

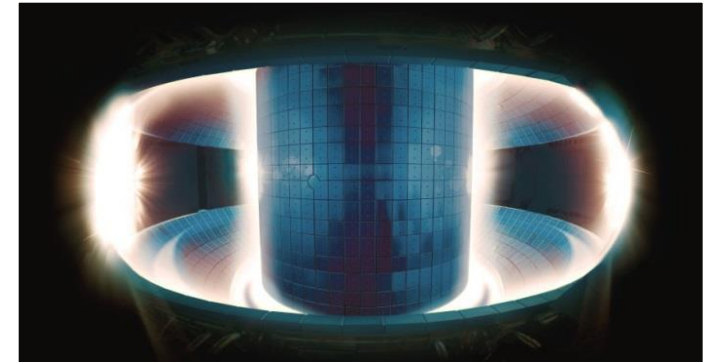
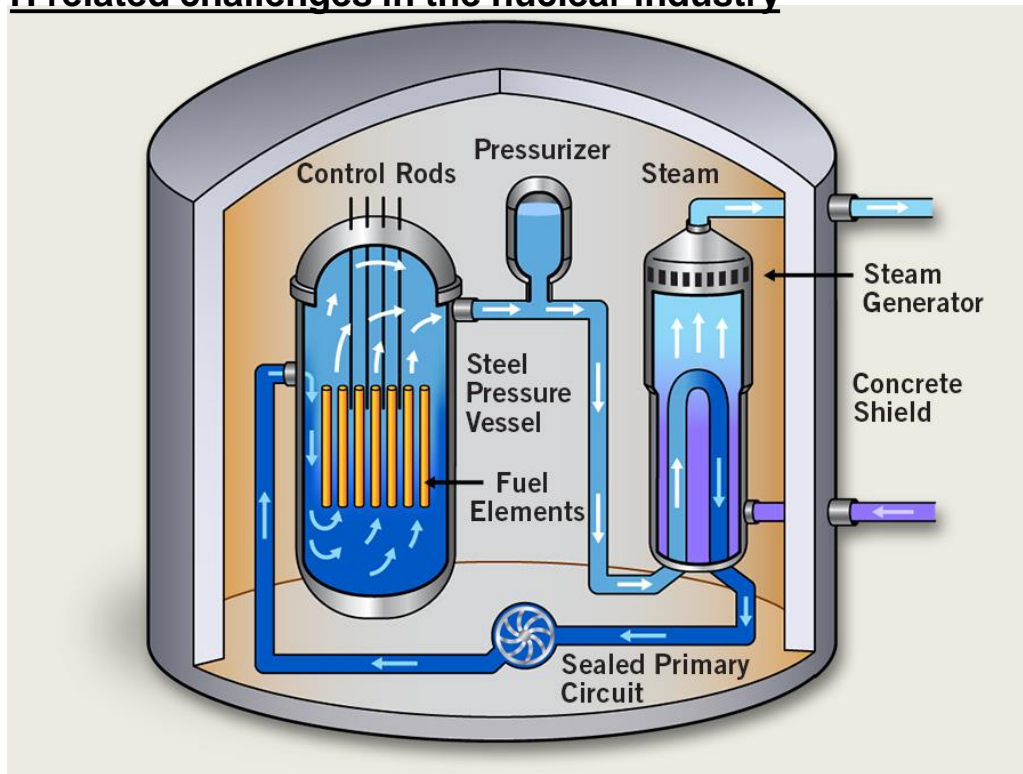
# ISOTOPIC TRACING OF HYDROGEN TRANSPORT AND TRAPPING IN NUCLEAR MATERIALS

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## H related challenges in the nuclear industry



Contamination → need of good assessment of the different barriers:

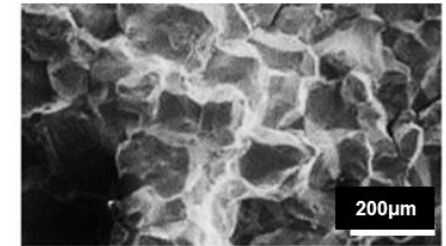
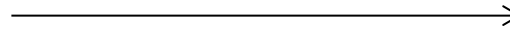
- mechanical integrity of the components (→ leaks?)
- tritium generation and wall permeation from core to secondary circuit
- tritium accumulation in component → maintenance & decommissioning

Tritium & deuterium recycling in tokamak or large devices dedicated to fusion

- loss of 'fuel'
- *in situ* creation of tritium by neutron-assisted transmutation

## H related challenges in the current nuclear industry

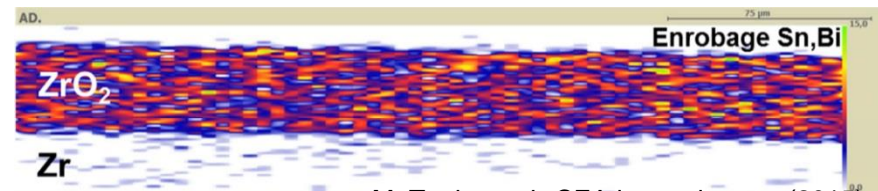
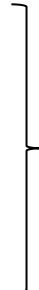
- Involvement of H in stress corrosion cracking mechanisms of fcc iron and nickel-base alloys



D. Symons, *et al.*, *J. Nucl. Mater.* 265(1999) pp. 225-23

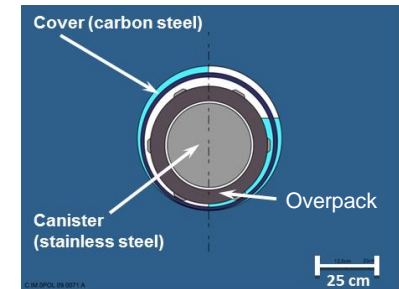
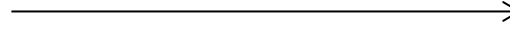
- Effect of hydride precipitates on the corrosion rate of Zr-base fuel cladding

- H absorption / desorption from used fuel claddings during storage and transport before recycling



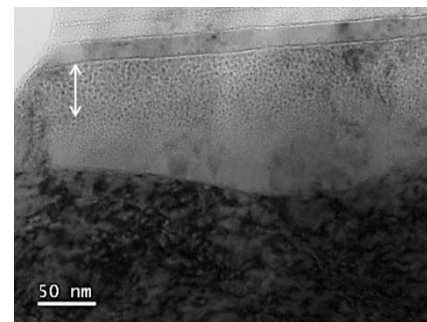
M. Tupin *et al.*, CEA internal report (2015)

- Role of H in the integrity of high radioactivity long life nuclear waste containers designed for long-term geological repositories



Référentiel Andra, 2006

- H behavior in materials exposed to neutron irradiation: in situ production of H, interaction with He and irradiation-induced defects, role in IASCC mechanisms



M. Dumerval, *PhD Thesis* (2014) Grenoble University, F.

- Nuclear power plants decommissioning and associated tritium hazards

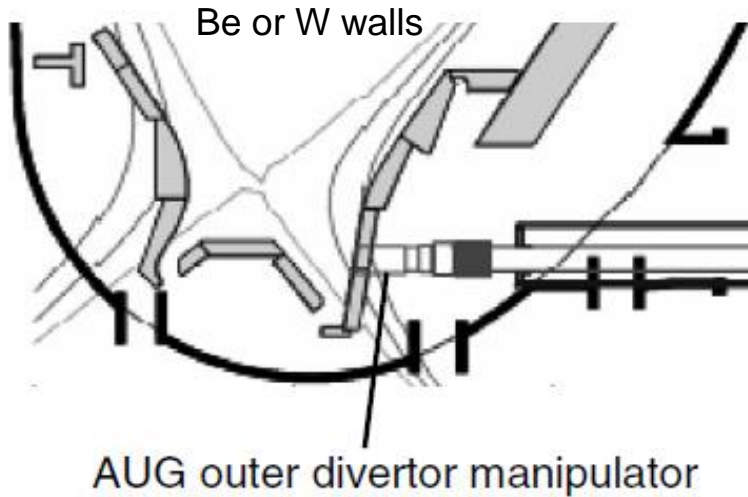
## H related challenges specific to nuclear materials:

- Continuous creation and annealing of defects
  - Irradiation defects (interstitials, vacancies, dislocation loops, stacking faults...)
  - Transmutation
  - Direct hydrogen implantation (plasma)
  
- Rapid transients of external surface H activity
  - Plasma transients
  - Rapid depassivation / repassivation
  
- Radiolysis
  
- Dynamic transient solicitations → non stationary boundary conditions
  - Plastic deformation / motion of microstructural defects
  - T transients
  - Microstructure transformation

## Interest of isotopic tracers:

- low natural abundance
  
- favorable cross section for nuclear reaction analysis
  
- radiation available for beta counting and autoradiography ( $^3\text{H}$ )
  
- large diffusion length for neutron scattering ( $^2\text{H}$ )
  
- in some cases, need for non radioactive tracer...

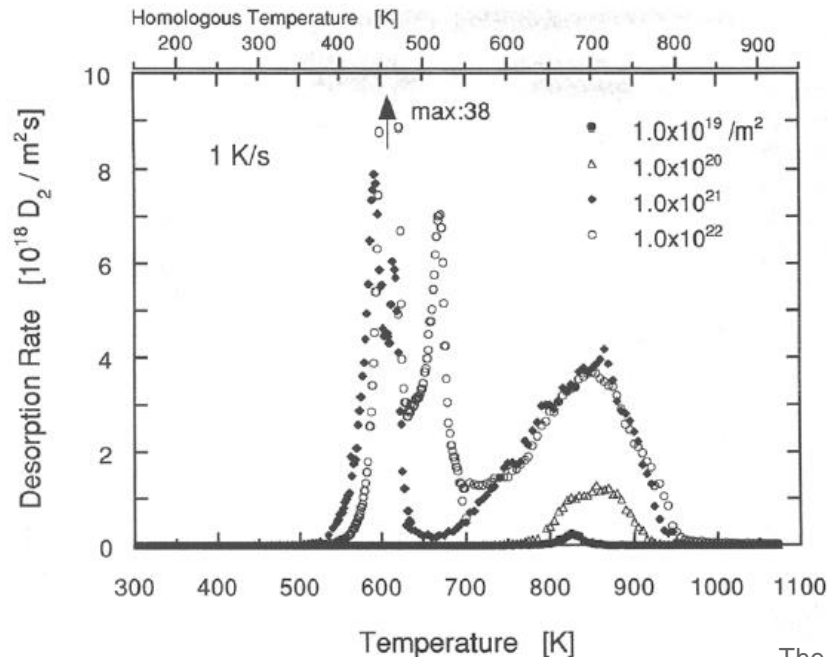
- **Hydrogen absorption in nuclear materials**
  - Hydrogen absorption by plasma-facing materials
  - Hydrogen absorption in Ni-base alloys in primary water PWR conditions
  
- **Hydrogen interactions with moving defects**
  - Hydrogen transport by dislocations
  
- **Discussion elements on possible isotopic effects**



K. Sugiyama *et al.*, *Phys. Scr.* **T145** (2011) 014033

### Be:

- + - Low atomic number
  - Excellent affinity for O (getter)
  - Ability to pump H continuously during short plasma discharges
- Transmutation from neutron irradiation → internal  $^3\text{H}$  formed → can be trapped or diffuse out of the wall (ext. part is problematic)
  - High inventory of  $^3\text{H}$  (up to 5kg for 10 years continuous exposure)



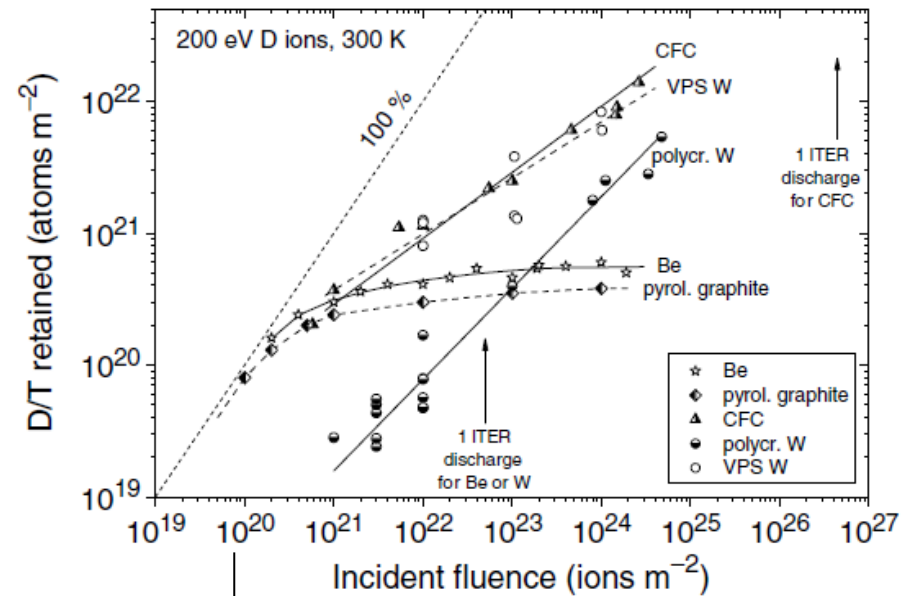
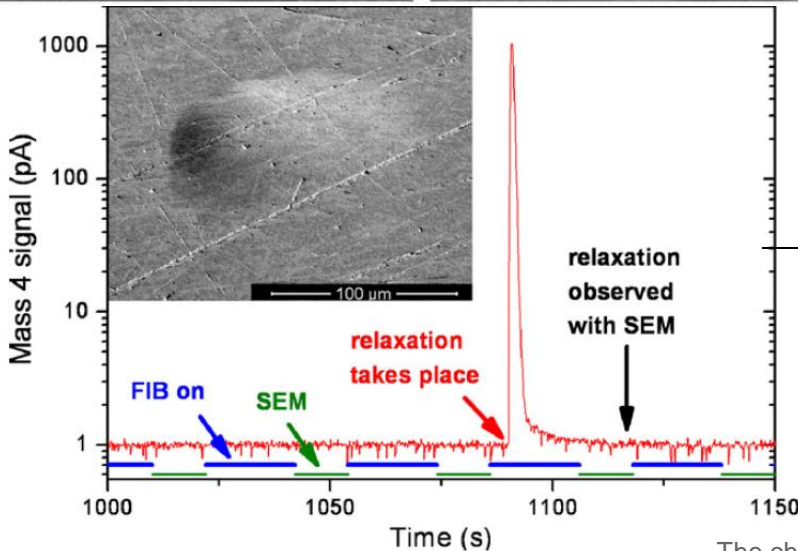
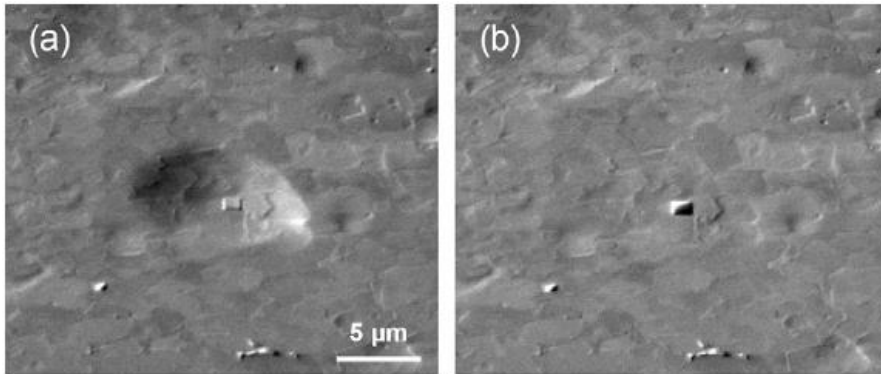
N. Yoshida *et al.*, *J. Nucl. Mater.* 233-237 (1996) pp. 874-879



**W:**

- + - Very high sputtering threshold
- High melting point
- Low H solubility

- Radiation loss in the plasma in presence of W
- W powder dust formation and redeposition  
→ potentially high specific surface



V. Alimov *et al.*, *Phys. Scr.* **T128** (2007) pp. 6-13

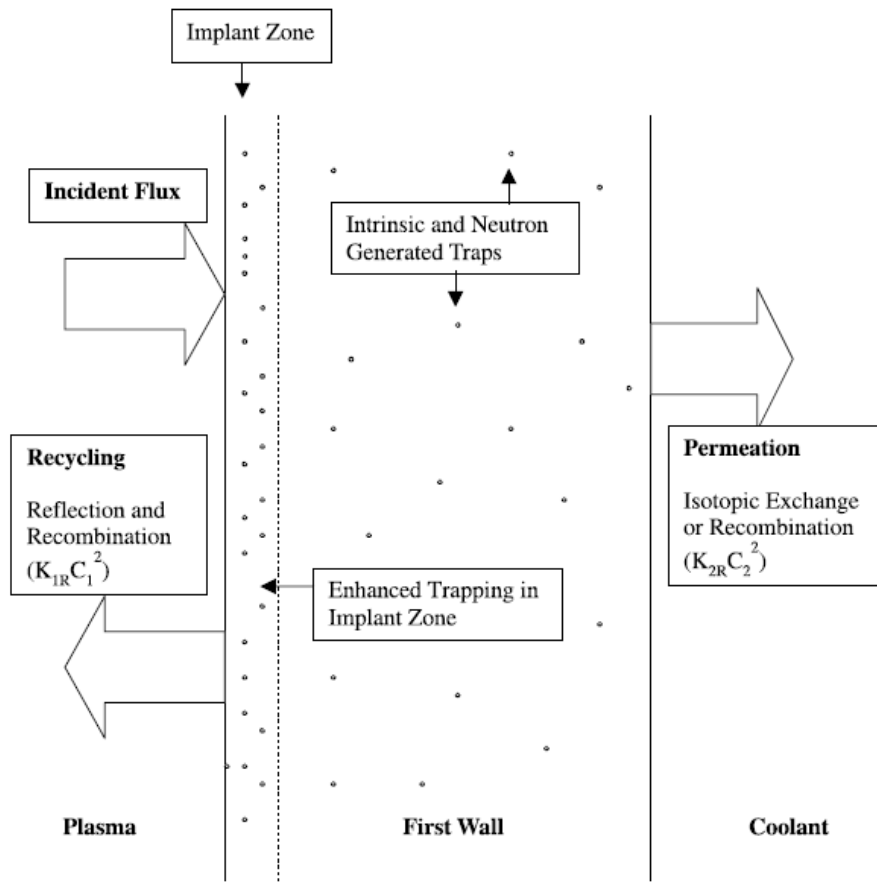
Increase of  $^2\text{H}/^1\text{H}$  retention with fluence (no saturation observed) → trapping?

Blisters on D-bombarded W surfaces:

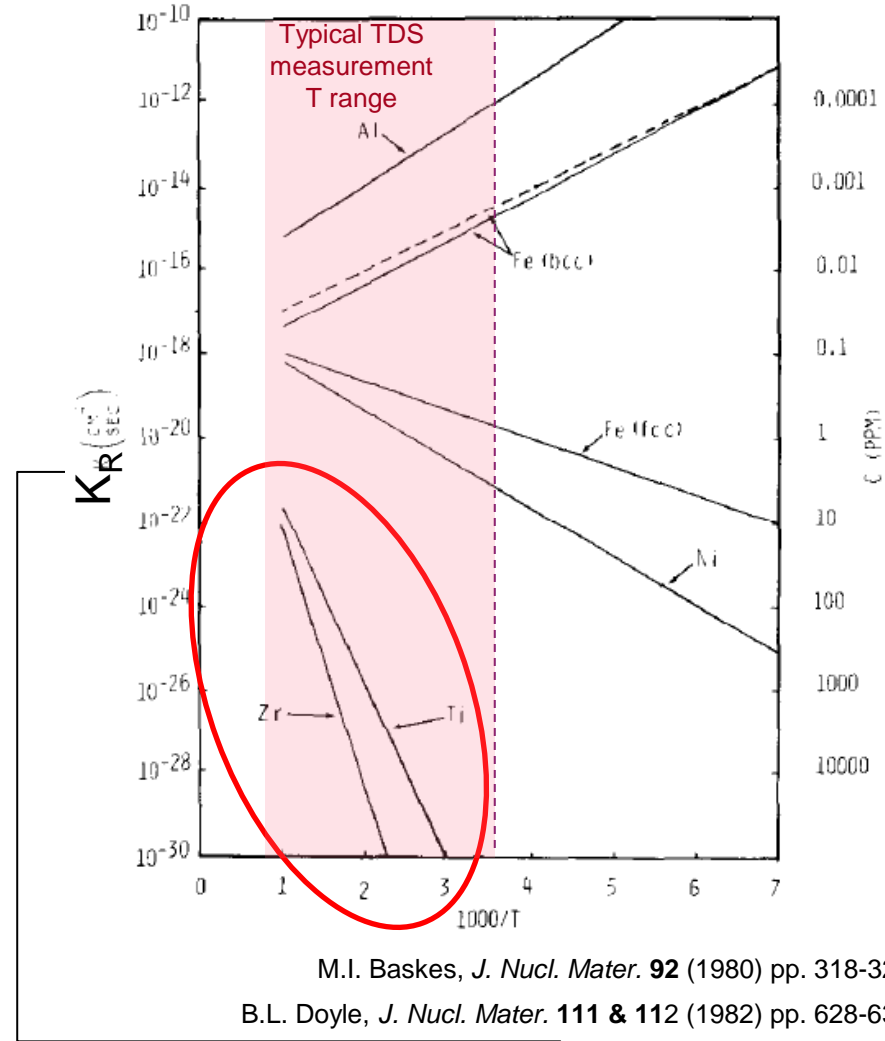
- Stable after end of irradiation
- Elastic deformation → SEM + FIB
- $^2\text{H}_2$  gas inside the blister evidenced by MS (+ possible quantification)
- May also induce some plastic deformation

**Hydrogen (or isotope) recycling matters**

Release rate =  $K_R C^2$  (atoms/m<sup>2</sup>s).



R. Causey, *J. Nucl. Mater.* **300** (2002) pp. 91-117



M.I. Baskes, *J. Nucl. Mater.* **92** (1980) pp. 318-324

B.L. Doyle, *J. Nucl. Mater.* **111 & 112** (1982) pp. 628-635

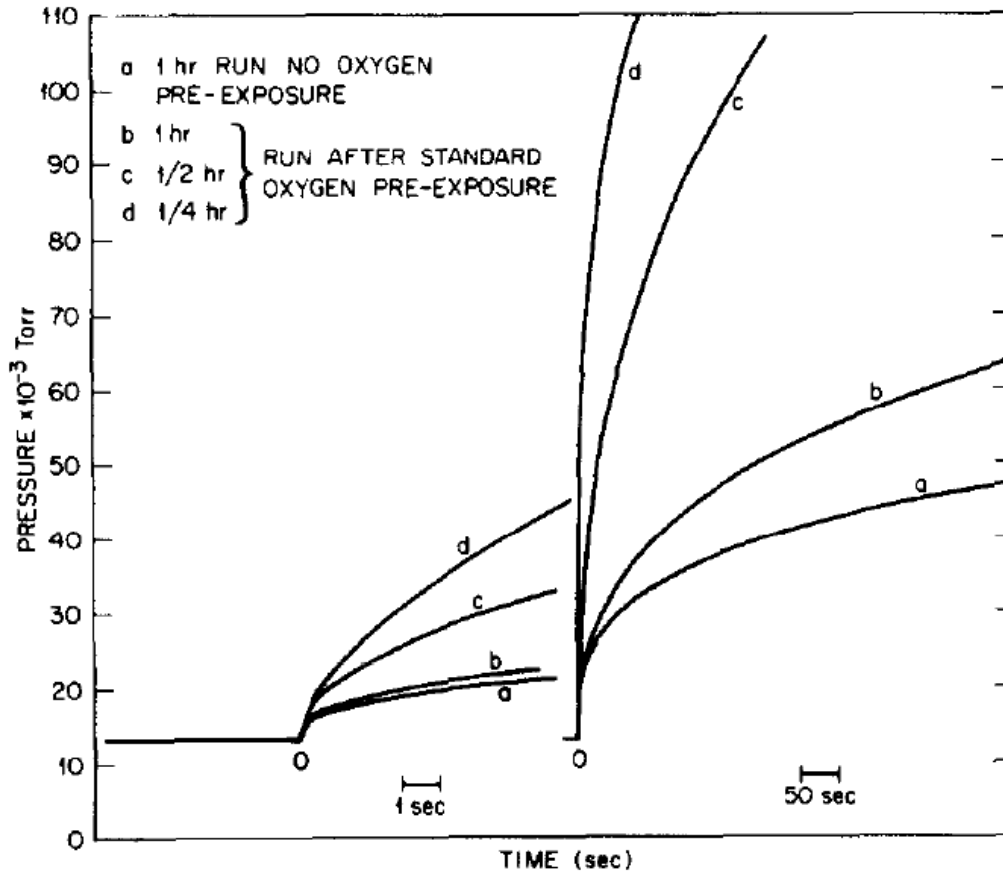
➔ Numerous models proposed by Baskes, Wilson and Doyle (Sandia National Labs, NM & CA)

➔ Analogy with cathodic charging & permeation topics ! (e.g. effect of surface recombination poisons)

The surface recombination step may be the limiting step to outgasing of H



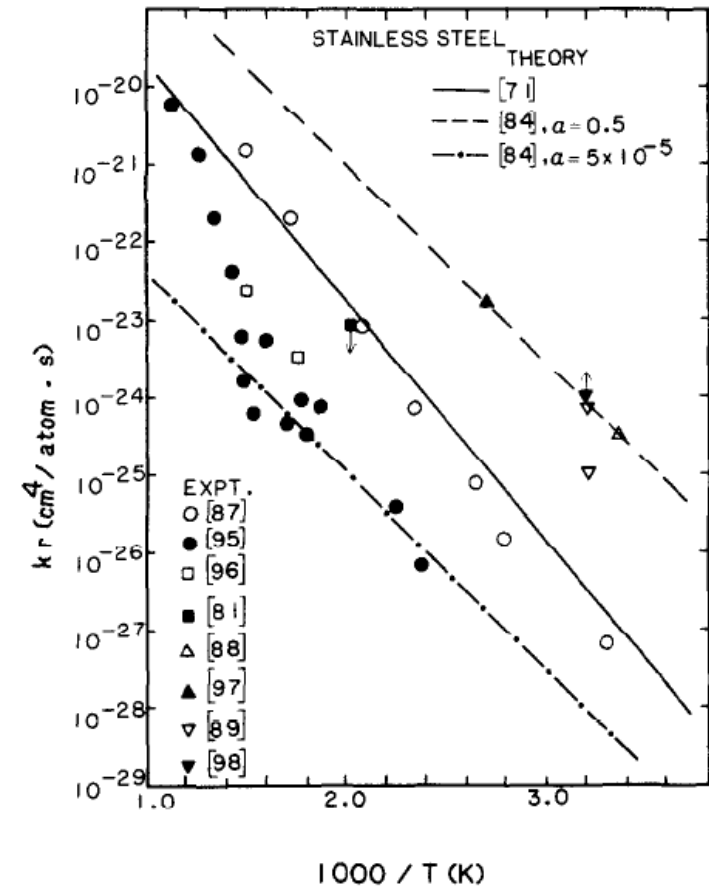
Hydrogen (or isotope) recycling matters



R. Clausing *et al.*, *J. Nucl. Mater.* **76 & 77** (1978) pp. 267-272

Evidence of the effect of an oxide layer on the recombination rate of hydrogen on the surface

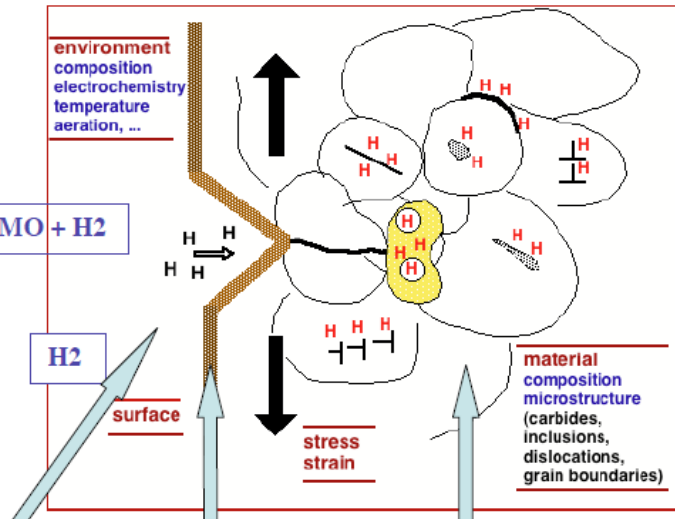
→ in addition to diffusion barrier layer, take into consideration potential rate-limiting step due to surface recombination slow reaction rate on the oxide layer



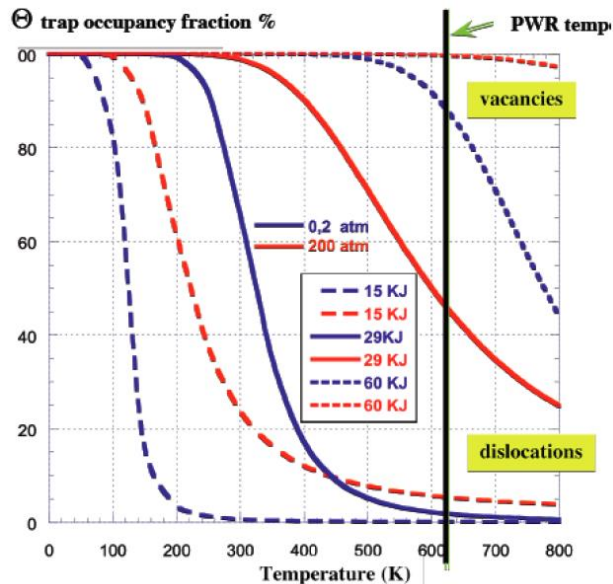
K. Wilson, *J. Nucl. Mater.* **103 & 104** (1981) pp. 453-464

High dispersion in  $K_R$  for stainless steels

- **Hydrogen absorption in nuclear materials**
  - Hydrogen absorption by plasma-facing materials
  - Hydrogen absorption in Ni-base alloys in primary water PWR conditions
  
- **Hydrogen interactions with moving defects**
  - Hydrogen transport by dislocations
  
- **Discussion elements on possible isotopic effects**



J. Chêne, in "The Coriou Effect", EFC Event 67, Woodhead Pub. (2016) pp. 295-311



## PWR primary circuit conditions:

Pure **water** /  $\langle T \rangle = 325 \text{ }^\circ\text{C}$  /  $P = 155 \text{ bar}$

1000 ppm B / 2 ppm Li

dissolved  $\text{H}_2$  : 35 cc/kg (NTP)  $\rightarrow$  eq.  $f(\text{H}_2) = 0.3 \text{ bar}$

dissolved  $\text{O}_2 < 5 \text{ ppb}$

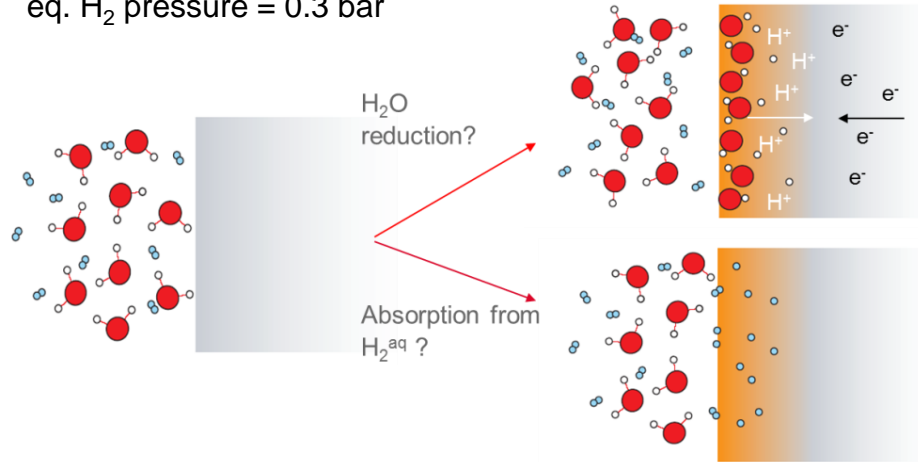
### main concerns are:

- Contribution to SCC propagation mechanisms?
- H-induced modification of mechanical properties?
- Effect of H in LTCP cases during cool down?
- H flux: towards what? What effect?

**$\rightarrow$  H.E. assisted cracking in primary media?**

Identification of the hydrogen source in primary water

$\langle T \rangle = 325 \text{ }^\circ\text{C}$  /  $P = 155 \text{ bar}$   
 eq.  $\text{H}_2$  pressure = 0.3 bar



Material:

- Single crystal of a A600-like alloy
- Composition: Ni – Cr:16.9 – Fe:5.7
- Surface : mirror-polished

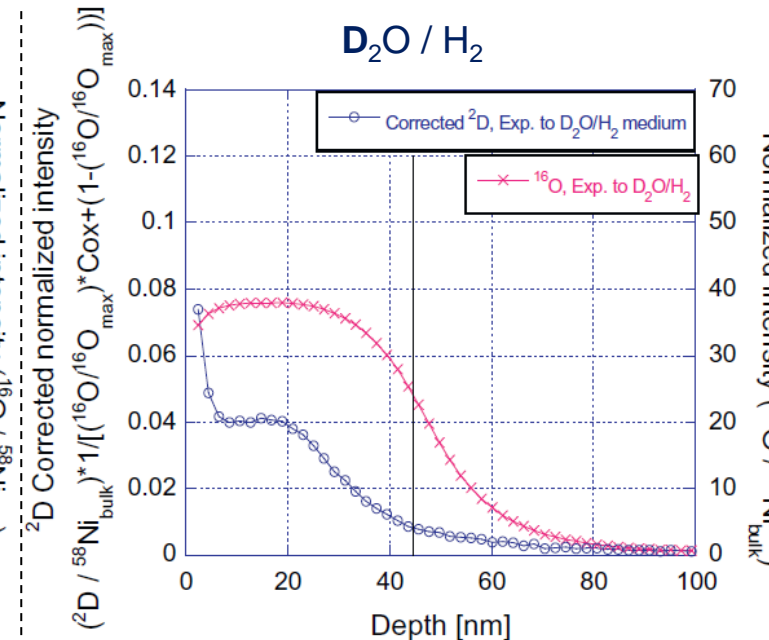
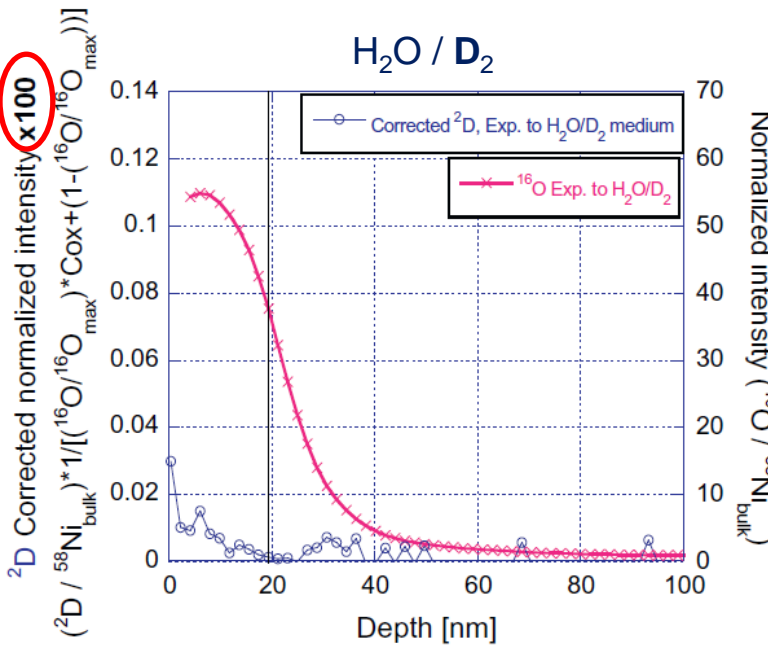


Method:

- Simulated primary media with deuterium (D)
- 2 experimental media tested for 45h exposure:

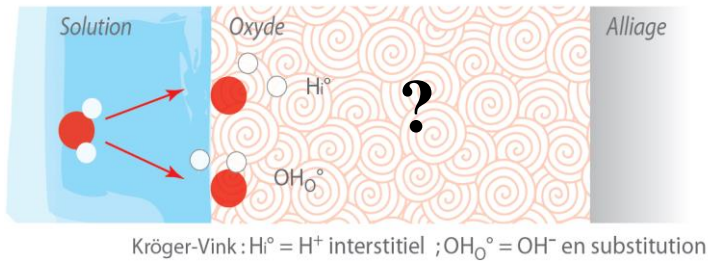
- 1)  $\text{H}_2\text{O} / \text{D}_2$
- 2)  $\text{D}_2\text{O} / \text{H}_2$

- SIMS D concentration profiling



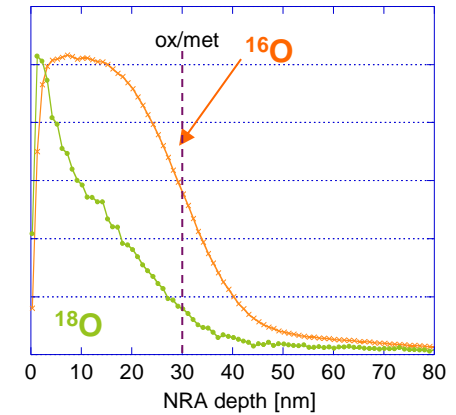
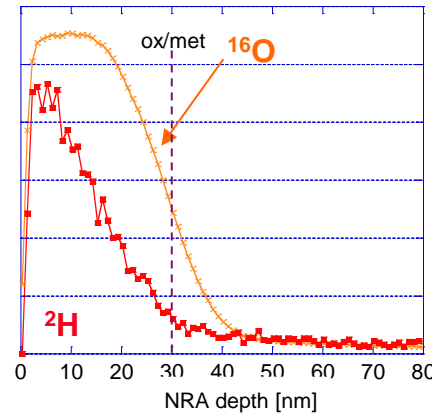
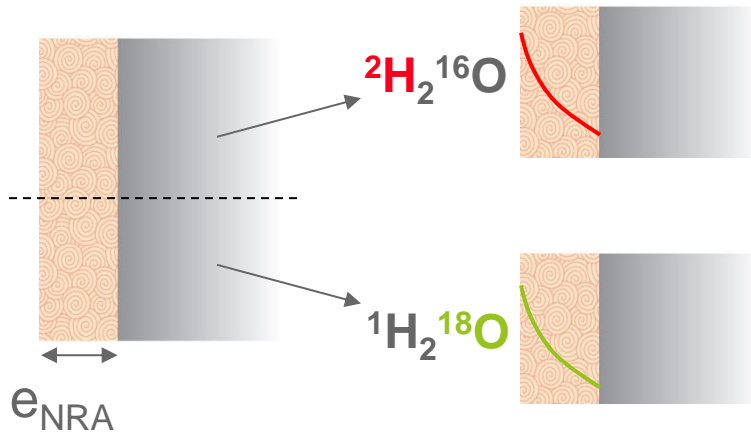
➔ Main source of H:  
 water molecules  
 dissociation /  
 reduction

## Identification of the hydrogen transport from the primary water towards the alloy



### Segmented experiment:

- 525 h pre-oxidation (PWR primary media, renewed conditions @325 °C)
- 9 h exposure in isotopically labelled media :  $^{18}O$  or  $^2H$
- high mass resolution SIMS concentration profiling



9h = short time exposure  
 → Harrison diffusion regime "C"  
 (diffusion by short-circuits)

$$c_{traceur}(x) = k \cdot \text{erfc} \left( \frac{x - P_1}{2\sqrt{D_{cc} \cdot t}} \right)$$

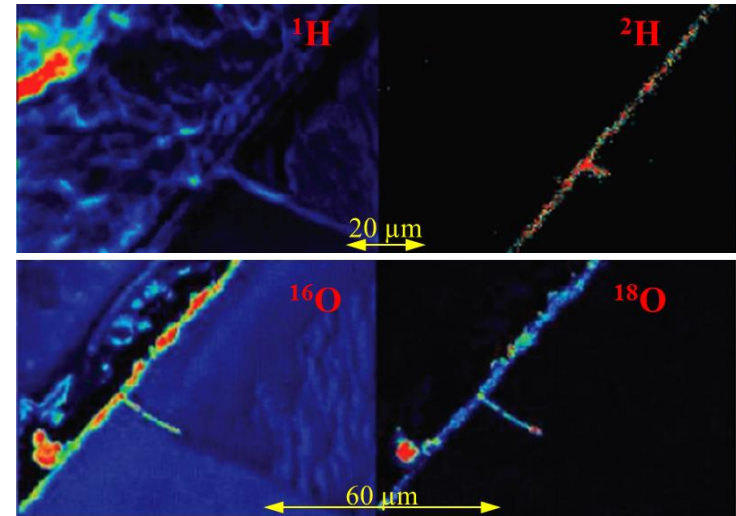
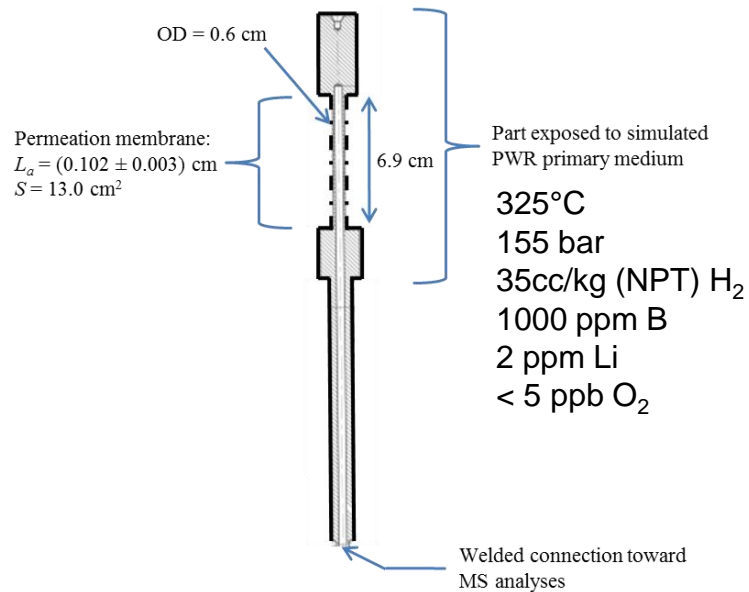
$$D_{cc}(^2H) = 5.2 \pm 1.2 \times 10^{-17} \text{ cm}^2/\text{s}$$

$$D_{cc}(^{18}O) = 4.6 \pm 0.9 \times 10^{-17} \text{ cm}^2/\text{s}$$

@ 325 °C

- H uptake mechanism based on the transport of  $OH_o^\circ$
- Very low  $OH_o^\circ$  diffusion coefficient in the oxide layer ( $cc \gg$  bulk) @ 325 °C → barrier effect

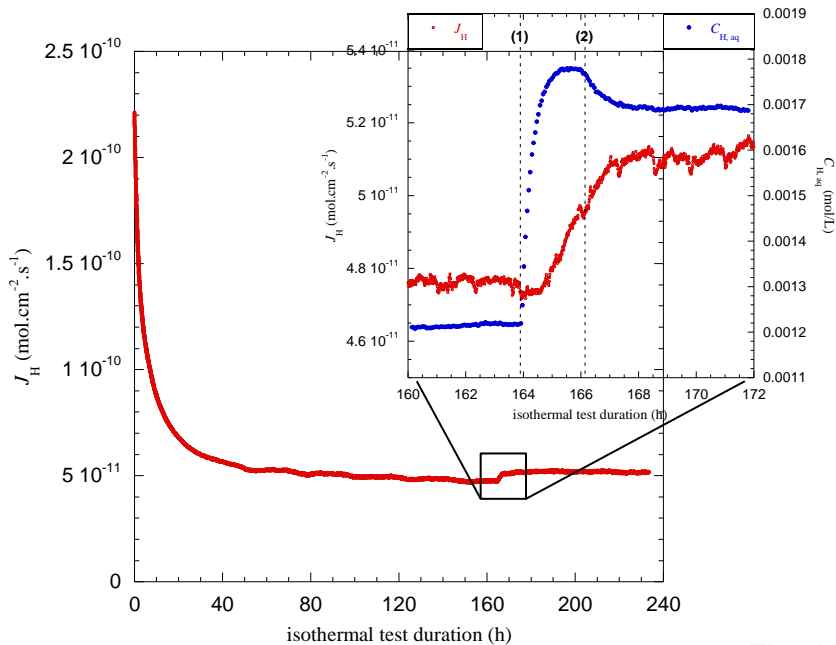
## Evaluation of the hydrogen fugacity associated with depassivation/repassivation processes in primary water



P. Laghoutaris, *PhD Thesis* (2008), Mines Paris

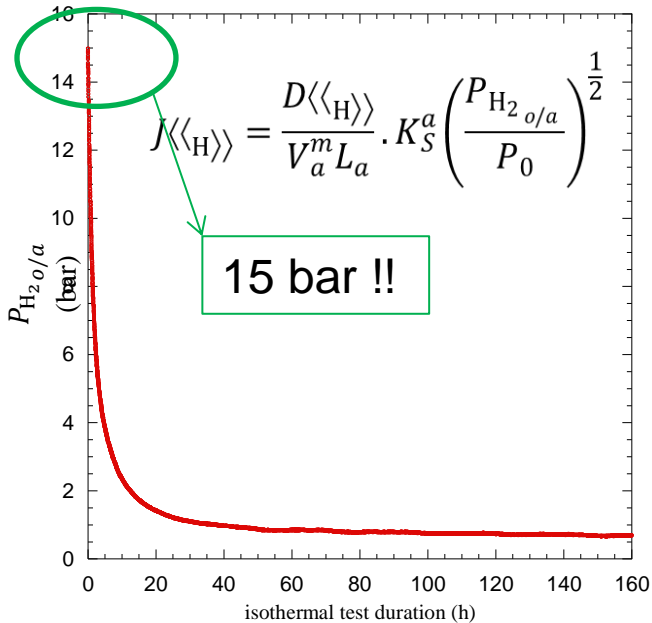
➔ Hydrogen penetration at crack tip embryo during ox. process

- Finite and non nil stationary permeation flux
- Hydrogen flux at first order governed by the oxidation rate
- Identification of the H carrier: charged species





## Evaluation of the hydrogen fugacity associated with depassivation/repassivation processes in primary water



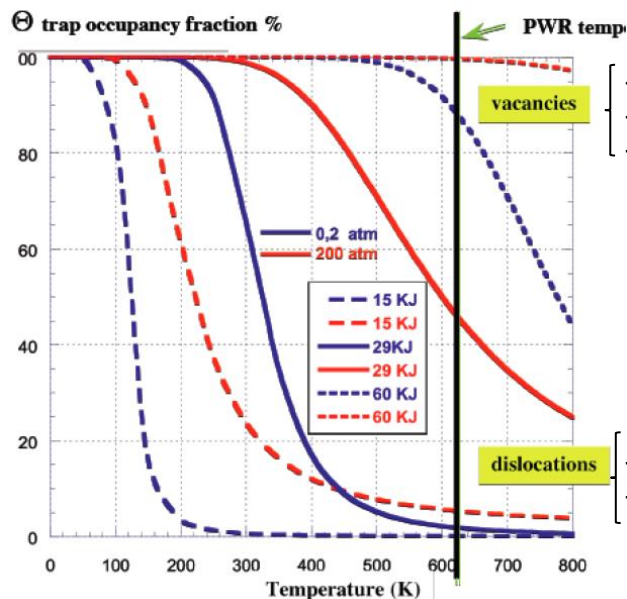
$K_S^a$  and  $D_{\langle\langle H \rangle\rangle}$  taken from Sakamoto *et al.*  
(*Fusion Sci Technol* 41 (2002) pp. 912-914)

→ much higher local hydrogen partial pressure would be expected when oxide film breaks at crack tip:

→ high injection rate of hydrogen directly into the material

→ high hydrogen partial pressure at alloy surface may induce, even @ such high temperatures, some traps filling

L. Marchetti *et al.*, to be submitted to *Corros. Sci* (2017)



- Brought by corrosion process  
- Irradiation defects  
- + cavities

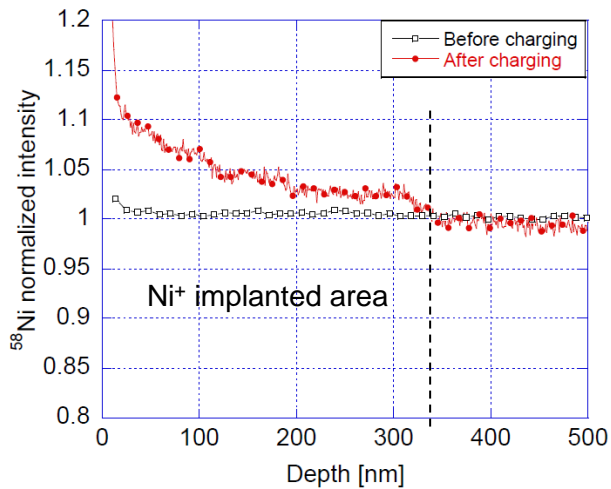
- Local plasticity at crack tip  
- Loops or stacking faults (irr. defects)

→ Possible effect of hydrogen in the mechanisms of crack propagation in SCC systems under primary water conditions

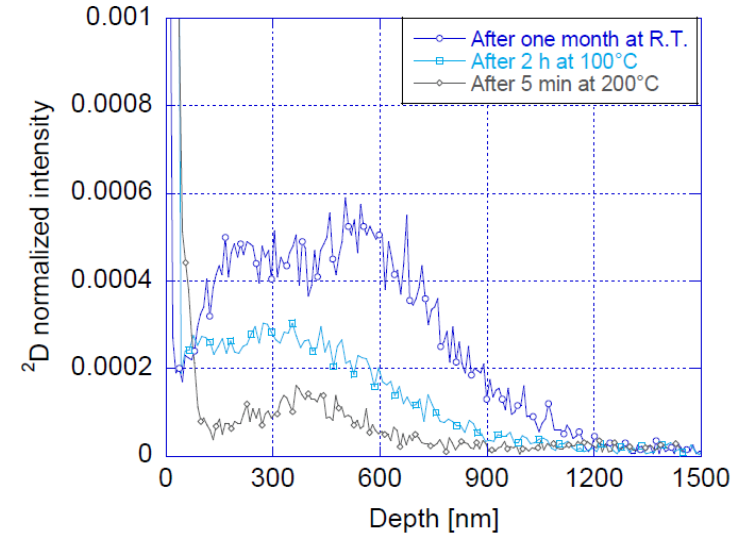
→ necessity to study diffusion and trapping in such materials

→ Diffusion and trapping / detrapping rate constants need to be addressed

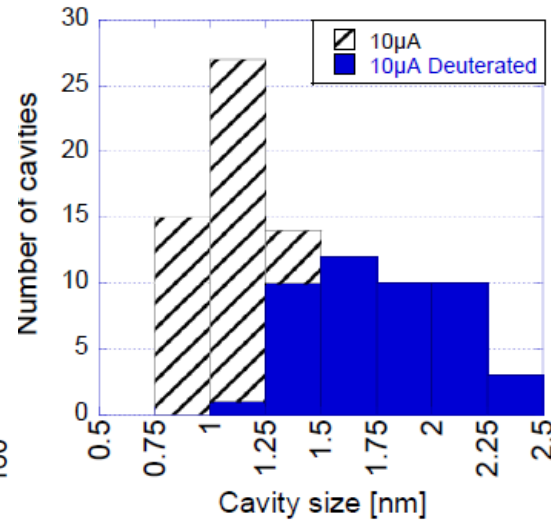
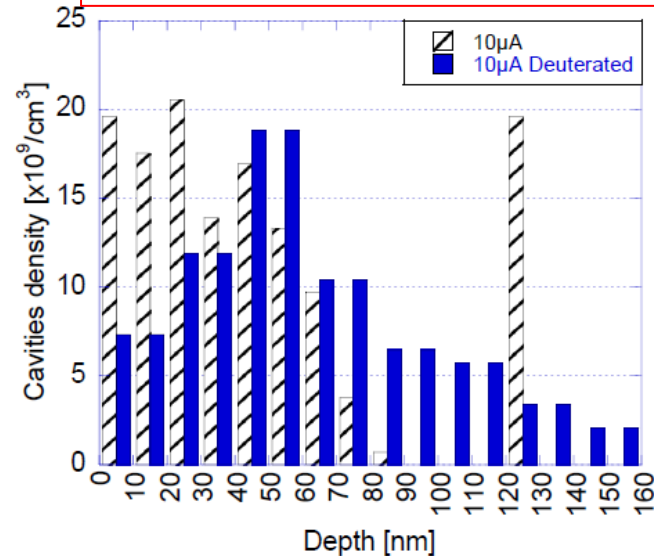
## Quantitative analysis of H interactions with microstructural defects in alloy A690



Evidence of metal – metal bonding weakening in presence of hydrogen (deuterium here)



Evidence of trapping and T-activated detrapping + still some detectable D trapped after 200°C heat treatment

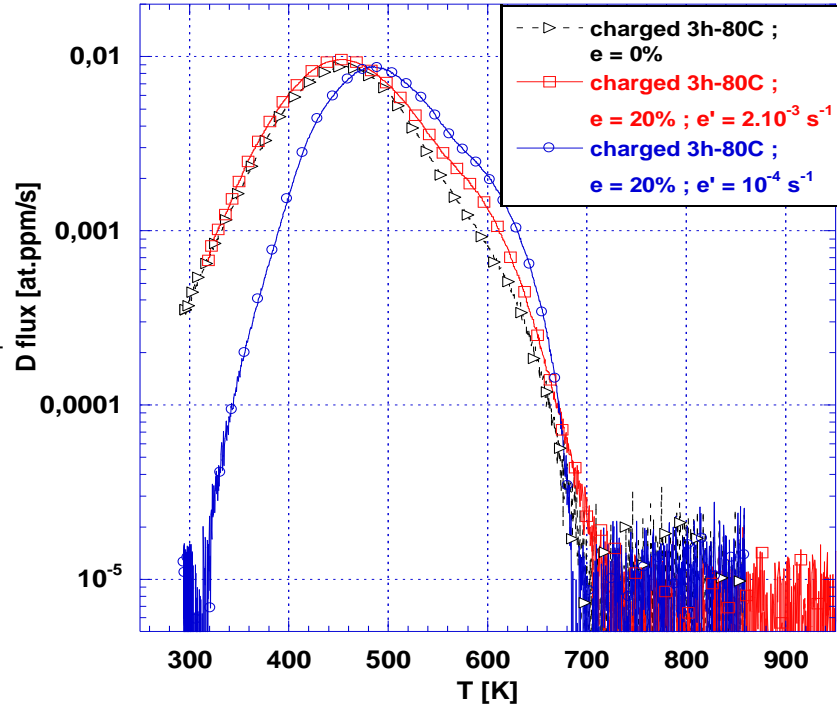


H-induced growth of faulted loops and cavities in [20;200] °C temp. range

Shows the **enhancement of the mobility of dislocations and point defects in presence of hydrogen**

→ Still valid for operational temp. in PWR?

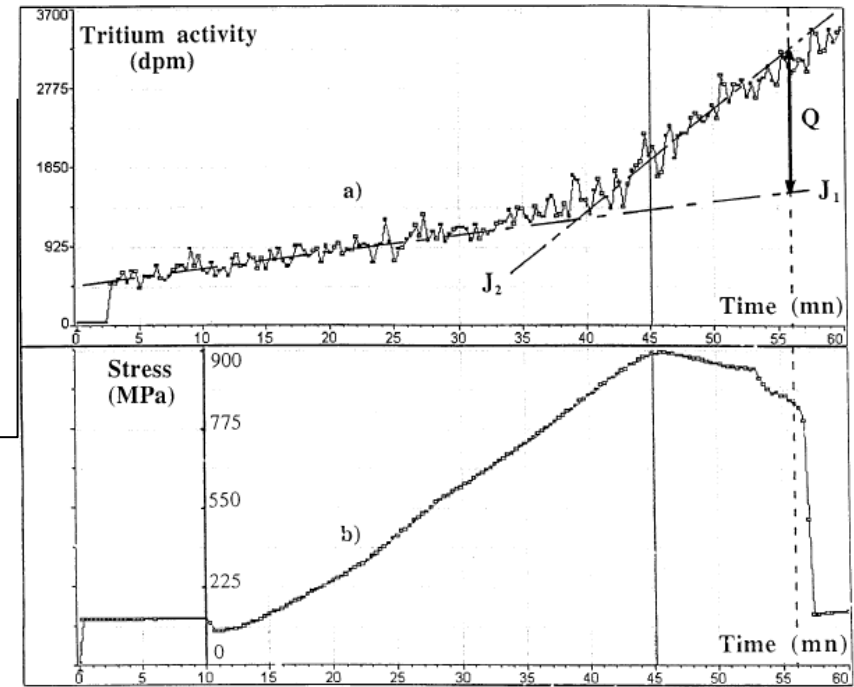
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pure Ni single crystal :  $^2\text{H}$  TDS

F. Martin *et al.*, *Proceedings: IHC* (2012) pp. 585-593

Assuming a closed system (limited deuterium desorption from interstitial sites during the tensile test):

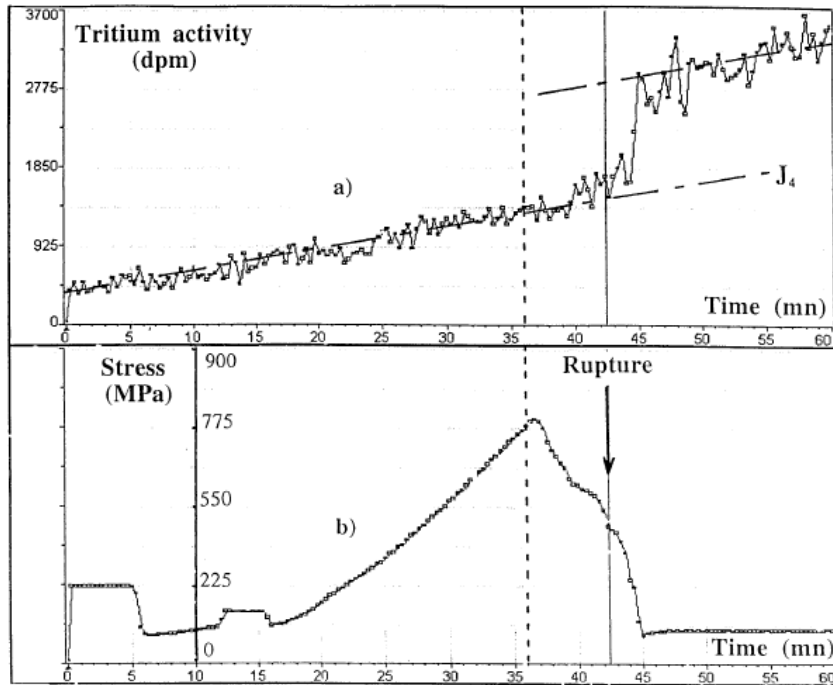
Evidence of elastic interactions between dislocations and interstitial deuterium  
 → Lattice hydrogen sweeping by dislocations

single crystal superalloy  $\gamma/\gamma'$ : tritium &  $\beta$  counting

J. Chêne *et al.*, *Scripta Mater.* **40** (1999) 537-542

- No elastic field-assisted desorption of tritium (lattice diffusion not modified by elastic strain)
- Plasticity enhances tritium desorption (by dislocation lines arriving at the surface) (starts in the microplasticity domain)
- Quantification possible (Q):  
 →  $\alpha_{\text{dislo}} < 50 \text{ at./b}$

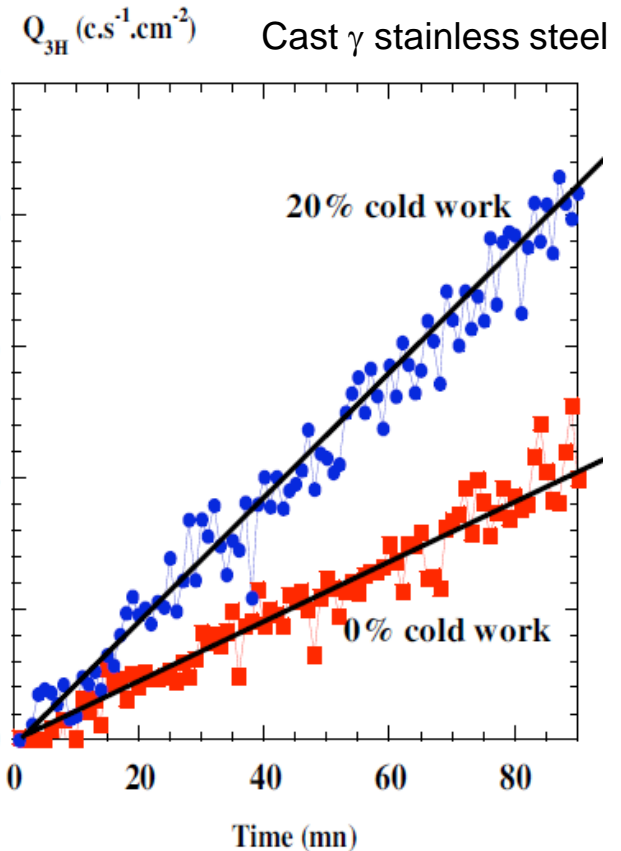
single crystal superalloy  $\gamma/\gamma'$ : tritium &  $\beta$  counting



J. Chêne et al., *Scripta Mater.* **40** (1999) 537-542

Tritium burst at rupture:

- liberation of tritium accumulated in the vicinity of the cracked area
- Enables quantification of local hydrogen concentration needed to weaken M-M bonds



J. Chêne, *Fusion Sci. Techn.* **54** (2008) pp. 506-509

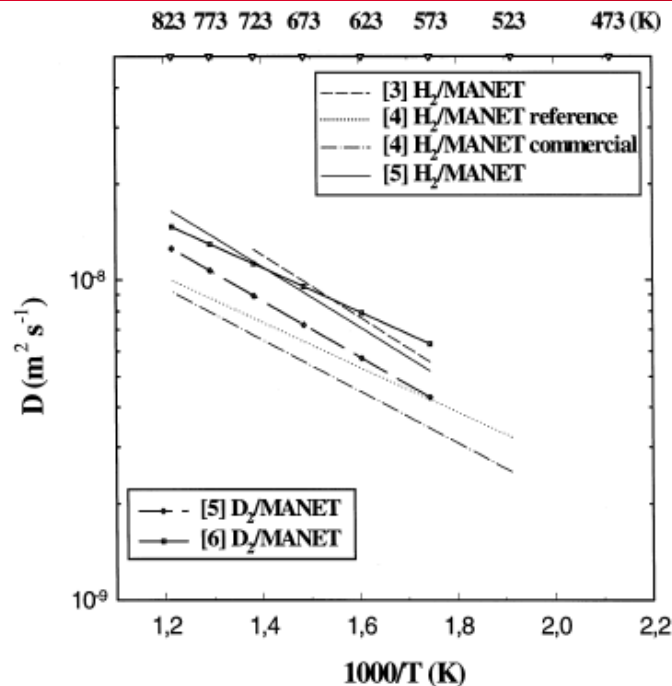
Possible effect of short circuit diffusion, @ RTI, due to the dislocation network formed by cold-working after tritium introduction

Hydrogen “pipe diffusion” along dislocations?

→ still controversy

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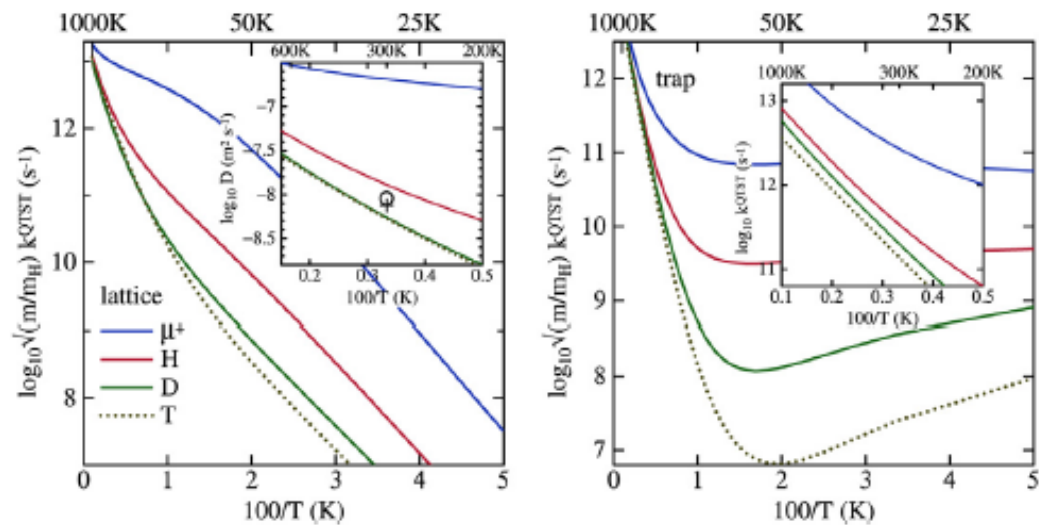
- Isotopic effect limited in usual exp. T range
- Within dispersion range of exp. data
- Effect lower than matrix effect

→ true for the majority of permeation / TDS / concentration profiles (NRA, SIMS) tests and analysis  
 → provided these experiments were carried @ elevated T

Anomalous isotopic effects (quantum effects)

→ especially at low T  
 → effect on trapping even @ RT

E. Serra et al., *J. Nucl. Mater.* **255** (1998) pp.105-115



<sup>2</sup>H or <sup>3</sup>H may be used to bring experimental evidence of such behavior  
 → at liquid N<sub>2</sub> temperature

Could this quantum effect (tunneling trapping) be responsible for an enhancement of the rate of hydrogen transport by mobile dislocations?

Quid of isotopic effects at surface during cathodic charging @ RT?

A. Paxton et al., *Acta Mater.* **103** (2016) pp.71-76