Tritium Control Using Carbon Outside of Core

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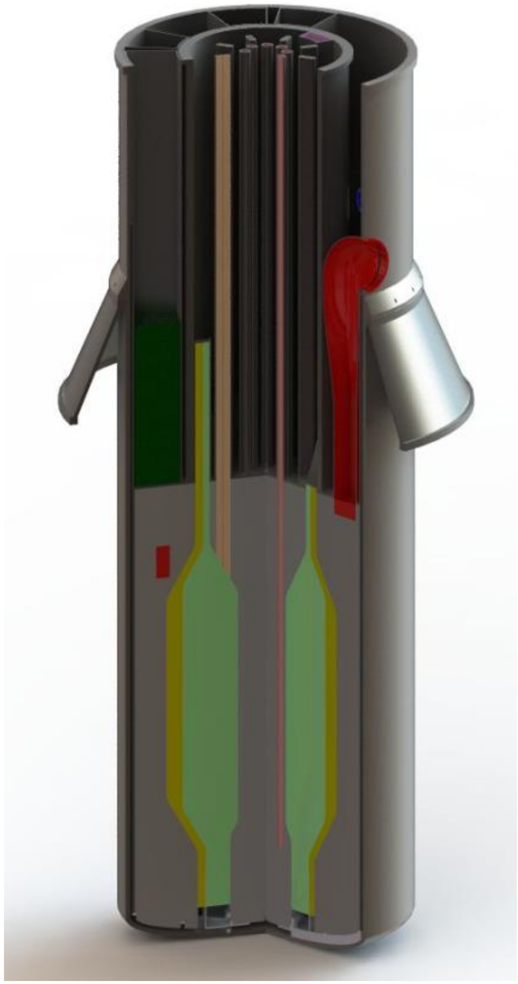

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Tritium Overview

Generation

- Thermal neutron transmutation of Li-6

$$ {}^{6}\mathrm{LiF} + n \rightarrow {}^{4}_{2}\mathrm{He} + {}^{3}_{1}\mathrm{HF} $$

- Initially 0.005 wt. % Li-6 in Flibe consumed but is continually produced by Be-9 transmutation:

$$ {}^{9}_{4}\mathrm{BeF}_2 + n \rightarrow {}^{4}_{2}\mathrm{He} + {}^{6}_{2}\mathrm{He} + 2\mathrm{F} $$

$$ {}^{6}_{2}\mathrm{He} \rightarrow {}^{6}_{3}\mathrm{Li} + e^{+} + \overline{\nu}_e \quad \left(t_{1/2} = 0.8\,\mathrm{sec} \right) $$

Concerns

- **Corrosion:** TF oxidizes chromium in stainless steel

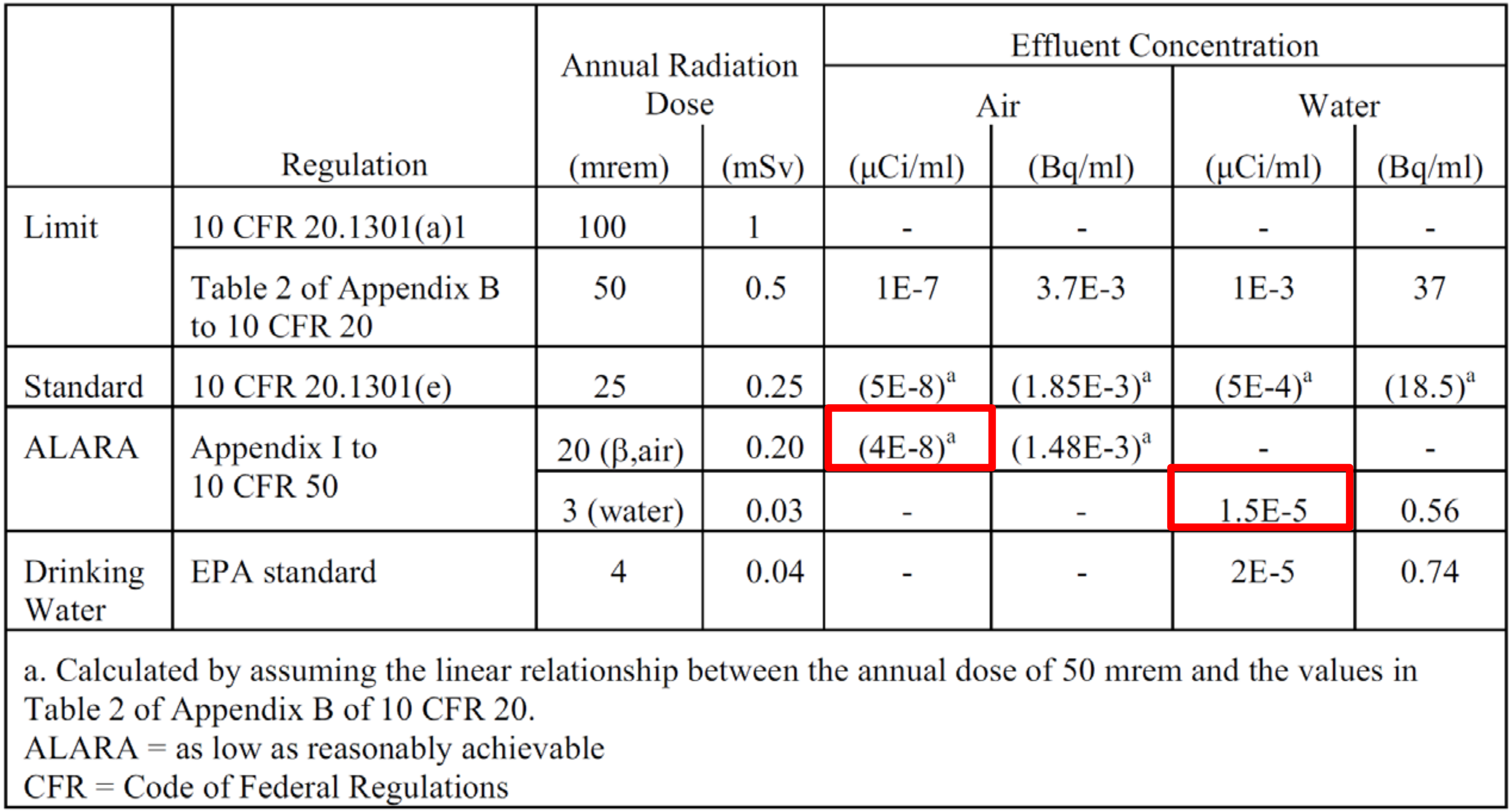
$$ 2\mathrm{TF}_{(d)} + \mathrm{Cr}_{(s)} \rightarrow \mathrm{CrF}_{2(d)} + \mathrm{T}_{2(g)} $$

- **Release:** T_2 diffuses through piping and escapes to environment
- **Uncertainty:** Lack of industrial experience with FHR

Regulatory Tritium Limits

Limit: Concentration limits in Effluent

Target: ALARA. Similar magnitude to existing commercial reactors



		Annual Radiation Dose		Effluent Concentration			
				Air		Water	
	Regulation	(mrem)	(mSv)	(µCi/ml)	(Bq/ml)	(µCi/ml)	(Bq/ml)
Limit	10 CFR 20.1301(a)1	100	1	-	-	-	-
	Table 2 of Appendix B to 10 CFR 20	50	0.5	1E-7	3.7E-3	1E-3	37
Standard	10 CFR 20.1301(e)	25	0.25	(5E-8)[a]	(1.85E-3)[a]	(5E-4)[a]	(18.5)[a]
ALARA	Appendix I to 10 CFR 50	20 (β,air)	0.20	(4E-8)[a]	(1.48E-3)[a]	-	-
		3 (water)	0.03	-	-	1.5E-5	0.56
Drinking Water	EPA standard	4	0.04	-	-	2E-5	0.74

a. Calculated by assuming the linear relationship between the annual dose of 50 mrem and the values in Table 2 of Appendix B of 10 CFR 20.

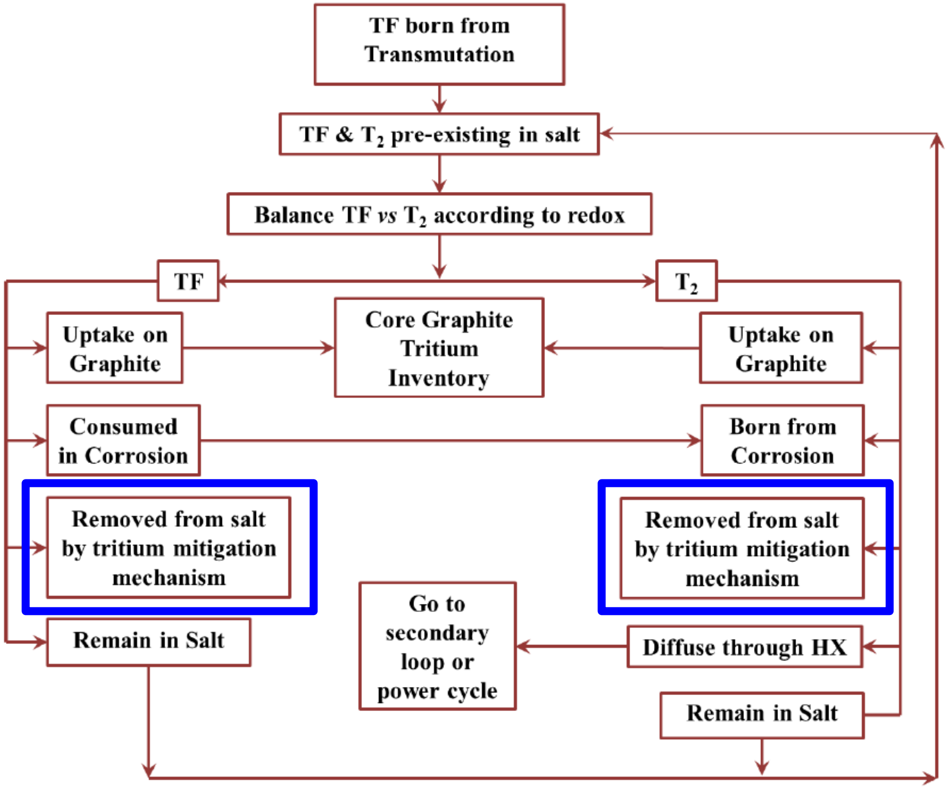
ALARA = as low as reasonably achievable

CFR = Code of Federal Regulations

"Sherman, S.R. Adams, T.M., "Tritium Barrier Materials and Separation Systems for the NGNP," WRSC-STI-2008000358, Rev.1, Savannah River National Laboratory, (2008)."

Tritium Modeling in FHR

Figure 1:TRIDENT Model Overview



TF born from Transmutation

TF & T_2 pre-existing in salt

Balance TF *vs* T_2 according to redox

TF

T_2

Uptake on Graphite

Core Graphite Tritium Inventory

Uptake on Graphite

Consumed in Corrosion

Born from Corrosion

Removed from salt by tritium mitigation mechanism

Removed from salt by tritium mitigation mechanism

Remain in Salt

Go to secondary loop or power cycle

Diffuse through HX

Remain in Salt

*"J. Stempien, "A Model of Tritium Transport and Corrosion in Salt-Cooled Reactors," Cambridge, 2015."

TRIDENT

Tritium Diffusion EvolutioN and Transport

Time dependent tritium in FHR model developed at MIT*:

- Tritium generation in core
- TF and T_2 Speciation (Redox)
- In-core graphite Up-take
- Corrosion consumption & generation
- Diffusion in coolant, vessels, heat exchangers, reflectors
- **Mitigation mechanisms**
- Tritium release to environment

Tritium Production Rates

Estimated Base Case FHR Without Mitigation

	Tritium Production Rates [Ci/GWd]
BWR*	12.3
PWR*	13.9
HTGR*	18.5
FBR*	24.9
HWR*	1176
FHR	**Beginning of Life: 11,000** **Equilibrium: 2,900**

"J. Stempien, "Tritium Transport, Corrosion, and Fuel Performance Modeling in the Fluoride Salt-Cooled High-Temperature Reactor," MIT, Cambridge, 2015."

*Other reactor values calculated from data in:

"Management of waste containing tritium and carbon-14", International Atomic Energy Agency, Technical Reports Series No. 421, Vienna, 2004.

Mechanisms and Release Rates

Tritium Capture Evaluation

- Without mitigation, release to environment peak at **2410 Ci/EFPD**
- Three mitigation mechanisms were evaluated in TRIDENT

1. Stripping Column

- 10 stage counter current column with 20,000 L/hr STP stripping gas
- Release rate with column: **436 Ci/EFPD**

2. Permeation Window

- Shell with permeation tubes (Nickel) with 2x heat exchanger area
- Release rate with window: **800 Ci/EFPD**

3 . Carbon Absorber Bed

- 1.2(R)x3.85(H)m bed nuclear grade graphite ISO-88 with 1 regen/30 days
- Release rate with bed: **7.5 Ci/EFPD** ← **Similar to a PWR**

Simplified Tritium Removal Analysis

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Numbers from "J. Stempien, "Tritium Transport, Corrosion, and Fuel Performance Modeling in the Fluoride Salt-Cooled High-Temperature Reactor," MIT, Cambridge, 2015."

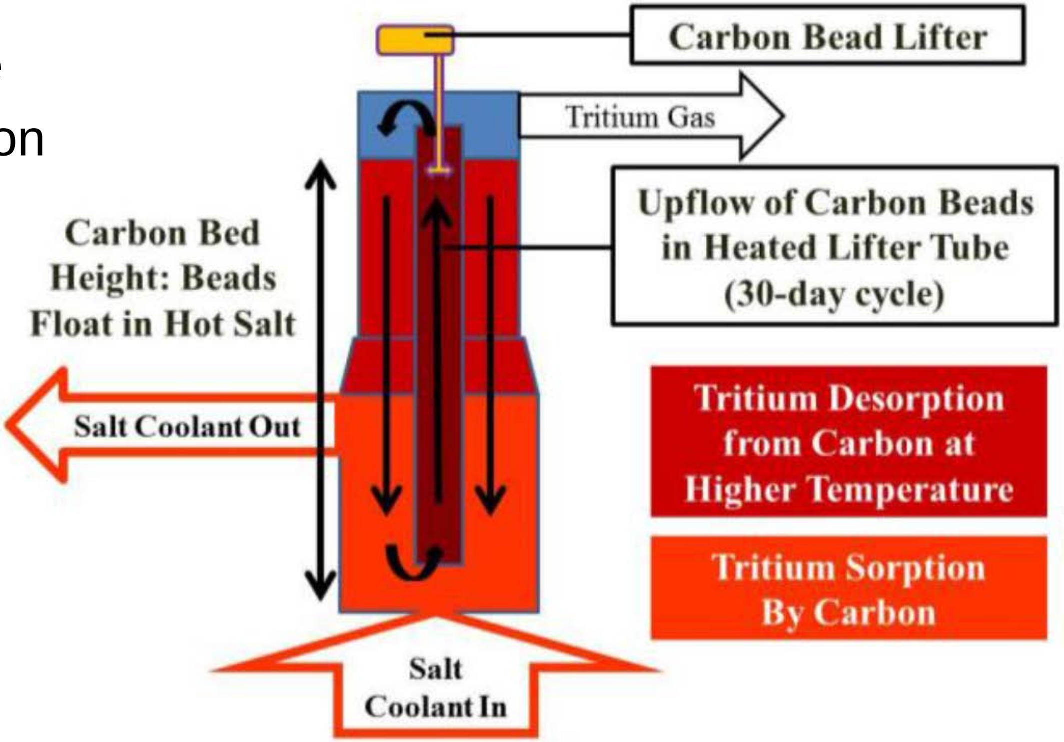
Carbon Absorber Bed

Concept

- Counter-current pebble bed absorber for coolant from core
- Continuous on-line regeneration
- Example: High temperature tritium de-gassing

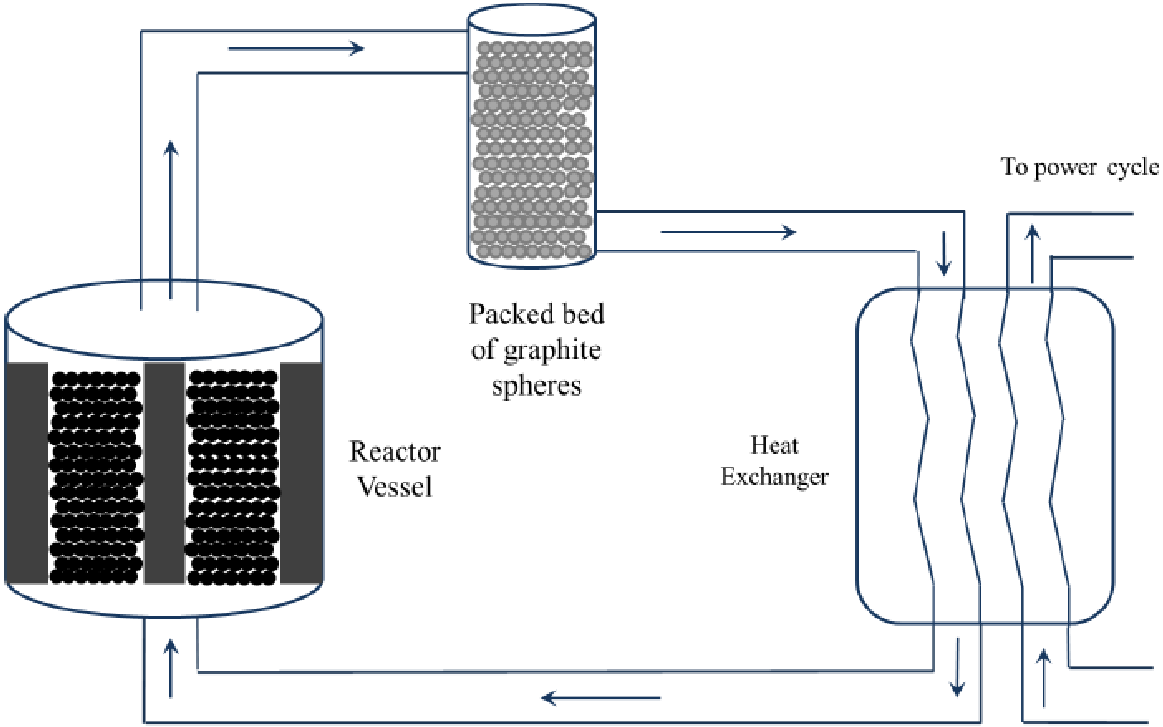
Specifications

- Bed size and flow rate (% of total primary molten salt flow)
- Operating temperatures
- Absorbent partial pressures
- Carbon type and area



“J. Stempien, "A Model of Tritium Transport and Corrosion in Salt-Cooled Reactors," Cambridge, 2015.”

Graphite Bed Location



Schematic of a PB-FHR Continuously regenerated carbon bed

Location

- Primary system before heat exchanger
- Full or partial flow

Current Modelling

- 1-D tritium diffusion through molten salt
- Graphite capacity limited
- **Graphite ISO-88 (Nuclear grade)**

“J. Stempien, "Tritium Transport, Corrosion, and Fuel Performance Modeling in the Fluoride Salt-Cooled High-Temperature Reactor," MIT, Cambridge, 2015.”

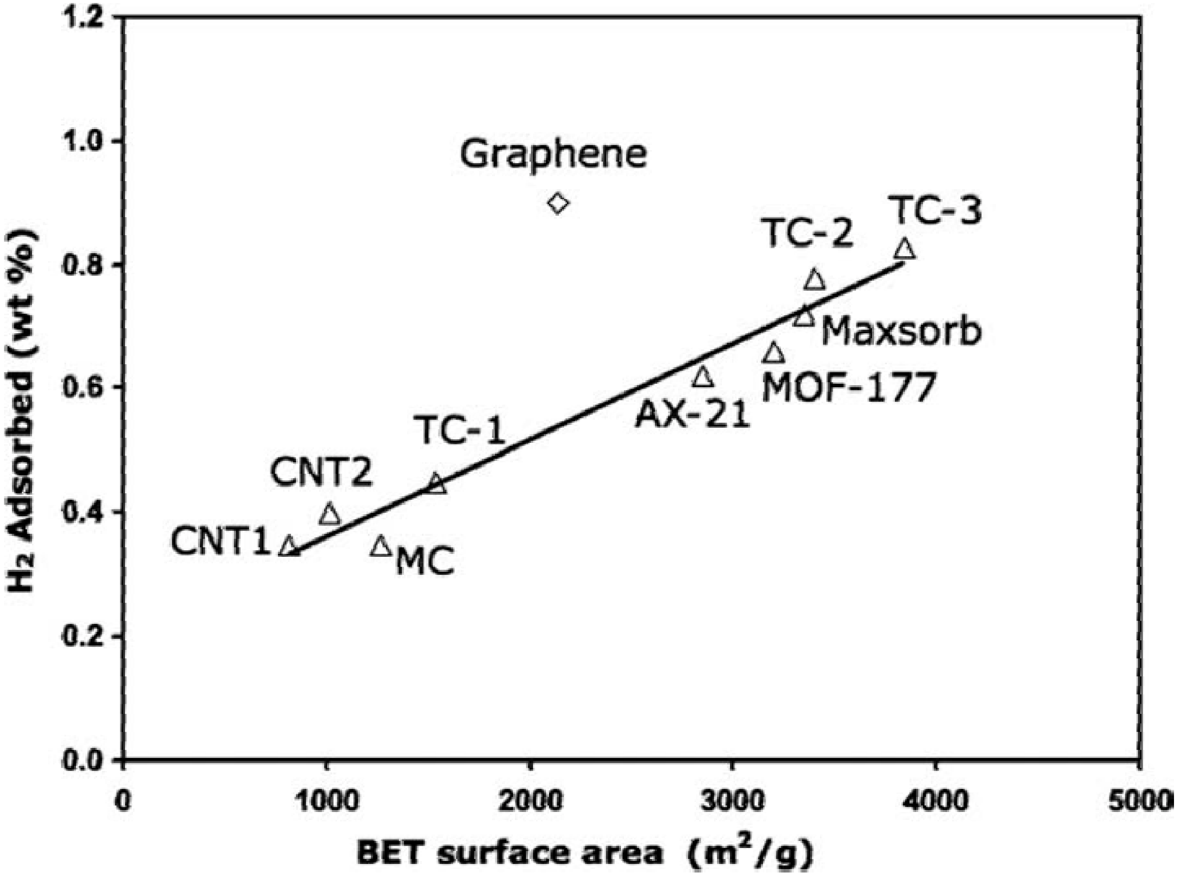
Choice of Absorbent

Considerations

- Non-nuclear grade (outside of core)
- Performance under operating conditions
- Long-term behavior in FHR

Carbon Properties

- Absorption rate
- Desorption rate
- Hydrogen Capacity:
  - BET Surface Area
  - **~1 vs. 3000 m^2/g** (nuclear graphite vs. activated carbon)



L. Wang, N. R. Stuckert and R. T. Yang, "Unique Hydrogen Adsorption Properties of Graphene,"

H_2 Uptake Completion Time

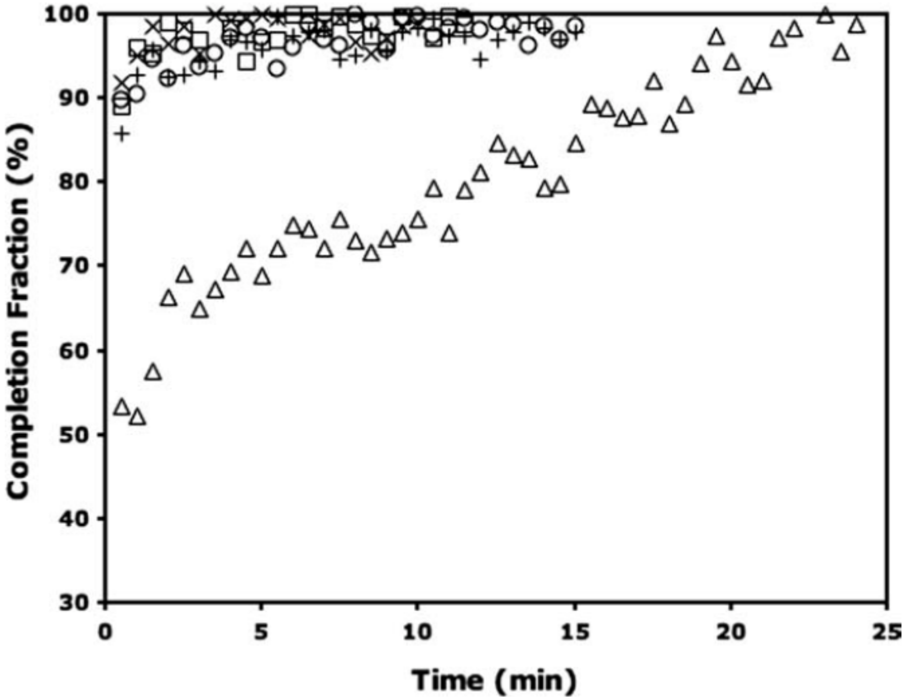


Figure 6. Fractional completion for hydrogen uptake at 298 K on AX-21 (×), Maxsorb (○), CNT (□), templated carbon (+), and graphene (Δ) at ~6 MPa end pressure.

L. Wang, N. R. Stuckert and R. T. Yang, "Unique Hydrogen Adsorption Properties of Graphene,"

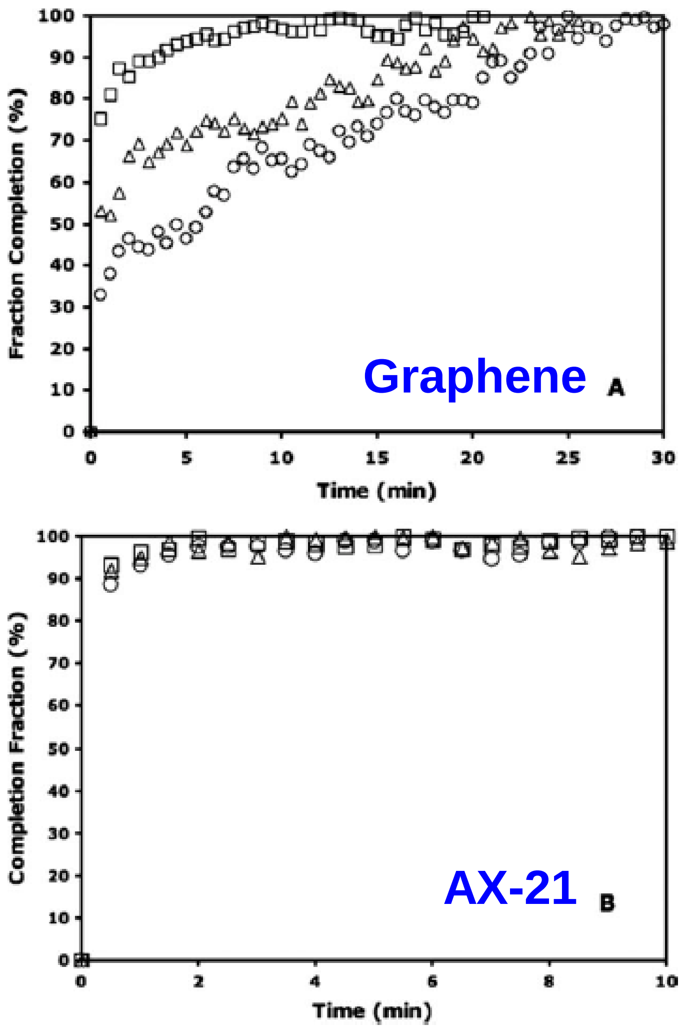
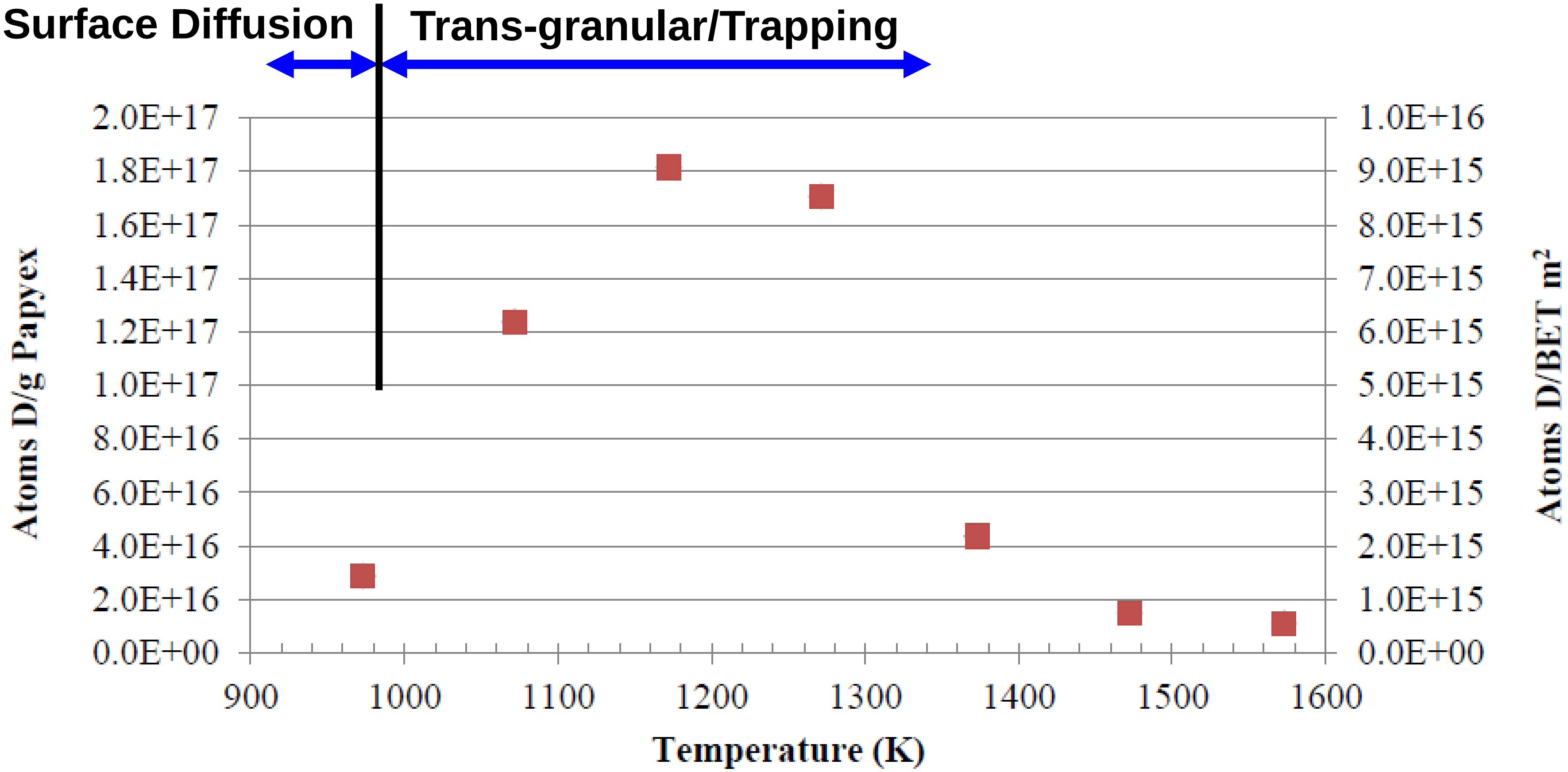


Figure 7. Adsorption fraction at 298 K on graphene (A) and AX-21 carbon (B) during each pressure ramp step at final pressures of: ~2 MPa (□), 6.2 MPa (Δ), and 7.9 MPa (○).

H_2 Capacity vs. Temperature



Surface Diffusion | **Trans-granular/Trapping**

Specific capacity of Papyex graphite under deuterium gas only at 0.66 Pa.

Engineering implications: Column size, percent flow, regeneration

Data converted “J. Stempien, "Tritium Transport, Corrosion, and Fuel Performance Modeling in the Fluoride Salt-Cooled High-Temperature Reactor," MIT, Cambridge, 2015.”
Original Data: CAUSEY, R.A., WILSON, K.L., “Retention of deuterium and tritium in Papyex graphite,” *Journal of Nuclear Materials*. **138**, 57–64 (1986).

FHR Conditions

Temperatures*	
Coolant Freezing	459°C (FliBe)
Operating Core Outlet	700°C
ATWS	<800°C
Coolant Boiling	**1400°C (FliBe)**
Pressures (primary loop)	*TRIDENT Simulation
p_{T2} Unmitigated	3.3-20 Pa
p_{T2} with Graphite Capture	**0.03-0.08 Pa** (Peak release 7.5 Ci/GW/d)
p_{TF} Unmitigated	0.03-0.075 Pa
p_{TF} with Graphite Capture	**0.0027-0.0045 Pa** (Peak release 7.5 Ci/GW/d)

Challenge: Low pressure and high temperature data

* “C. Andreadas, et. Al. "Technical Description of the "Mark 1" Pebble-Bed Fluoride-Salt-Cooled High-Temperature Reactor (PB-FHR) Power Plant," University of California, Berkeley, Berkeley, 2014.”

Next Steps

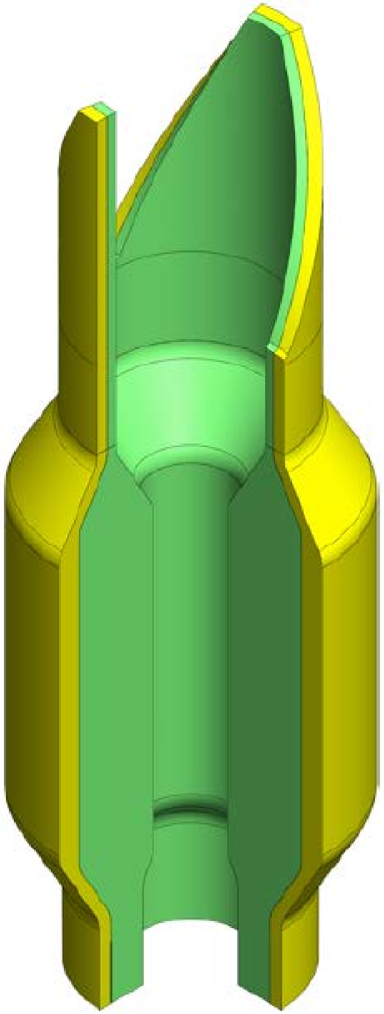
1. **Design and construct experiment for testing performance of different carbons in FHR conditions**
   - Vacuum chamber
   - Temperature and pressure controls, etc.

2. **Data collection to understand hydrogen uptake mechanics**
   - Absorption-Desorption kinetics (trapping, diffusion, etc.)
   - Behavior in high temperature exposure, cycling

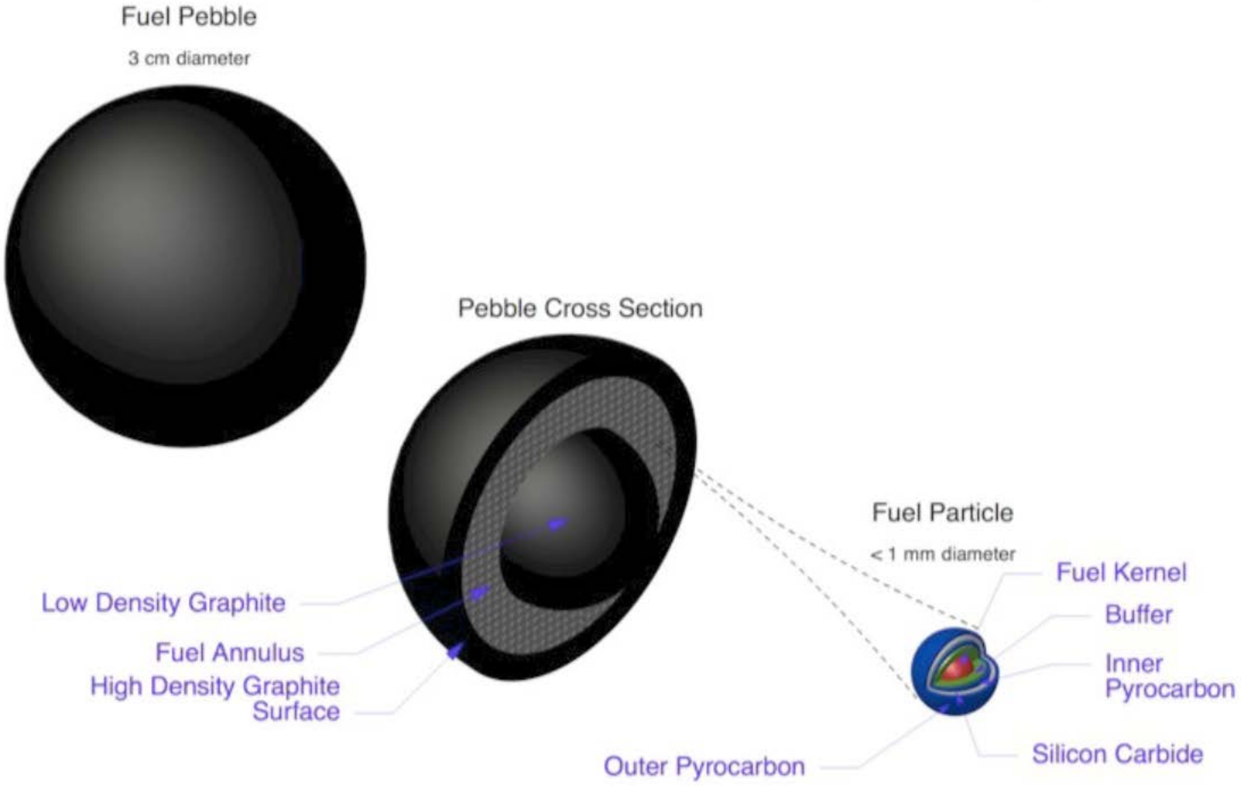
3. **Modeling and technology qualification**
   - Use new data to reduce model uncertainty
   - Improve predictive capability

Questions

In-Core Graphite



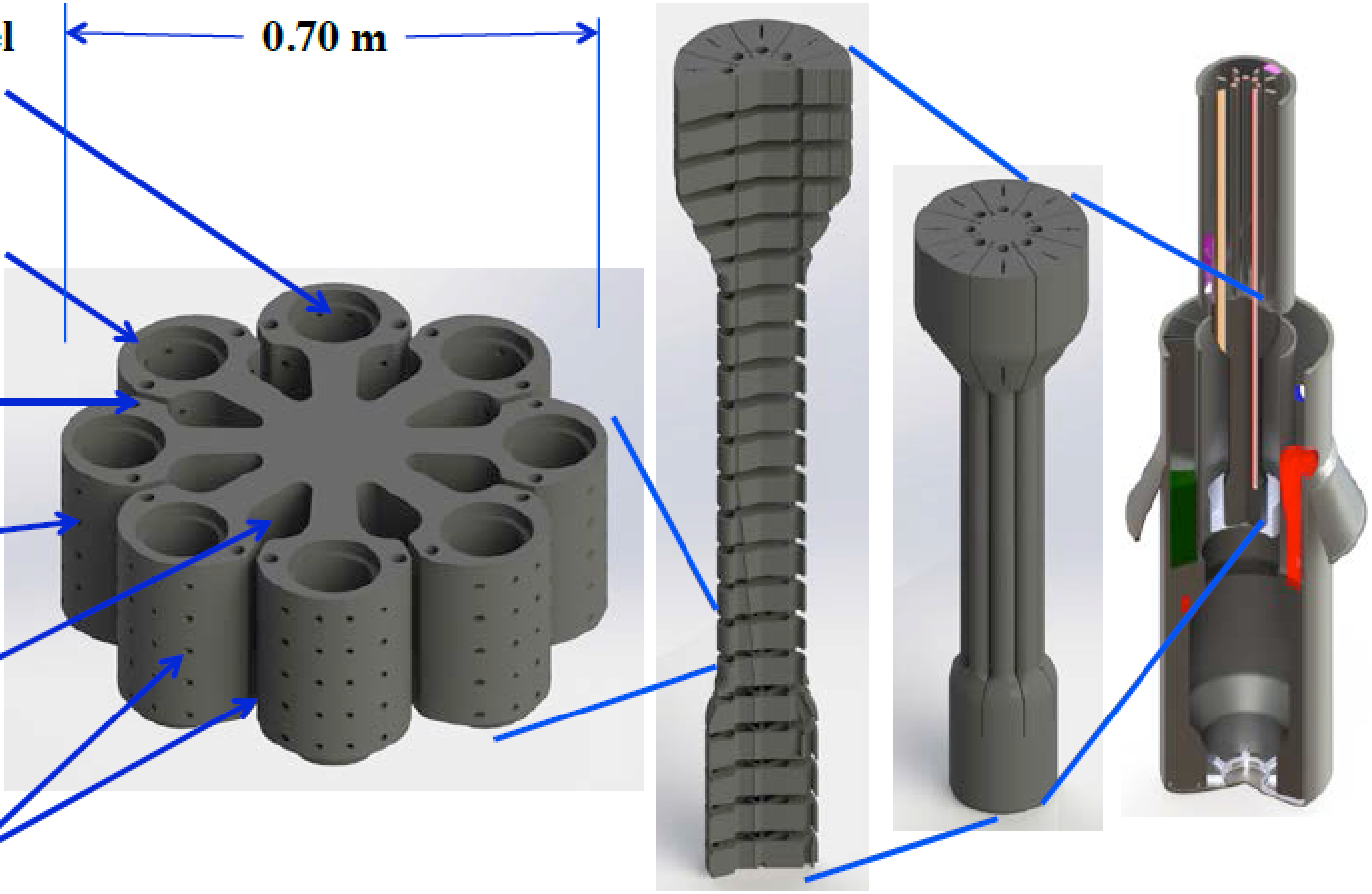
(Left) Mk1 pebble core geometry showing fuel pebble (green) and graphite reflector pebble (yellow) regions



(Above) A PB-FHR pebble fuel element

ANDREADES, C., CISNEROS, A.T., CHOI, J.K., CHONG, Y.K., FRATONI, M., HONG, S., ET AL., “Technical Description of the ‘Mark 1’ Pebble-Bed Fluoride-Salt-Cooled High-Temperature Reactor (PB-FHR) Power Plant,” UCBTH-14-002, University of California-Berkeley, (2014).

In-Core Graphite



Control rod channel keyed to maintain block alignment

8 lobes reduce neutron irradiation induced stress

16 instrument guide tubes

Control channel coolant injection holes

Center coolant flow channel

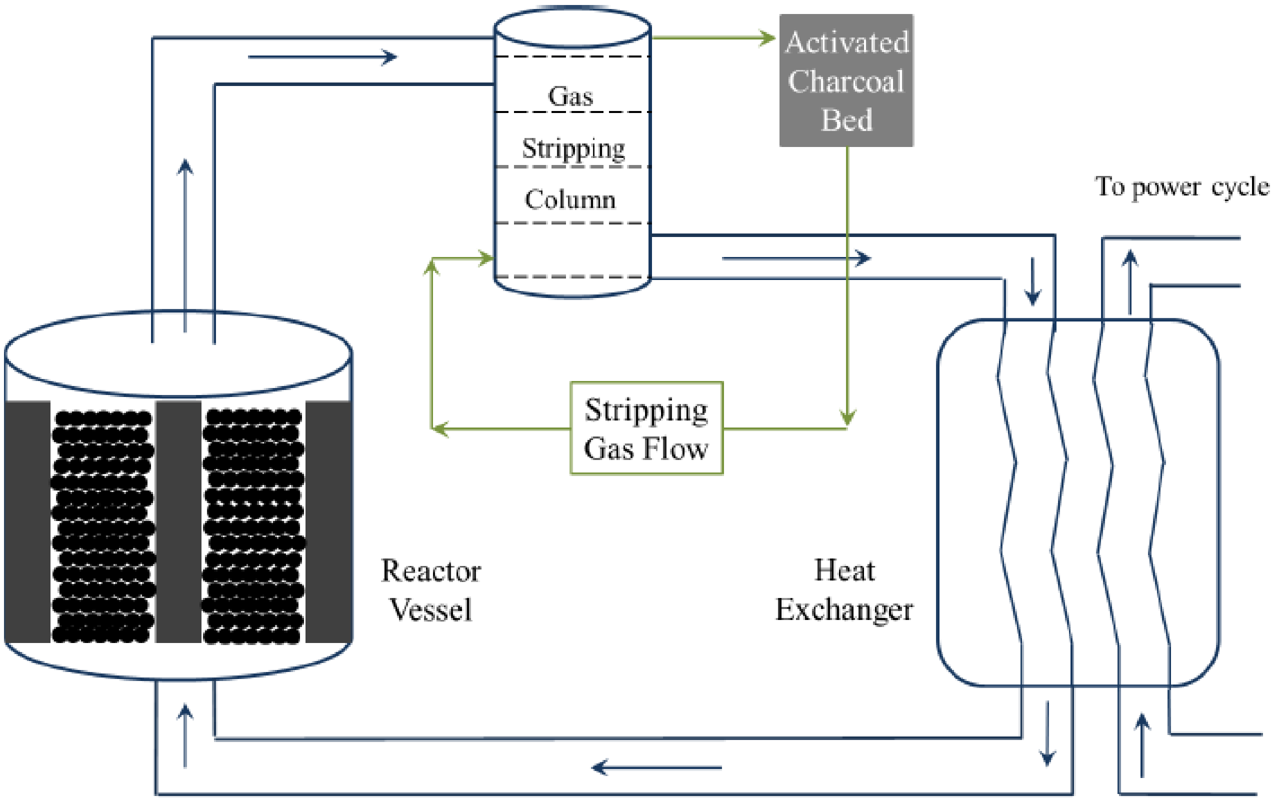
Center channel coolant injection holes and slot

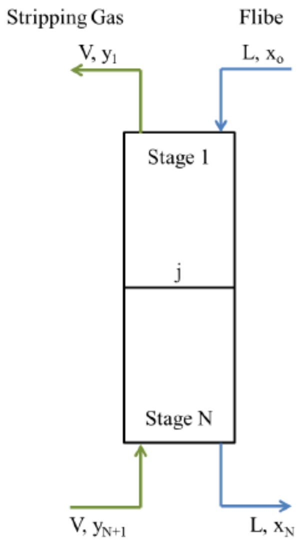
Exploded View

Replaceable Mk1 center graphite reflector

ANDREADES, C., CISNEROS, A.T., CHOI, J.K., CHONG, Y.K., FRATONI, M., HONG, S., ET AL., “Technical Description of the ‘Mark 1’ Pebble-Bed Fluoride-Salt-Cooled High-Temperature Reactor (PB-FHR) Power Plant,” UCBTH-14-002, University of California-Berkeley, (2014).

Gas Stripping Column



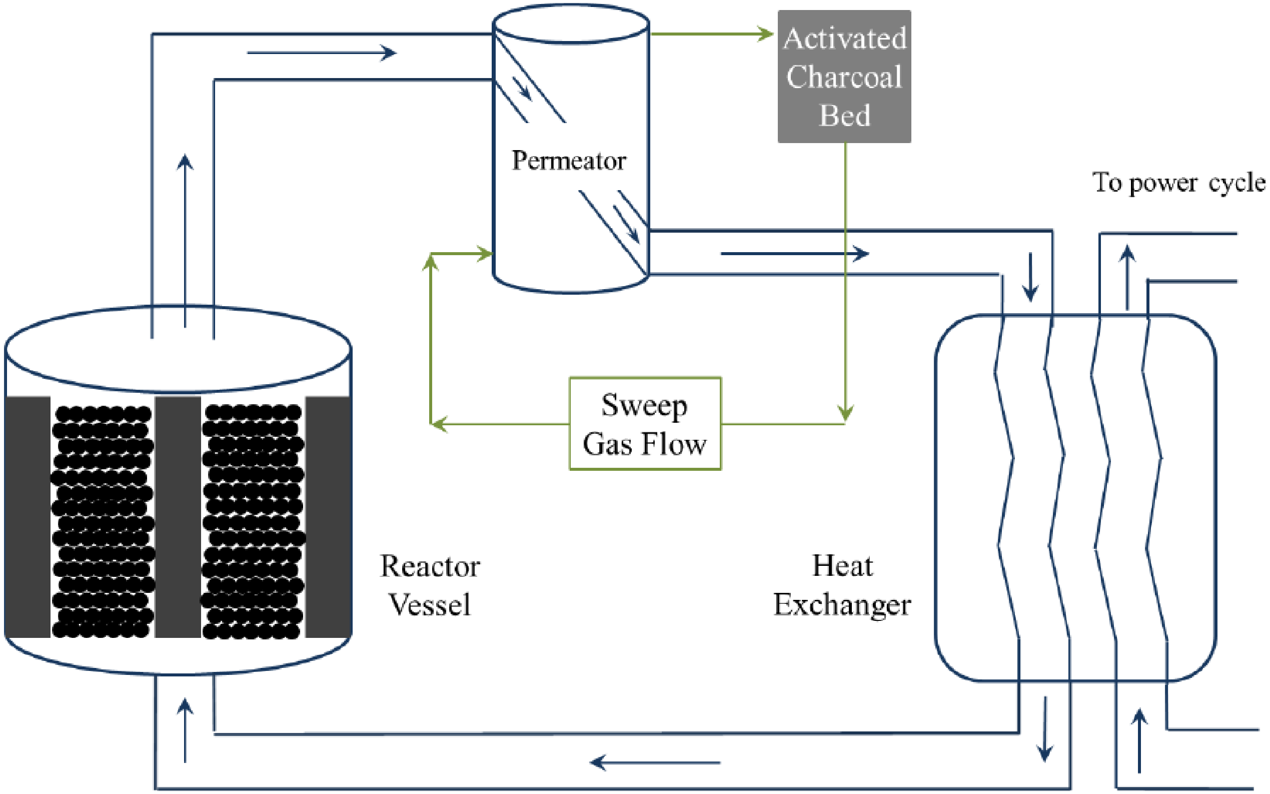


Equilibrium Stage

Schematic of a PB-FHR with multi-stage counter current gas stripper and charcoal bed

Numbers from “J. Stempien, "Tritium Transport, Corrosion, and Fuel Performance Modeling in the Fluoride Salt-Cooled High-Temperature Reactor," MIT, Cambridge, 2015.”

Permeation Window



- **1-D diffusion through Ni Tubes**
- **20,000 m^2 surface area**
- **27,360 permeation tubes**
- **Permeation tubes OD: 0.00635**

Schematic of a PB-FHR Permeation Window and Activated Charcoal bed for gas recovery

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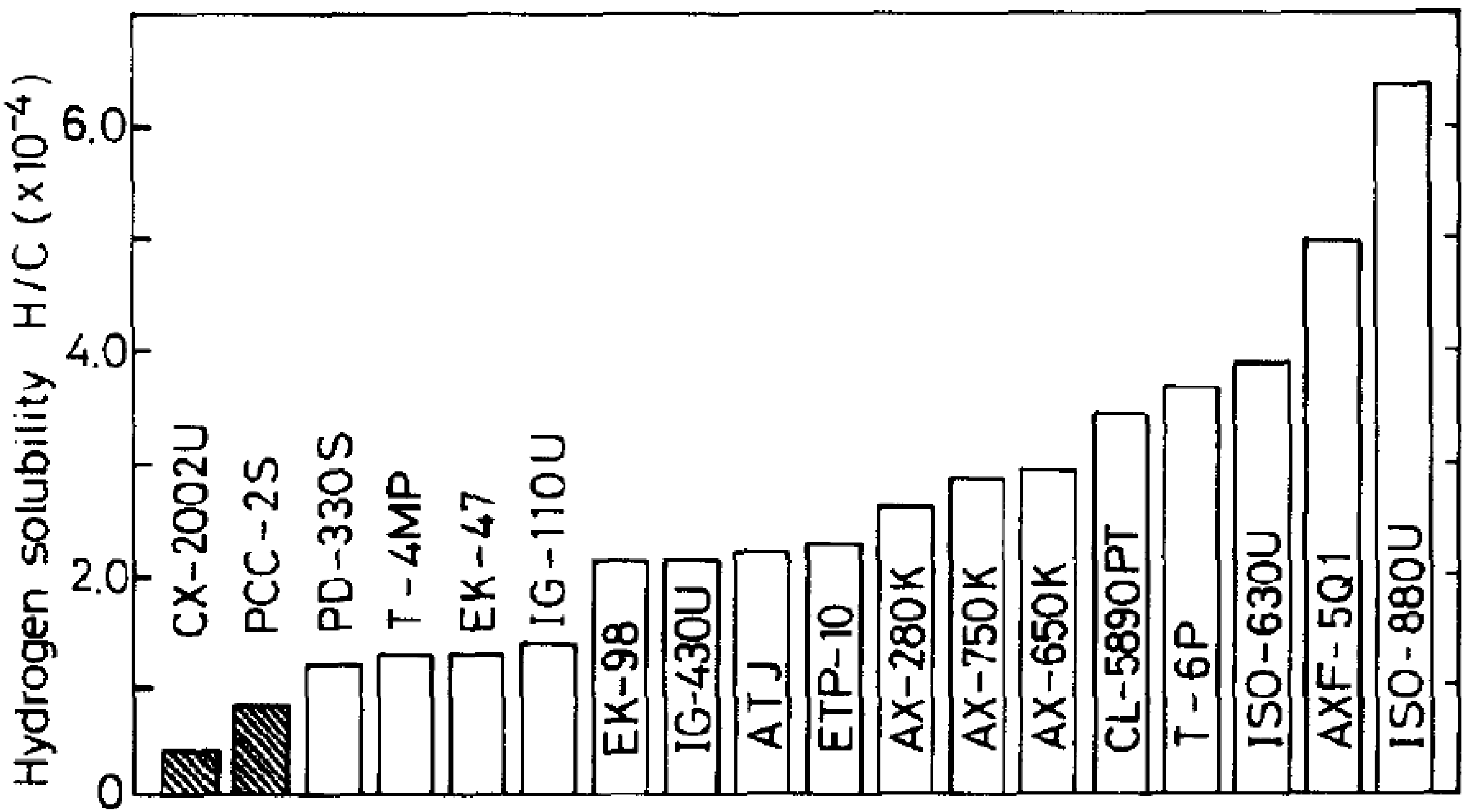
“J. Stempien, "Tritium Transport, Corrosion, and Fuel Performance Modeling in the Fluoride Salt-Cooled High-Temperature Reactor," MIT, Cambridge, 2015.”

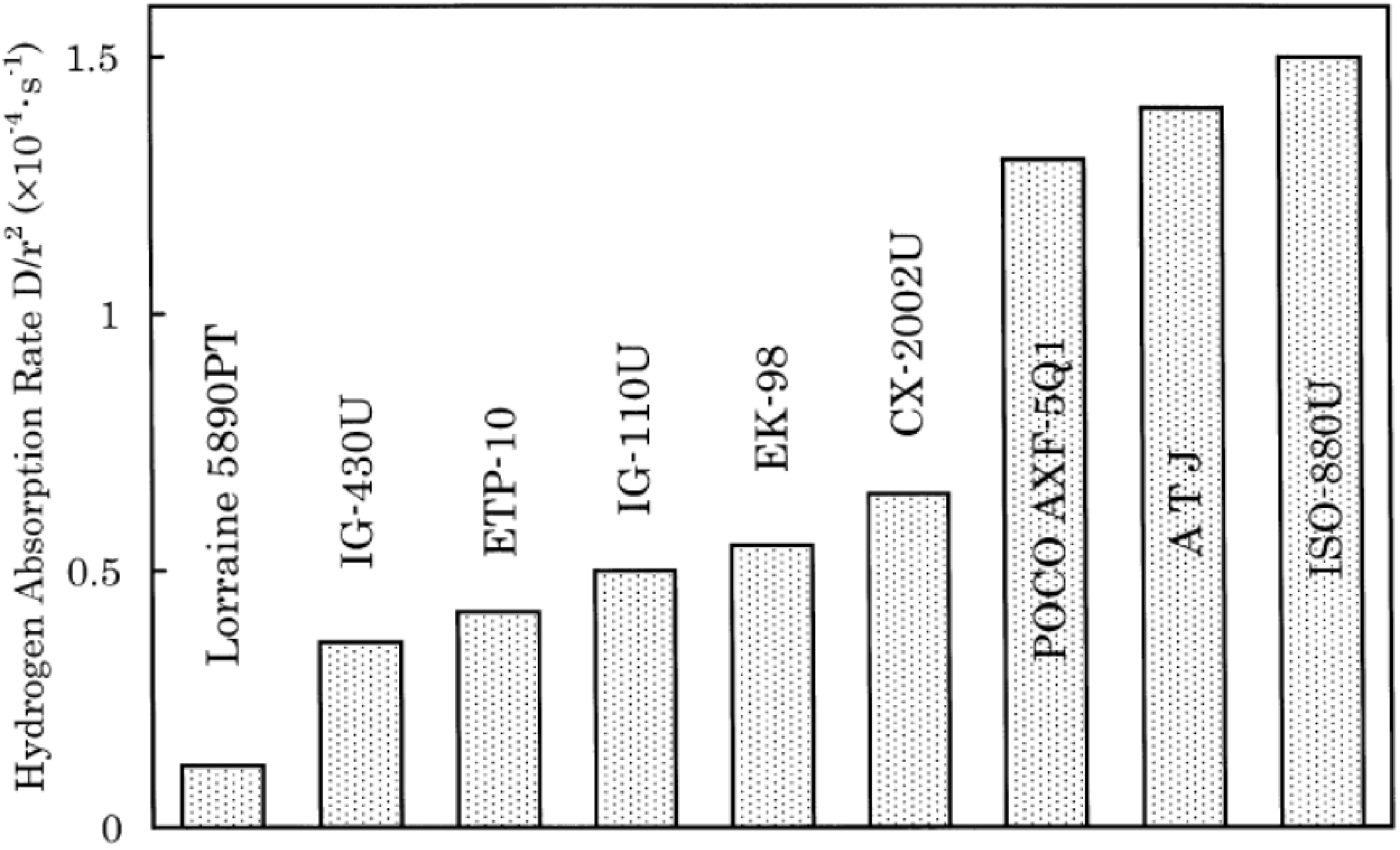
Hydrogen Solubility



Hydrogen solubility of different carbons at 1000 ºC and 101 kPa

"Astumi, H., Iseki, M., Shikama, T., "Trapping and detrapping of hydrogen in carbon-based materials exposed to hydrogben gas,' Journal of Nuclera Materials. 212-215, 1478-1482 (1994) "

Hydrogen Absorption Rates

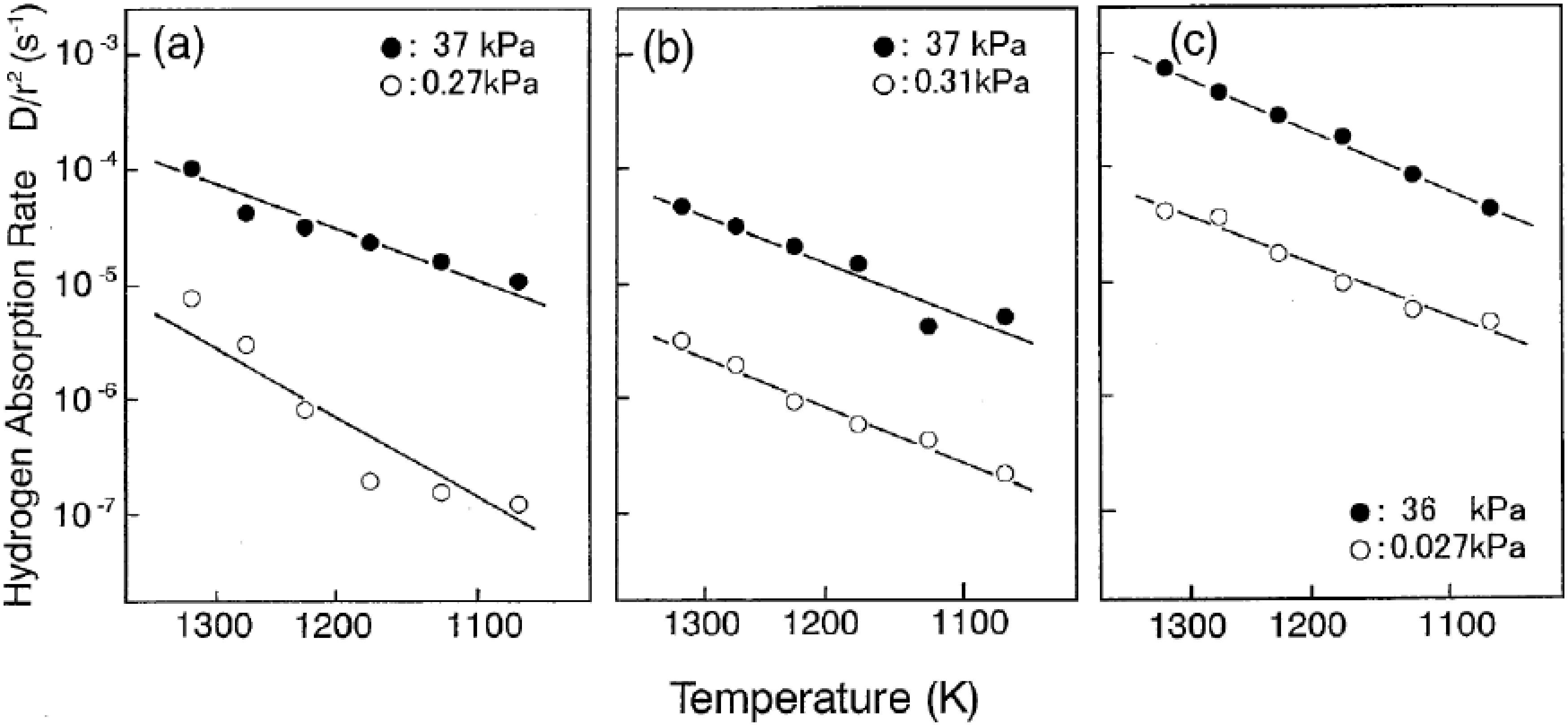


Hydrogen absorption rates in graphite and the CFC CX-2002U. T = 1273 K and P = 10 kPa.

ATSUMI, H., ISEKI, M., "Hydrogen absorption process into graphite and carbon materials," *Journal of Nuclear Materials*. **283–287, Part 2**, 1053–1056 (2000).

Absorption Rate vs. Temperature

- Increasing absorption **rate** with increasing temperature

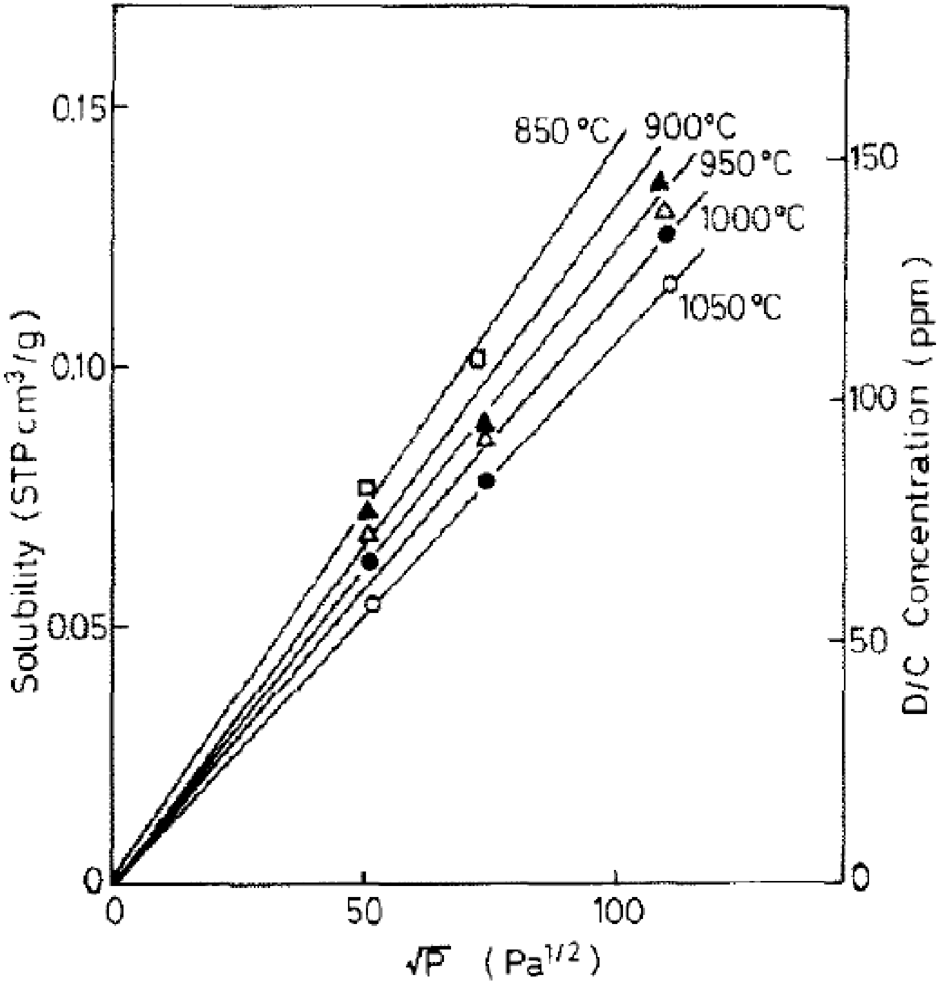


Hydrogen absorption rate in (a.) IG-110U, (b.) IG-430U, and (c.) ISO-880U.

ATSUMI, H., “Hydrogen bulk retention in graphiet and kinetics of diffusion,” *Journal of Nuclear Materials*. **307-311**, 1466–1470 (2002).

Solubility vs. Temperature

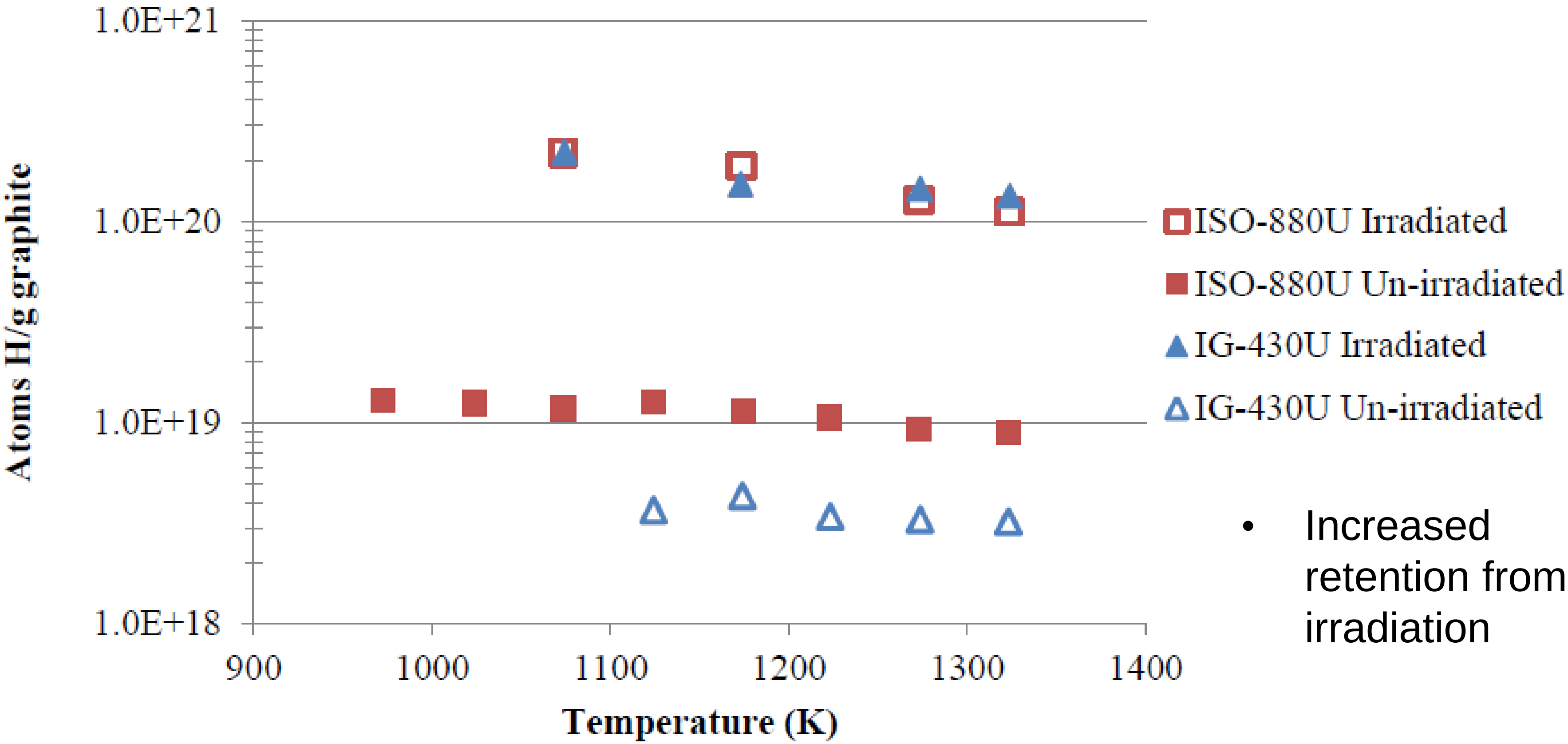
Solubility isotherms for deuterium adsorption on ISO-88 graphite



- Decreasing solubility with increasing temperature

ATSUMI, H., TOKURA, S., MIYAKE, M., “Absorption and desorption of deuterium on graphite at elevated temperatures,” *Journal of Nuclear Materials*. **155–157, Part 1**, 241–245 (1988).

Tritium Retention vs. Irradiation



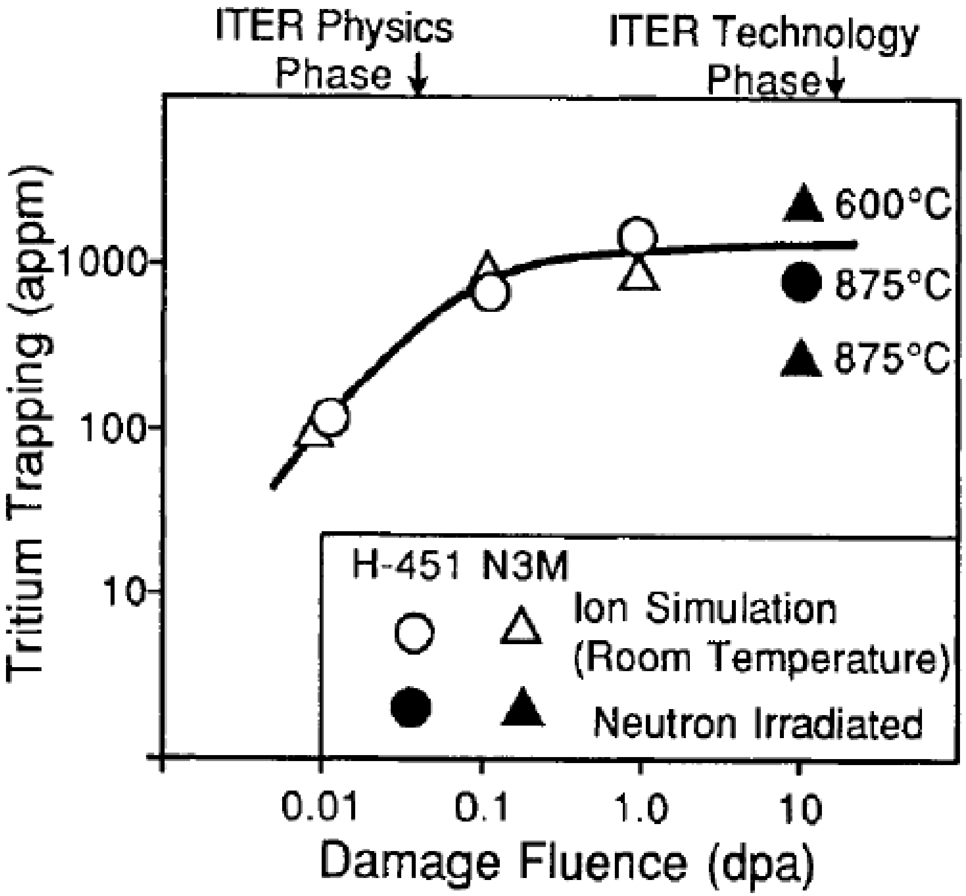
- Increased retention from irradiation

Hydrogen retention in ISO-880U and IG-430U. Irradiation was to 0.047 dpa.

Data converted “J. Stempien, "Tritium Transport, Corrosion, and Fuel Performance Modeling in the Fluoride Salt-Cooled High-Temperature Reactor," MIT, Cambridge, 2015.”

Original: ATSUMI, H., TANABE, T., SHIKAMA, T., “Bulk hydrogen retention in neutron-irradiated graphite at elevated temperatures,” *Journal of Nuclear Materials*. **390–391**, 581–584 (2009).

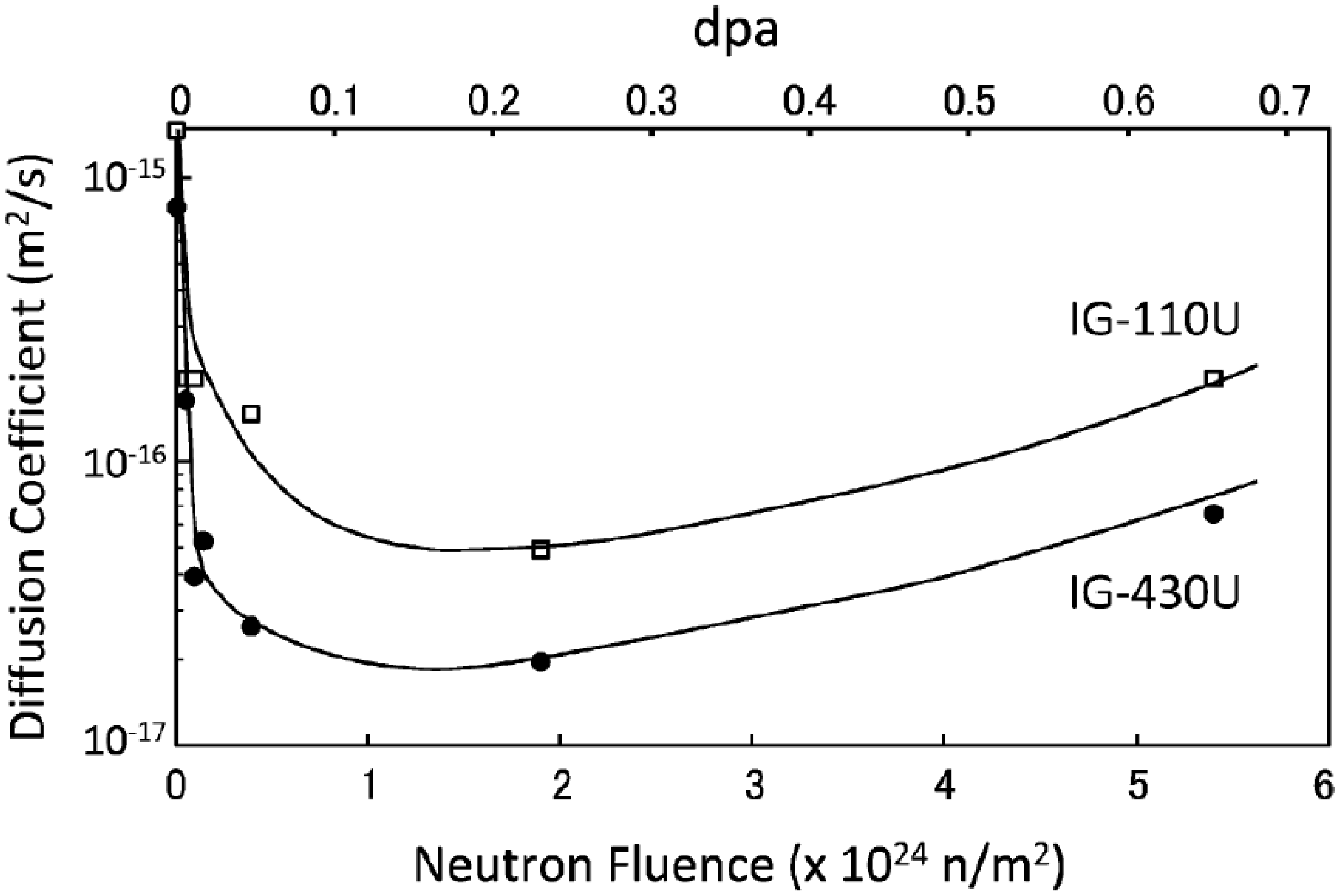
Tritium Trapping vs. Irradiation



Tritium Trap Concentration (atom ppm) for H-451 and N3M

CAUSEY, R.A., WILSON, K.L., WAMPLER, W.R., DOYLE, B.L., "The Effects of Neutron Irradiation on the Trapping of Tritium in Graphite," *Fusion Science and Technology*. **19**, 1585–1588 (1991).

Hydrogen Diffusion vs. Irradiation



Hydrogen Diffusion with Neutron Flux at 1273K and 10 kPa

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ATSUMI, H., TANABE, T., SHIKAMA, T., “Hydrogen behavior in carbon and graphite before and after neutron irradiation – Trapping, diffusion and the simulation of bulk retention–,” *Journal of Nuclear Materials*. **417**, 633–636 (2011).