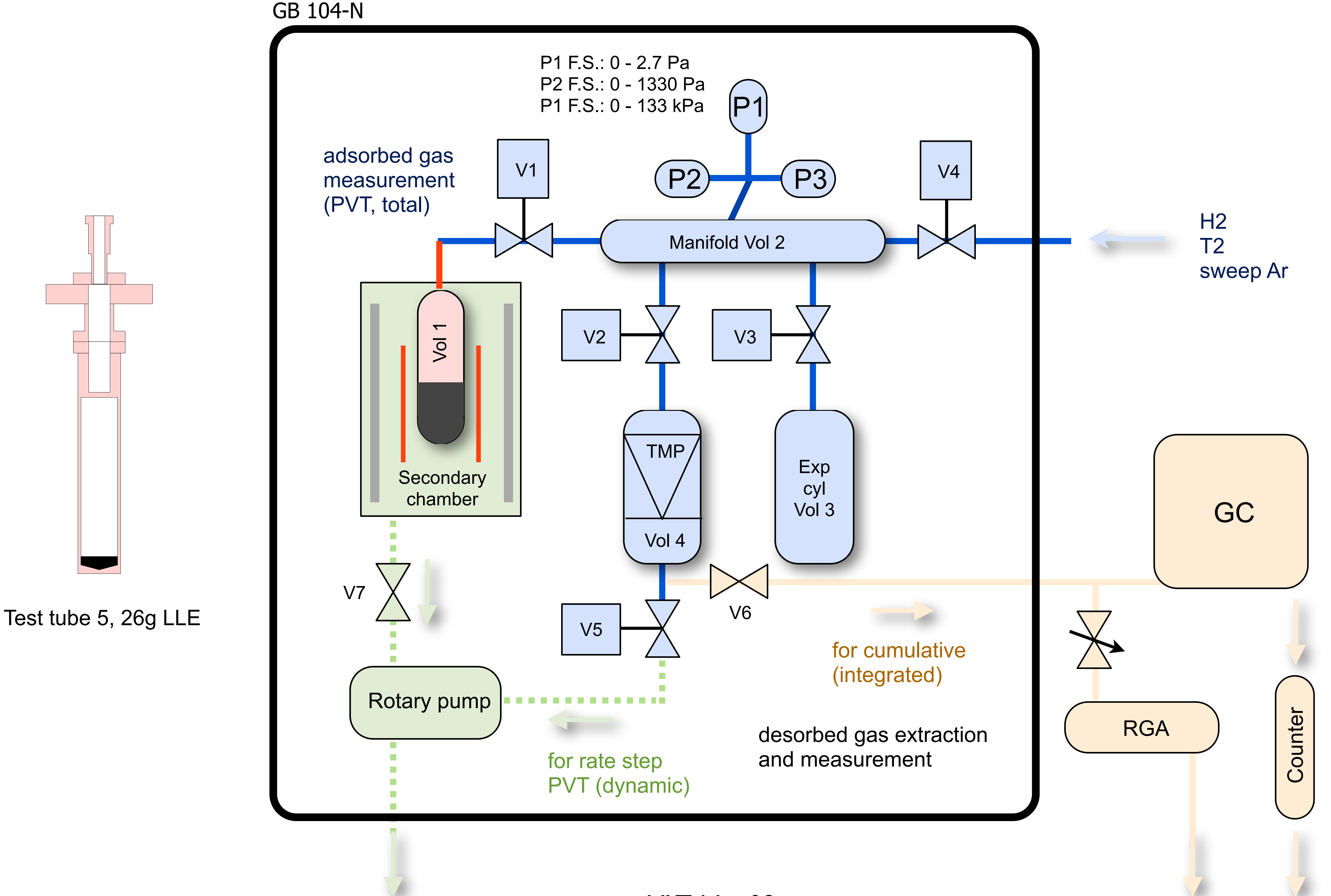
A closer look at the available database and design requirements for TITAN experiments

- Different experimental approaches led to systematic differences in measured solubility because of different impact of parasitic phenomena and other intrinsic errors:
  - desorption - small sample mass (10 g), initial evacuation, system outgassing, ...
  - adsorption - large sample mass (1 kg), parasitic adsorption, losses, ...
  - indirect (permeation) - all of the above, interface phenomena, ...
- Simultaneous measurement by independent diagnostics (PVT, gravimetry, gas chromatography, beta detection) and test procedure evaluation to ensure equilibrium conditions are met are essential
- Focus on reversibility of adsorption/desorption process to eliminate systematic uncertainties

Why testing with tritium for low partial pressure (< 10 Pa) components design

- Experimental evaluation of isotopic effects on transport properties and impact of isotopic exchange phenomena on tritium behavior in LLE and system interfaces
- Testing in relevant hydrogen isotopes partial pressures ranges (deviation from Sievert’s law, rate-controlling process transition, interface phenomena)
  - ‘Natural’ hydrogen background in small-scale laboratory facilities
  - Sensitivity/accuracy limitation of measuring instruments
  - Practical laboratory tests require $p_{H2/D2}$ > 100 Pa (available database $1x10^3 < p_{H2} < 1x10^5$)
- Radiation counters for tritium detection (recently purchased Tyne monitors with 1ηCi/m^3 sensitivity in 1 liter chamber) have practically no sensitivity limits - determined by experiment design (purge flow, background, ...)

Experiment diagram

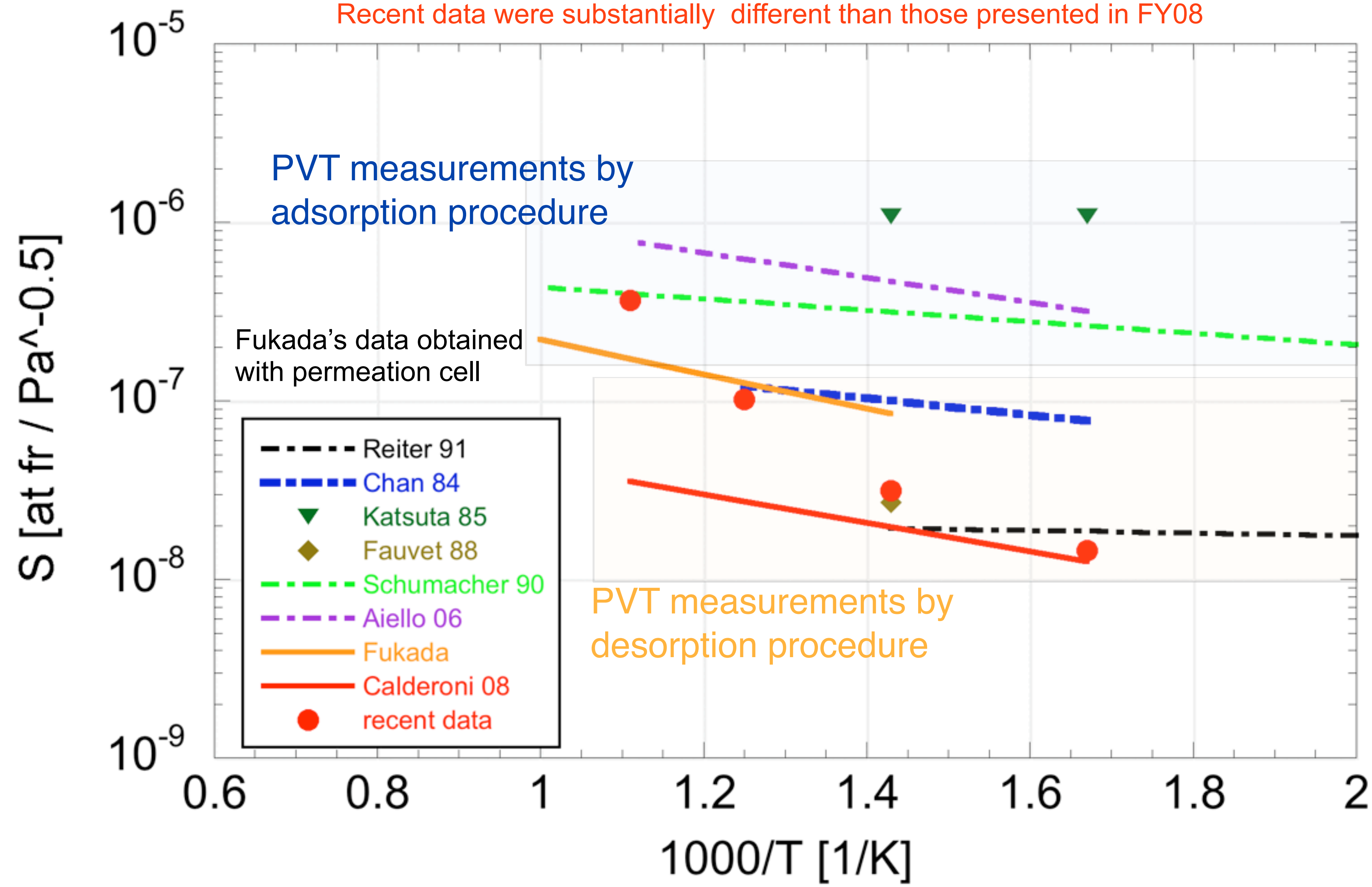


Test tube 5, 26g LLE

TITAN data compared to references for H2 solubility

T	T	1000/T	Ks H2								
K	C	1/K	at fr / Pa^-0.5								
			Reiter 91 1e3 - 1e5 Pa	Chan 84 1e4 Pa	Katsuta 85 1e4 - 1e5 Pa	Fauvet 88 1e3 - 1e4 Pa	Schumacher 90 1e4 - 1e6 Pa	Aiello 06 1e3 - 1e5 Pa	Fukada 1e3 - 1e5 Pa	INL 08 1 - 1e5 Pa	INL 09 1 - 1e5 Pa
500	227	2.00	1.76E-08				2.07E-07				
600	327	1.67	1.86E-08	7.73E-08	1.08E-06		2.64E-07	3.17E-07		1.26E-08	1.45E-08
700	427	1.43	1.93E-08	1.00E-07	1.08E-06	2.70E-08	3.15E-07	4.66E-07	8.44E-08	1.96E-08	3.14E-08
800	527	1.25		1.21E-07			3.59E-07	6.21E-07	1.26E-07	2.73E-08	1.02E-07
900	627	1.11					3.97E-07	7.77E-07	1.72E-07	3.53E-08	3.65E-07
1000	727	1.00					4.31E-07		2.21E-07		

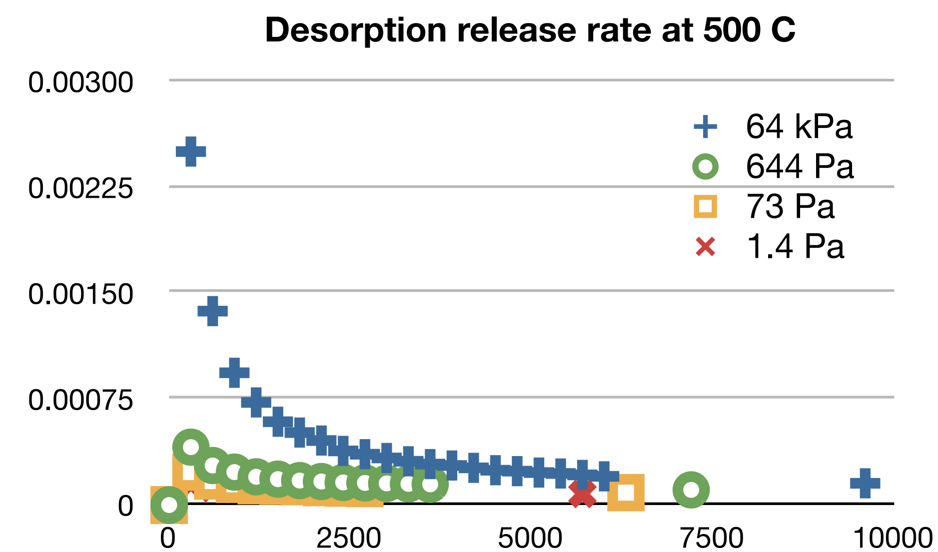
Recent data were substantially different than those presented in FY08

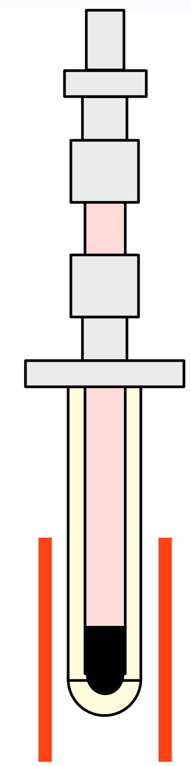


- In the range of applicability (<500 C) Reiter data are verified by desorption experiments based on PVT measurements
- Different liquid column geometry shows impact of surface to volume ratio is negligible - diffusion controlled process
- High temperature data are still unreliable
  - Interaction with the alumina crucible above 500 C is likely responsible for the high apparent solubility because of the formation of Li-Al alloys, as demonstrated by corrosion tests performed by B. Pint at ORNL (presented at ICFRM14)

Ongoing experiment modifications:

- quartz crucibles (with optional moly liners)
- improved heating system (induction or IR)
- gas chromatographic analysis in parallel with PVT measurements
- integrated test mode vs rate-step mode
- TMAP modeling for data analysis





Planned FY10 activities to complete task objectives:

- increase sample mass to observe reversible adsorption/desorption
- finalize a critical assessment of referenced and ongoing experiments within IEA collaboration to identify optimal test procedure for tritium tests
- test different batches of LLE from different sources within IEA collaborative agreement on material reference specifications
- perform tritium solubility tests

Outlook of planned experimental activities

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- Additional resources for a mid-sized (10 L) forced convection loop with independent test sections (material, temperature, flow conditions) have not materialized
- Main objective of Phase II activities remains the experimental investigation of tritium extraction from LLE with the vacuum permeator as reference concept

  Ongoing analysis effort to design a smaller (1 L) loop design with dedicated test section enclosed in available GB - main issues: tubes material (commercial ferritic steel, quartz), permeating window material (ferritic steel, coated refractory metal), pump (non contact EM, contact EM)
- Focus could be shifted to tritium permeation tests in metals and coatings