Tritium permeation control and extraction- perspectives from fusion systems studies

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Workshop on Tritium Control and Capture in Salt-Cooled Fission and Fusion Reactors

Salt Lake City, Utah

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Idaho National Laboratory

Outline

- Tritium in fission and fusion reactors: similarities and differences
- Overview of breeding concepts for fusion
- Tritium management in fusion
- Concepts for tritium extraction from liquids
- Permeation barriers
- Permeation scaling with pressure
- Conclusions and recommendations for future research

Tritium generation in fission and fusion reactors

- Tritium generation in salt-cooled fission reactors is large relative to other fission reactors, but several orders of magnitude less than fusion

	PWR[1]	**CANDU[1]**	**Gas-cooled reactor[1]**	**Molten salt reactor[1]**	**ITER**	**FNSF**	**DEMO**
T generated (kg/y)	0.000075	0.1	0.002	0.09	0.0042	1 - 10	100 - 167

- Fusion consumes ~55 kg of tritium per GW-year of fusion power, and must necessarily breed this amount from lithium
- Tritium is very mobile and will permeate through solids at high temperature; losses must be limited to < 20 Ci/day (very roughly 1 g/yr)
- A fusion reactor must recover and separate bred tritium for re-use as fuel; in a fission reactor is it a waste product
- Strategies for tritium permeation control and extraction investigated for fusion should apply to salt-cooled fission reactors

[1] H. Schmutz, INL/EXT-12-26758, 2012

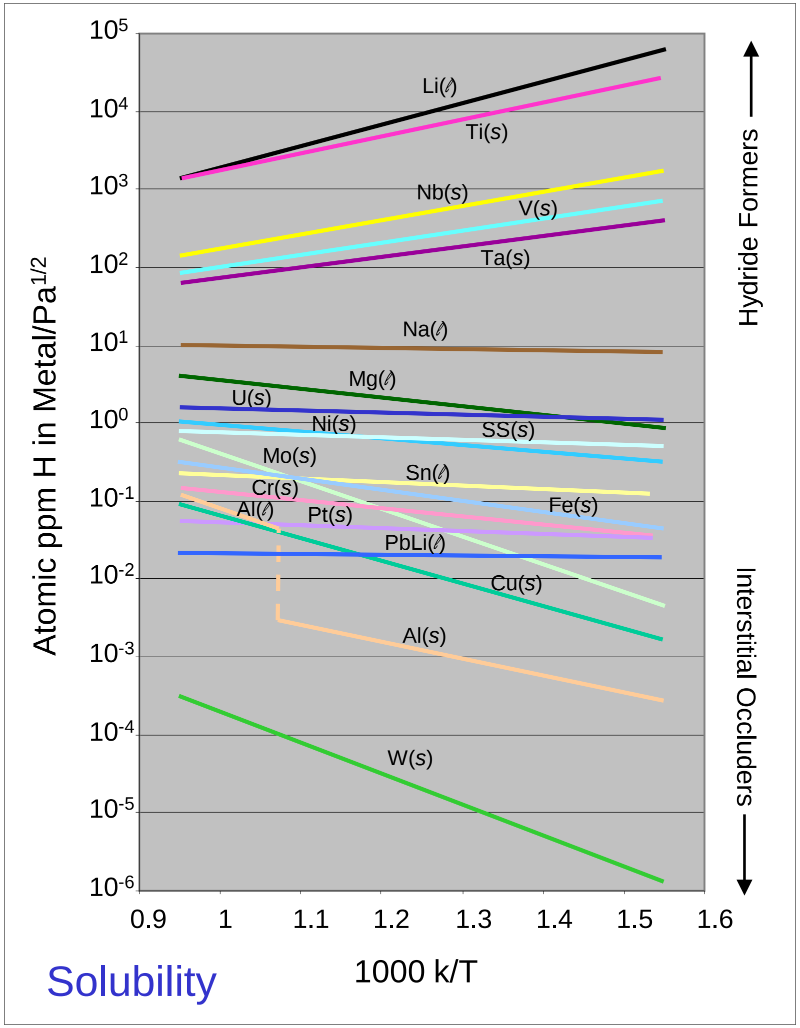
Tritium breeding materials in fusion

- Tritium is bred via neutron interactions with materials enriched in lithium-6
- Solid breeders (beds with ~1 mm diameter pebbles)
  - Li_4SiO_4 or Li_2TiO_3 ceramic breeder
  - Be or $Be_{12}Ti$ (lower chemical reactivity) neutron multiplier
- Liquid breeders
  - Li liquid metal
  - PbLi eutectic (Pb is a multiplier; less chemically reactive than Li)
  - FLiBe (requires additional Be multiplier)
- Current research is focused on solid ceramic (European, Japanese, Korean, Chinese, and Indian TBMs in ITER) or PbLi breeders (EU, Indian TBMs)
- The US does not have a TBM program, but our reference design is based on a PbLi breeder

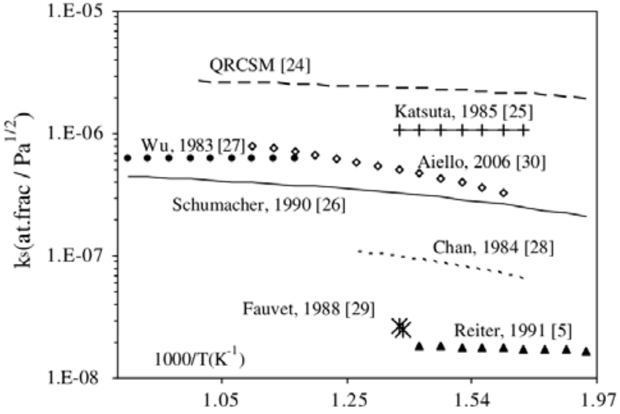
PbLi breeder concepts

- Structural material: reduced activation ferritic-martensitic (RAFM) steel
  - Limited to 550 °C operation, maybe lower (~480 °C) due to PbLi corrosion
- Helium-cooled lead-lithium (HCLL)
  - EU ITER TBM design and DEMO concept
  - PbLi breeder flows very slowly and serves no cooling function
    - High tritium partial pressure; permeation barriers required
  - Cooling is provided entirely by separate helium channels
- Dual-coolant lead-lithium (DCLL)
  - US TBM conceptual design (not pursued) and DEMO concept
  - Higher PbLi flow rates
    - Low tritium partial pressures *if extraction system is highly efficient*
  - ~50% of power extracted from PbLi, ~50% from separate helium coolant
  - SiC flow channel inserts for thermal (potential PbLi temp ~700 °C), and electrical (mitigate MHD forces) insulation, and corrosion barrier

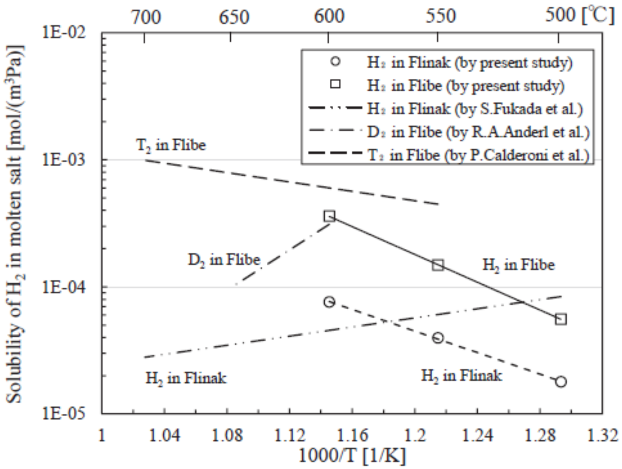
Tritium solubility in PbLi, FLiBe, and metals



PbLi: E. MAS DE LES VALLS et al., *Journal of Nuclear Materials*, **376**, 353 (2008).



Molten Salt: A. NAKAMURA al., *Journal of Plasma Fusion Research SERIES*, **11**, 25 (2015).



Tritium control in fusion

- Both PbLi and FLiBe have low tritium solubilities- this results in a higher tritium partial pressure and tends to drive permeation losses through solid structures
- Extraction concepts therefore attempt to do the following:
  - Provide a medium (purge gas, getter, etc.) where tritium will preferentially accumulate, relative to structural materials
  - Maximize the contact area of the breeder/coolant with this medium
  - Minimize the transport distance through the breeder/coolant to reach this medium
  - Maximize the residence time in the extraction system (i.e. reduce the flow rate)
- These same ideas for PbLi should be applicable to FLiBe or other molten salts (chemistry may complicate things somewhat)
- Additionally, one can apply permeation barriers (e.g. in the form of coatings) to structural materials- probably necessary for fusion, not for fission

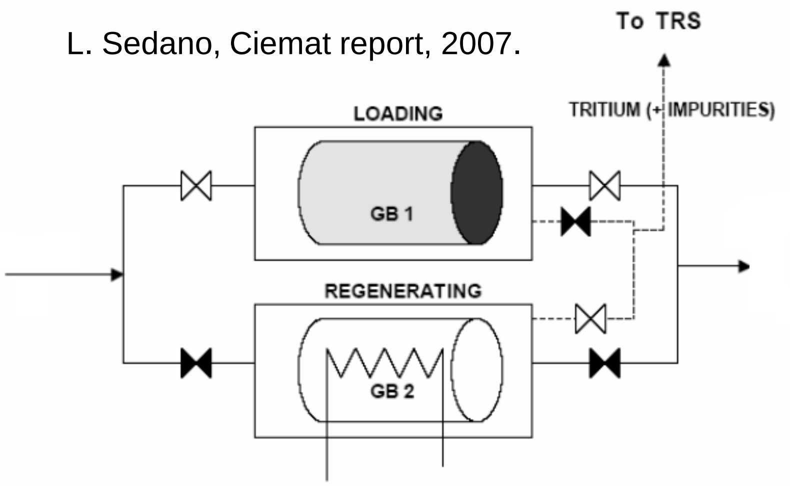
Tritium extraction concepts

- Immersed getters
- Liquid getter/cold trap
- Release to purge gas or vacuum
  - Bubblers, spray/droplets, extraction columns
- Vacuum permeator

Immersed Getters

- Getters such as U, Zr(Co), Pd, Ti, etc. are commonly used to remove tritium from gases (Example: a 60g U bed can hold 2g tritium)
- Immersed getters (V, Nb, Ta) have been proposed in the past to remove tritium from PbLi
- Principle demonstrated at small scale with V in PbLi, though not to saturation[1]

L. Sedano, Ciemat report, 2007.



- Issues:
  - Integrity of material (getter beds for gases are reduced to fines and require ceramic filters)
  - Lifetime of beds under cyclic loading (e.g. daily)
  - Deleterious effects of impurities including oxygen

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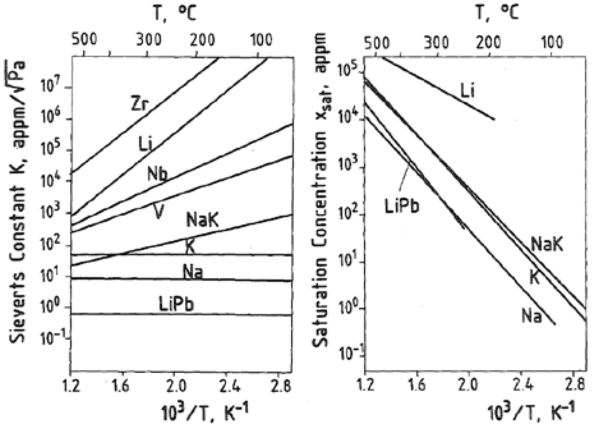
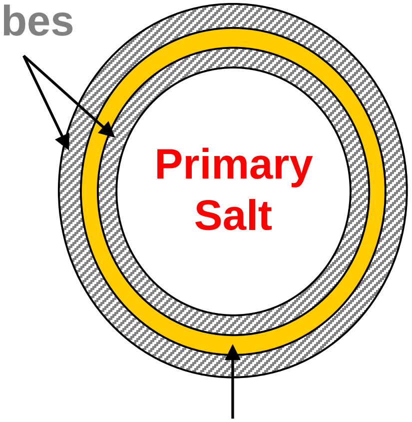
[1] H. Feuerstein, *Fusion Technology (14th SOFT),* 1986, p. 646

Liquid metal getter with cold trap

- Concept investigated at KIT in the 1980s
  - Intermediate NaK loop proposed, which acts as a tritium getter
  - NaK cooled so as to precipitate solid hydrides
  - Tritium removed from solid hydrides by vacuum pumping
- Might also take the form of a thin film between concentric HX tubes
  - Processing rate required for fusion may imply large heat loss
  - Salt-cooled fission reactors may require only infrequent batch processing and have minimal impact on HX performance
  - Li suitable for fission reactors where subsequent extraction is unnecessary
    - High saturated concentration
    - Less chemically reactive than Na/NaK

J. Reimann, *Fusion Technology (14th SOFT)*, 1986, p. 1579





Concentric HX Tubes

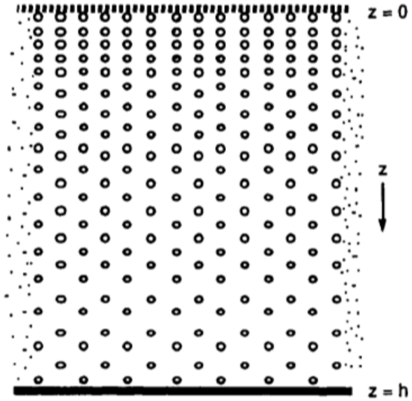
Intermediate/ Secondary

Primary Salt

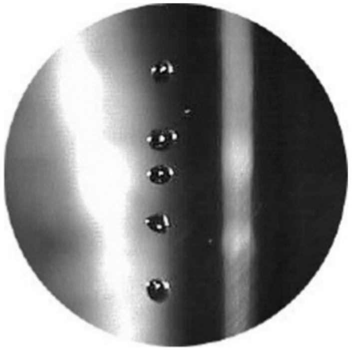
Alkaline metal film (Na, NaK, or Li)

Droplets in vacuum

- Concept: spray coolant as small droplets into a purge gas or vacuum
- Small droplets provide high surface area and small transport distance
- “Vacuum Disengager” proposed for HYLIFE-II IFE design study[1]
- Analytical solution and numerical models suggested 99.9% efficiency; no experiments performed
- Now under investigation for PbLi (as “Vacuum Sieve Tray”)[2]
- Different analytical solution and numerical models suggest 70% efficiency achievable
- Measured extraction was lower than predicted by 10x, but models depend on (uncertain) solubility and diffusivity



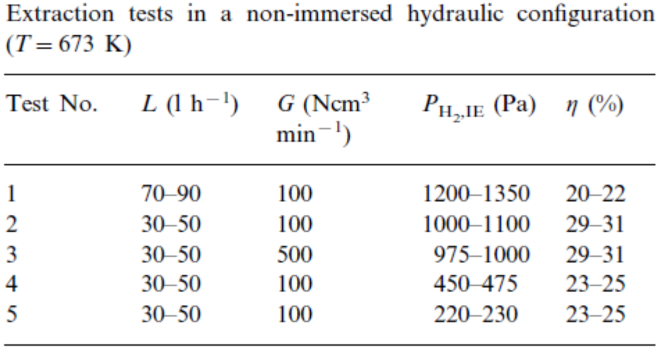
[1] T. Dolan, *Fus. Tech.* **21** (1992) 1949-1954



[2] F. Okino, *FED* **87** (2012) 1014-1018

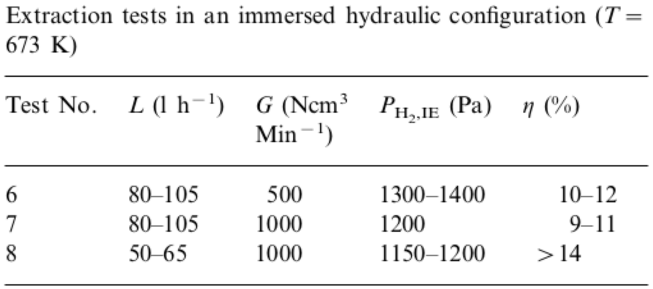
Compact Mass Extractor

- Gas/Liquid Contactor – planned for HCLL (TBM and DEMO)
- Structured packing disperses PbLi flow and creates a large interfacial area between PbLi and gas
- ≤ 30% efficiency for single column as tested in MELODIE loop[1]



Extraction tests in a non-immersed hydraulic configuration ($T = 673$ K)

Test No.	L (l h^{-1})	G (Ncm^3 min^{-1})	$P_{H_2,IE}$ (Pa)	η (%)
1	70–90	100	1200–1350	20–22
2	30–50	100	1000–1100	29–31
3	30–50	500	975–1000	29–31
4	30–50	100	450–475	23–25
5	30–50	100	220–230	23–25

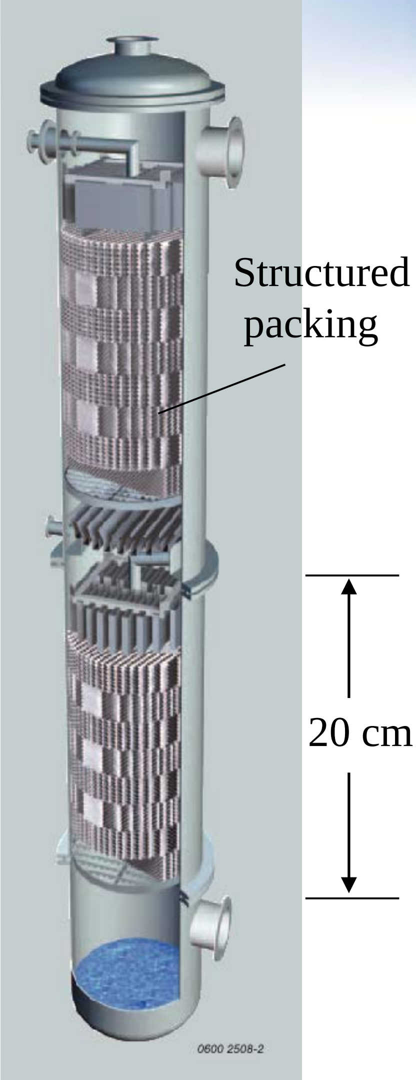


Extraction tests in an immersed hydraulic configuration ($T = 673$ K)

Test No.	L (l h^{-1})	G (Ncm^3 Min^{-1})	$P_{H_2,IE}$ (Pa)	η (%)
6	80–105	500	1300–1400	10–12
7	80–105	1000	1200	9–11
8	50–65	1000	1150–1200	> 14

[1] N. Alpy et al. *FED* **49-50** (2000) 775-780

- HCLL DEMO (14 inventory re-circulations per day) requires at least 80% efficiency[2] even with permeation barriers (with ~100x reduction factor)
- Larger scale tests, optimization planned at TRIEX loop (ENEA) but no results as of yet

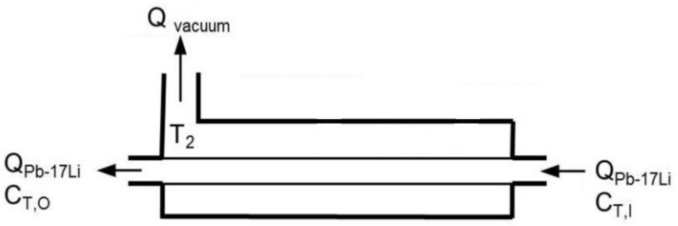


Sulzer Column

[2] O. Gastaldi et al. *FED* **83** (2008) 1340–1347

Vacuum permeator

- For a PbLi-cooled (e.g. DCLL) or salt-cooled fission or fusion reactor, higher flow rates must be processed
  - Simple scaling from most efficient MELODIE tests indicates that for a DCLL blanket (~470 inventory re-circulations/day), 240,000 extraction columns would be required[1] (!)
- DCLL flow rates are much higher (~470 inventory re-circulations/day required)
- Similar performance in a much smaller device is potentially achievable with a vacuum permeator
- Concept: a shell-and-tube mass exchanger with tritium-laden primary, vacuum secondary, and high-permeability, thin-walled tubes
- Required efficiency depends on the reactor design (losses), but:
  - What is achievable?
  - How does it scale?



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[1] B. Merrill, 2005/06/15 ARIES meeting

Permeator extraction efficiency[1]

- Transport processes in a permeator tube:
  - Advection in PbLi in the axial direction
  - Convective mass transport in PbLi in the radial direction
  - Permeation (Diffusion) through solid in the radial direction
- Can be solved analytically: $\eta = 1 - \exp\left(-\frac{\tau\zeta}{1+\zeta}\right)$
- ζ and τ are dimensionless numbers that indicate the relative importance of three transport phenomena

$$\zeta = \frac{\Phi_s}{K_T K_l r_i \ln\left(r_o / r_i\right)}$$

$$\tau = \frac{2K_T L}{v r_i}$$

r_i – inner diameter of tubes

r_o – outer diameter of tubes

L – length of tubes

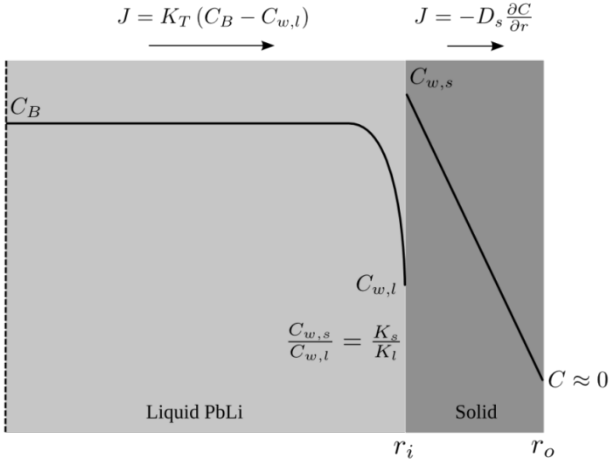
v – PbLi velocity

K_l – PbLi solubility

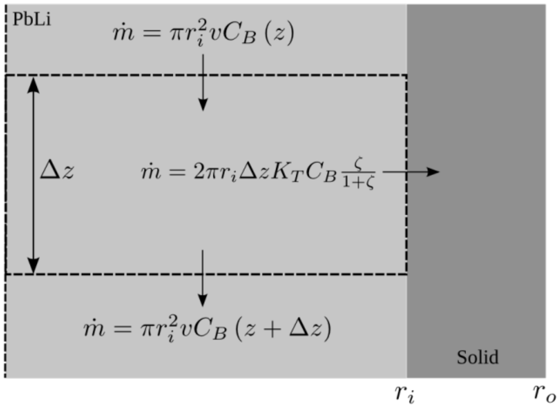
K_T – mass transport coefficient

Φ_s – permeability of solid tube

Radial Transport



Axial Transport



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[1] P. Humrickhouse *Fusion Science and Technology* **68** (2015) 295-302

Significance of ζ and τ

- ζ indicates whether radial transport is limited by mass transport in PbLi, or by permeation through the solid tube wall
- When $\zeta << 1$: Diffusion in the solid is limiting; there is no dependence on the PbLi transport property K_T
- When $\zeta >> 1$: Mass transport in the PbLi is limiting; there is no dependence on the solid transport properties Φ_s, r_o or PbLi solubility K_l
- τ is a ratio of axial to radial transport times:

$$\tau = \left(L/v\right)/\left(r_i/2K_T\right)$$

- When $\tau >> 1$, tritium is swept through the length of the permeator tube before it has a chance to migrate radially
- Need to evaluate K_T…

Mass Transport Correlations

- K_T is defined by the Sherwood number: $\mathrm{Sh} = dK_T / D_l$
- Sherwood number correlations have the form $\mathrm{Sh} = \beta \mathrm{Re}^a \mathrm{Sc}^b$
- For PbLi at 470-700 ˚C, 10 < Sc < 150 $\left(\mathrm{Sc} = \mu / \rho D_l\right)$
- The correlations below are remarkably consistent with each other, and with the heat transfer analogy- this approach is valid
- The choice of correlation is not a significant source of uncertainty in this analysis relative to other parameters

β	a	b	Range	Reference	Notes
0.023	4/5	1/3		Colburn 1933	Heat transfer analogy
0.023	0.83	0.44	2000 < Re < 35000 0.6 < Sc < 2.5	Gilliland and Sherwood 1934	Vaporization of nine different liquids in air
0.0328	0.77	0.33	3000 < Re < 40000 0.5 < Sc < 3	Johnstone and Pigford 1942	Distillation of five different substances in a wetted-wall column
0.023	0.83	1/3	2000 < Re < 70000 1000 < Sc < 2260	Linton and Sherwood 1950	Solution of benzoic acid, cinnamic acid, and beta-naphthol in water
0.0163	0.83	0.44	Sc ~ 0.6	Kafesjian et al. 1961	Vaporization of water in a wetted-wall tower
0.0096	0.913	0.346	10000 < Re < 100000 430 < Sc < 100000	Harriott and Hamilton 1965	Benzoic acid in glycerin-water, and hydroxymethycellulose solutions

Permeator Optimization

- Regardless of the transport regime, permeator efficiency is always increased by:
  - Increasing the temperature, T
  - Increasing the tube length, L
  - Decreasing the permeator velocity, v (e.g. by increasing the number of permeator tubes)
  - Decreasing the tube diameter, d
- Using the analytical solution, we can optimize the design (minimize the total volume)
- The following slide does so for different materials and temperatures, subject to the following constraints (from ARIES-CS):

$$\eta \geq 0.7 \qquad \mathrm{d} \geq 0.01\mathrm{m} \qquad \dot{m} = \rho N \pi r_i^2 v = 26000\,\mathrm{kg/s} \qquad \Delta p = f\frac{L}{d}\frac{\rho v^2}{2} \leq 1\ \mathrm{MPa}$$

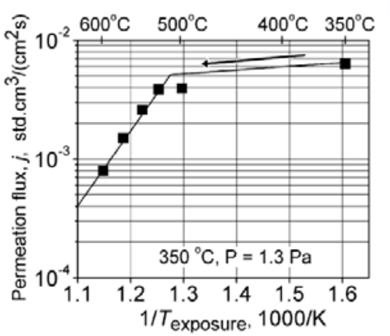
Tube material comparison

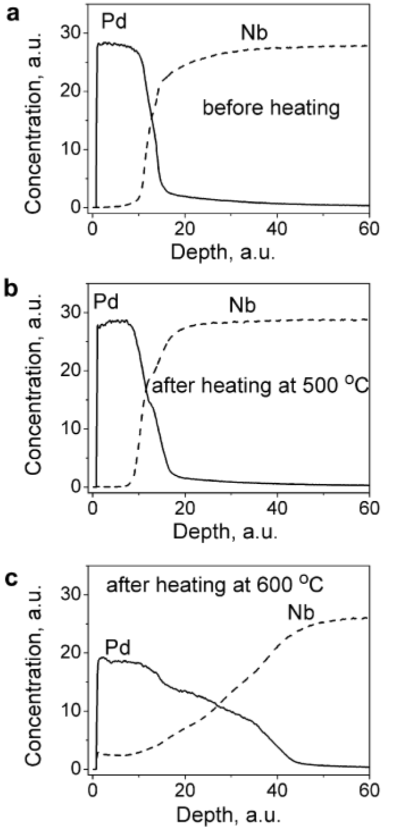
	B&W PWR steam generator	RAFM 470 ˚C	RAFM 470 ˚C	RAFM 470 ˚C	Vanadium 400 ˚C	Vanadium 500 ˚C	Vanadium 600 ˚C	Vanadium 700 ˚C
η (low solubility)		0.7	0.7	0.7	0.7	0.7	0.7	0.7
Tubes (#)	15,000	343,521	68,704	19,432	13,347	10,136	8,274	7,095
Tube length (m)	20.7	8.54	16.61	37.3	18.25	11.15	7.65	5.7
v (m/s)		0.1	0.5	1.77	2.55	3.4	4.22	4.98
Total volume (m^3)	61.8	278.7	108.42	69.0	23.15	10.74	6.01	3.84
ζ		4.85	1.27	0.45	1681	425	148	65
η (high solubility)		0.10	0.04	0.03	0.47	0.36	0.29	0.23

- There is a significant size/cost advantage to high-permeability materials

Group 5 Metals - oxidation

- Group 5 metals have very high tritium permeabilities and from that standpoint are promising tube materials
- They are compatible with PbLi, but the oxygen partial pressure on the vacuum side must be kept below 10^{-10} Pa to prevent oxidation[1]
- Application of a Pd coating can prevent this, and commercial hydrogen purifiers based on this concept are available
- They have a very narrow range of operation around 400 °C
  - At lower temperatures, hydrides form and embrittle the structure
  - At higher temperatures, Pd and substrate diffuse together, reducing (irreversibly) the tritium permeability





V. Alimov, *International Journal of Hydrogen Energy* **36** (2011) 7737-7746

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[1] R. Kurtz, 2005 ITER TBM meeting

Potential solutions

- Inter-diffusion of Pd and substrate can be prevented by an intermediate layer that separates them
  - Such composites are being actively investigated in the hydrogen energy research community
  - These are typically ceramics with some porosity so as not to prevent tritium permeation
  - Al_2O_3, Nb_2C, HfN, YSZ, etc. mentioned in literature
- Alloys?
  - V-Ni, Pd-Cu, V-Ti, V-Cu, others mentioned in literature
- Other coatings- Pd is necessary for separation from other gases, but we only need to prevent oxidation

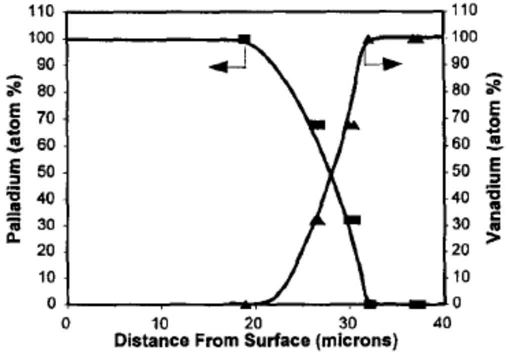


Fig. 6. Cross-sectional analysis of a palladium-coated vanadium membrane after 22 h under argon showing some diffusion of vanadium into the palladium layer. Test conditions: 700°C, membrane stored under 100-psig argon.

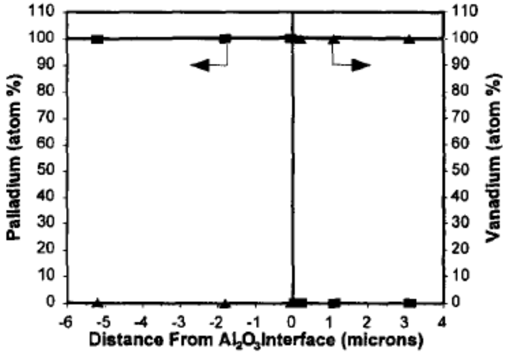
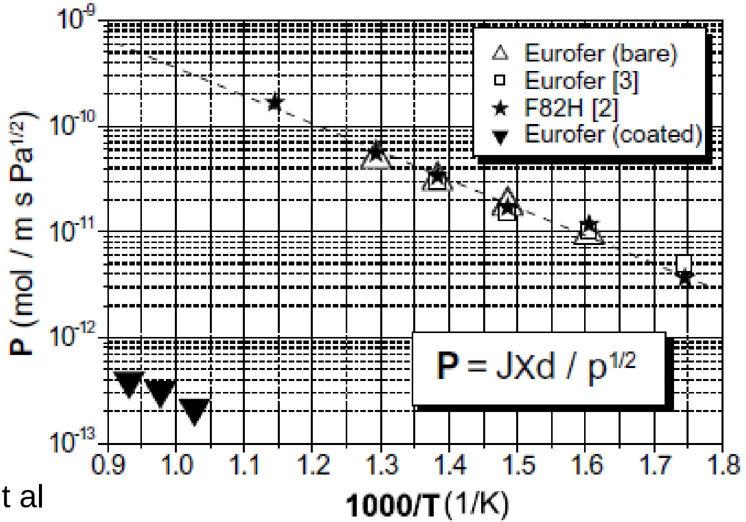


Fig. 7. Cross-sectional analysis of the palladium and vanadium layers of a three-component composite-metal membrane incorporating a porous aluminum oxide intermediate layer operated for 76 h. Test conditions: 700°C, 100-psig hydrogen feed pressure, permeate hydrogen at ambient pressure.

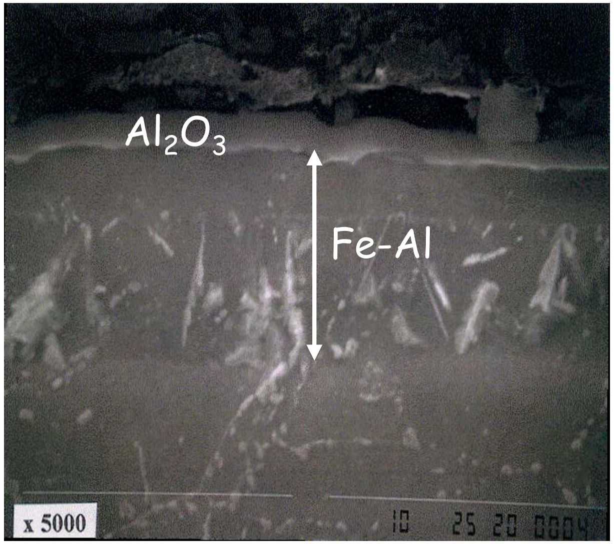
Edlund, *Journal of Membrane Science* **107** (1995) 147-153

Permeation Barriers

- Even under relatively optimistic assumptions for the extraction system, fusion systems studies usually find a permeation reduction factor (PRF) of 10-1000 on structures is necessary to meet release limits
- Many barriers have been investigated experimentally, such as low-permeability metals (e.g. aluminum) or ceramics such as Al_2O_3, Cr_2O_3, Er_2O_3
- These have achieved permeation reduction factors as high as 10,000 in the laboratory



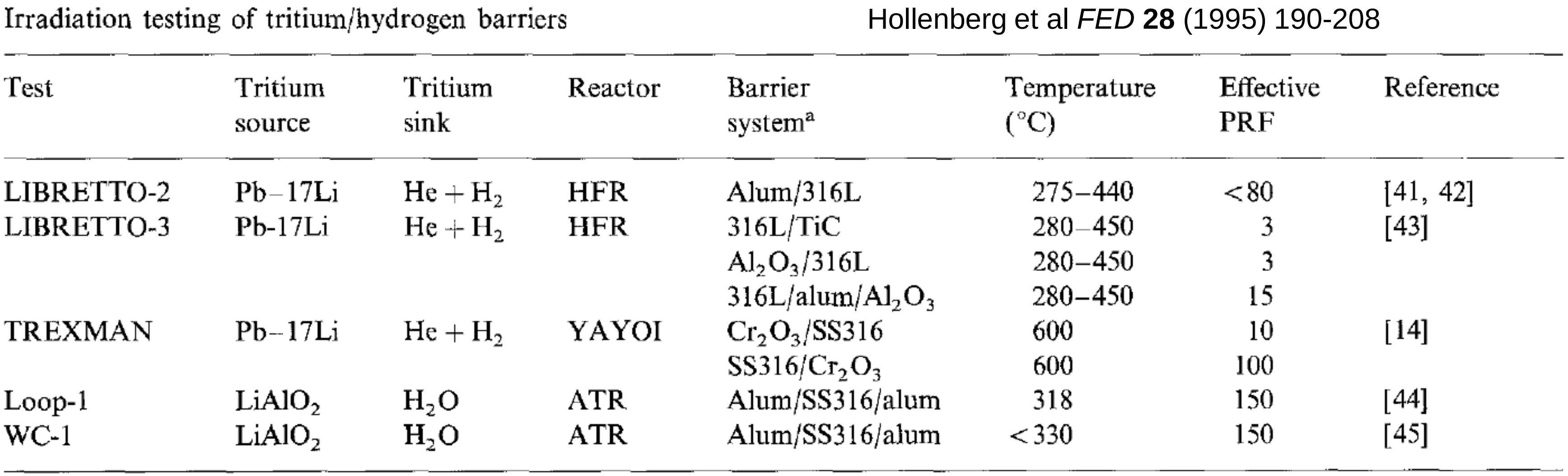
Levchuck et al
JNM **328** (2004) 103



Al_2O_3 deposition by CVD - Jürgen Konys

Permeation Barriers in a Radiation Environment

- While permeation reduction factors up to 10,000 have been measured in the laboratory, reactor tests on the same materials have not achieved this



Irradiation testing of tritium/hydrogen barriers

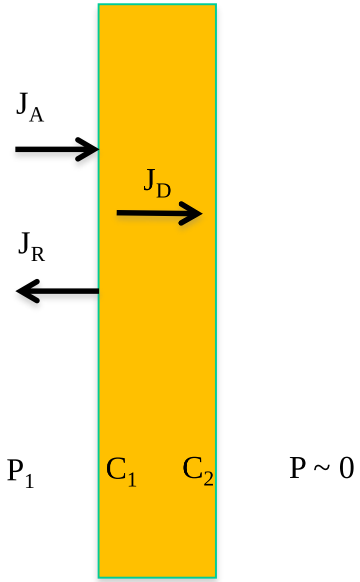
Hollenberg et al *FED* **28** (1995) 190-208

Test	Tritium source	Tritium sink	Reactor	Barrier system[a]	Temperature (°C)	Effective PRF	Reference
LIBRETTO-2	Pb–17Li	He + H_2	HFR	Alum/316L	275–440	<80	[41, 42]
LIBRETTO-3	Pb-17Li	He + H_2	HFR	316L/TiC	280–450	3	[43]
				Al_2O_3/316L	280–450	3	
				316L/alum/Al_2O_3	280–450	15	
TREXMAN	Pb–17Li	He + H_2	YAYOI	Cr_2O_3/SS316	600	10	[14]
				SS316/Cr_2O_3	600	100	
Loop-1	$LiAlO_2$	H_2O	ATR	Alum/SS316/alum	318	150	[44]
WC-1	$LiAlO_2$	H_2O	ATR	Alum/SS316/alum	<330	150	[45]

- This reduction may result from damage (e.g. cracking) of the barrier, an increase in defects, or some other effect under irradiation

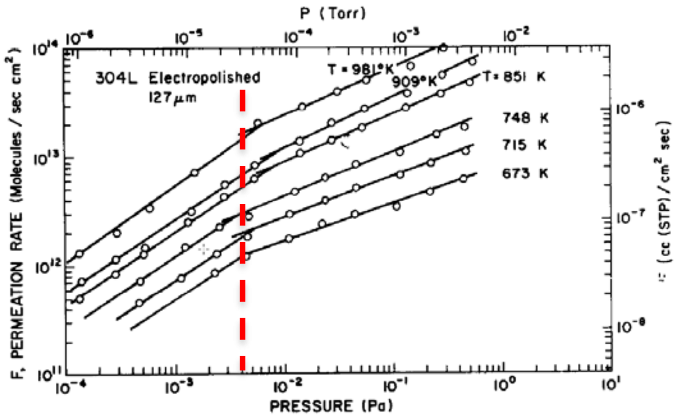
Permeation scaling with pressure

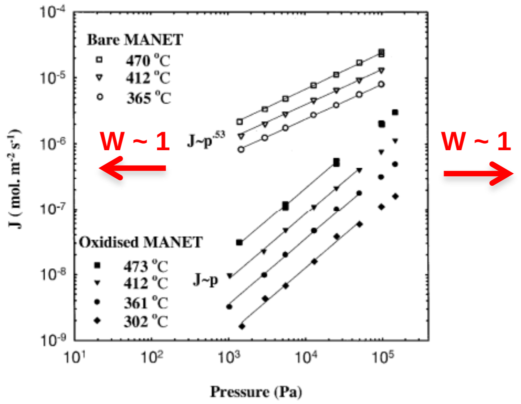
- Permeation usually scales with the square root of partial pressure, implying that it is limited by diffusion through the solid
- Low pressures or surface changes can result in surface-limiting and a change to linear dependence on partial pressure
- Systems designed to achieve low tritium partial pressures need to investigate this experimentally
    - Dimensionless number governs transition:



$$W = \frac{K_A x\sqrt{P}}{K_S D}$$

Ali-Kahn et al *JNM* **76/77** (1978) 337-343.





Perkins and Noda *JNM* **71** (1978) 349-364.

Serra and Perujo *JNM* **240** (1997) 215-220.

Conclusions

- A number of tritium capture/extraction concepts have been proposed for fusion over the last several decades
- Some of these have been investigated experimentally, but none on the scale (size, tritium inventory) or under the conditions (radiation, high temperatures, long times) necessary for fusion
- Because of the low solubility of tritium in both PbLi and molten salts (including FLiBe), extraction techniques developed for PbLi are likely applicable to salt-cooled fusion and fission reactors as well
- Tritium generation will be orders of magnitude lower in fission reactors, for which tritium is a much more manageable problem
  - Tritium must be captured, but not necessarily separated/purified
  - Extraction systems may only need to process a fraction of the coolant on each pass
  - Permeation barriers may be unnecessary; for fusion it will be difficult to keep losses sufficiently low without them