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Hydrogen Permeability of Additively Manufactured Stainless Steel

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Tritium Focus Group,
Albuquerque, New Mexico
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Hydrogen permeation in metals

- Atomic hydrogen permeates through all metals
- Driven by a concentration gradient
- Follows Fick's and Sieverts Laws
  - *Fick's law can be derived using a random walk*
- In crystalline materials hydrogen is present both interstitially and at defects
- Arrhenius temperature dependence $\Phi=\Phi_0 e^{-E_a/RT}$
- Can be measured electrochemically or by gas driven diffusion

Fick's Law

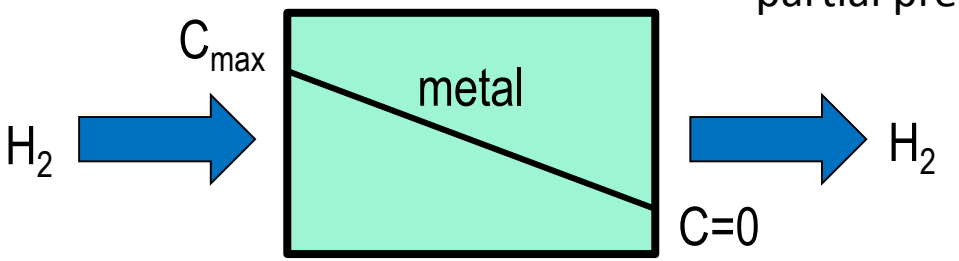
$$J = -D\nabla\varphi$$

Flux is proportional to concentration gradient

Sievert's Law

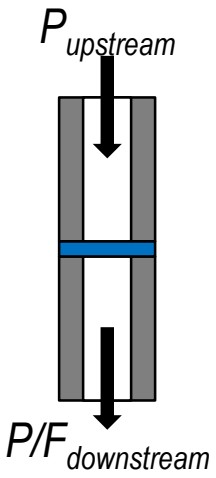
$$c_{at} = \sqrt{K p_{mol}}$$

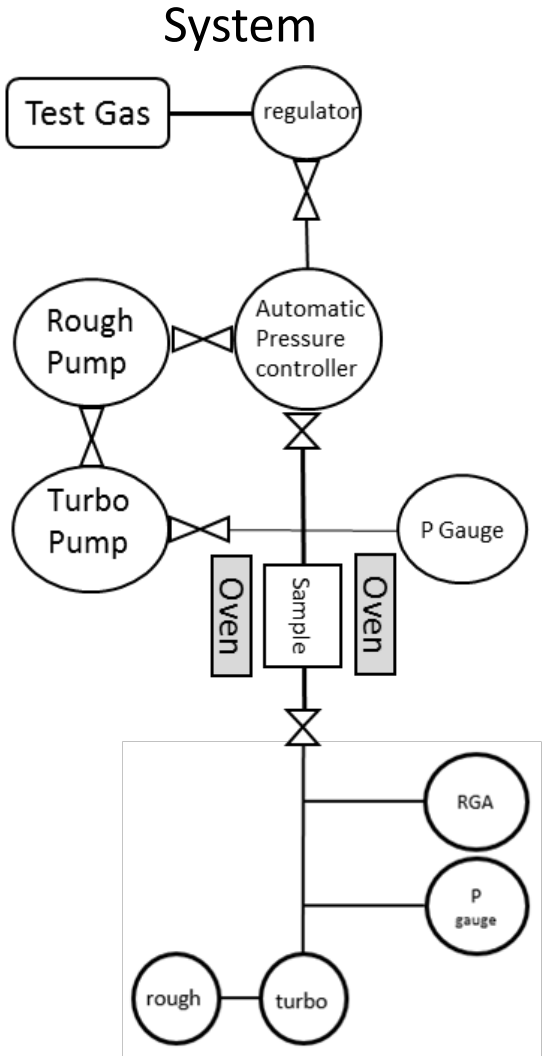
Surface concentration is proportional to square root of partial pressure

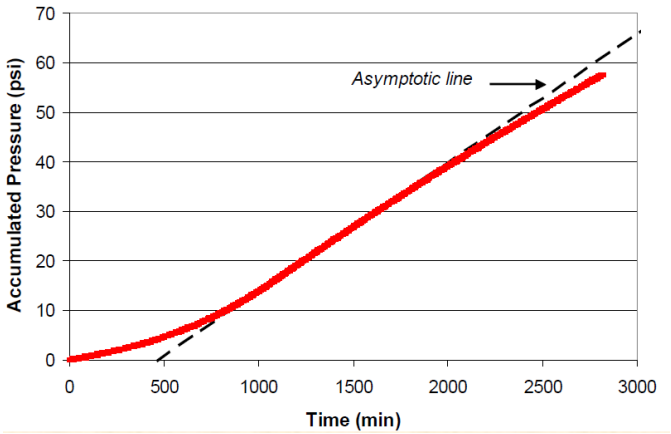


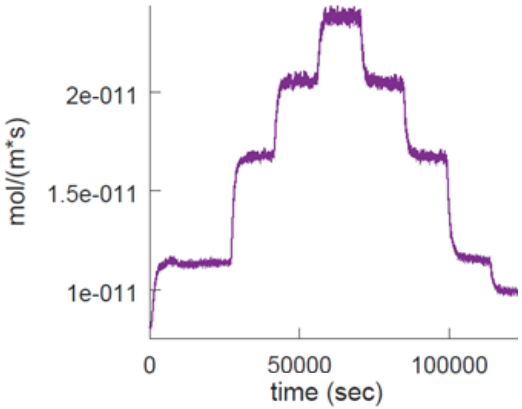
Gas driven hydrogen permeability

1. H_2 partial pressure is controlled such that it is higher upstream than downstream
2. Atomic hydrogen diffuses through the sample
3. Hydrogen flux through the sample is measured as a function of time
   - Our system measures the hydrogen **flow rate** rather than the total hydrogen that has passed through the sample (rate of rise).







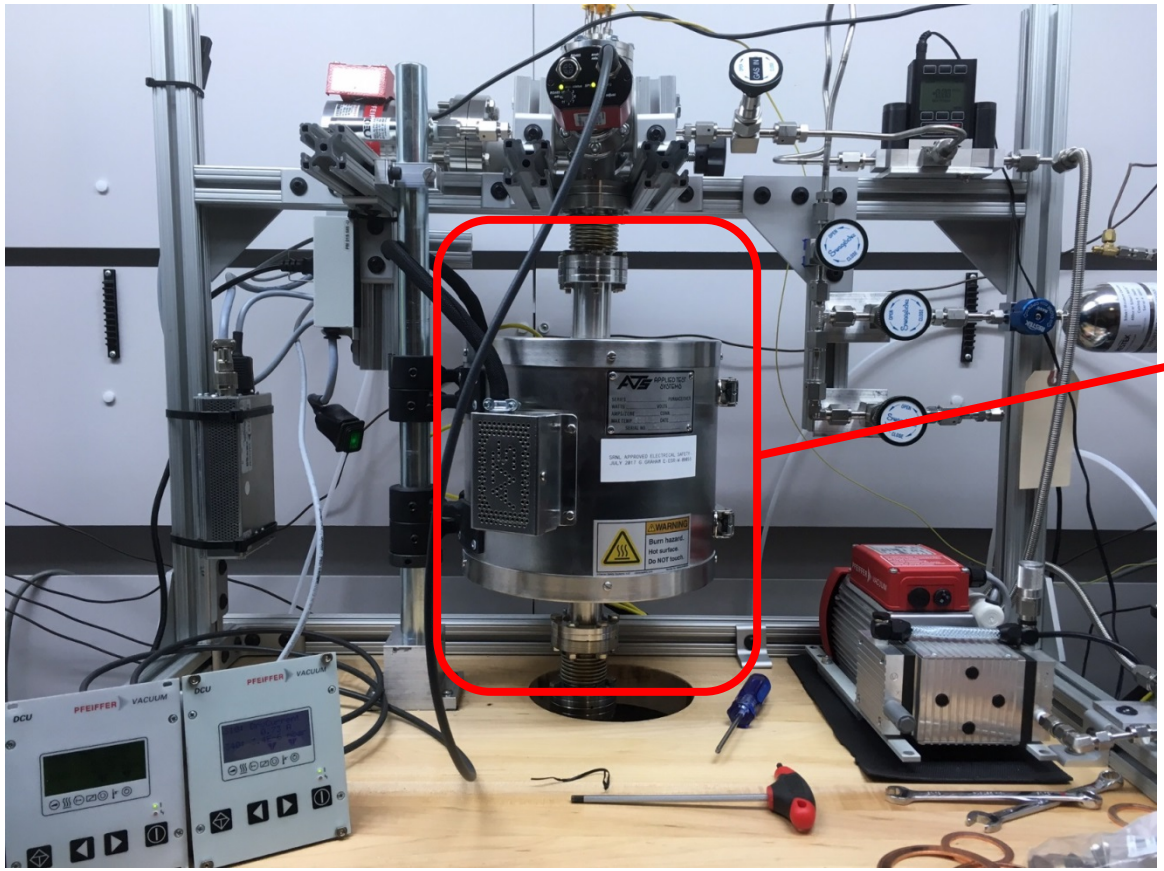


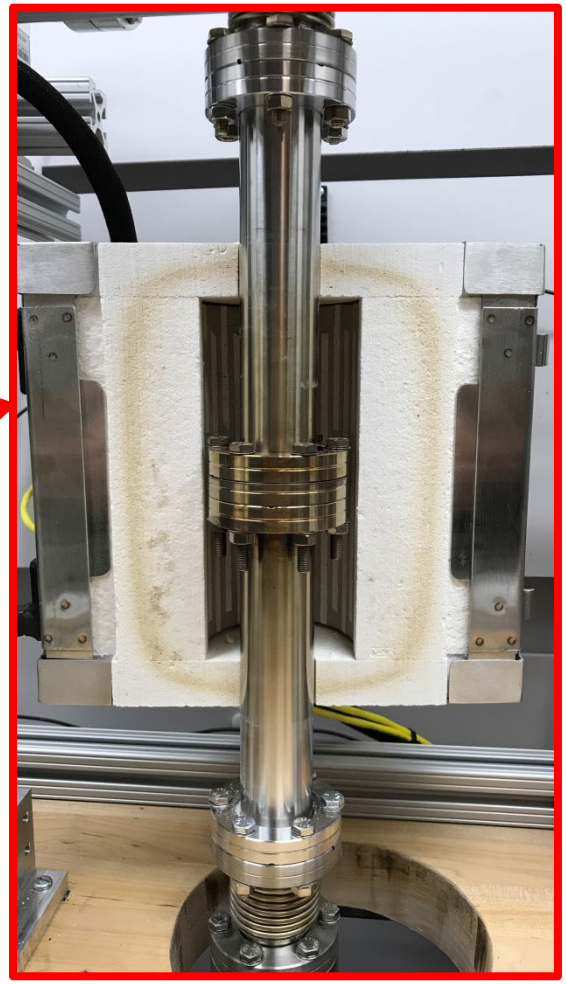
Z. Fent et al. “Hydrogen Permeability and Integrity of Hydrogen Delivery Pipelines”

Sample Temperature Control via Oven

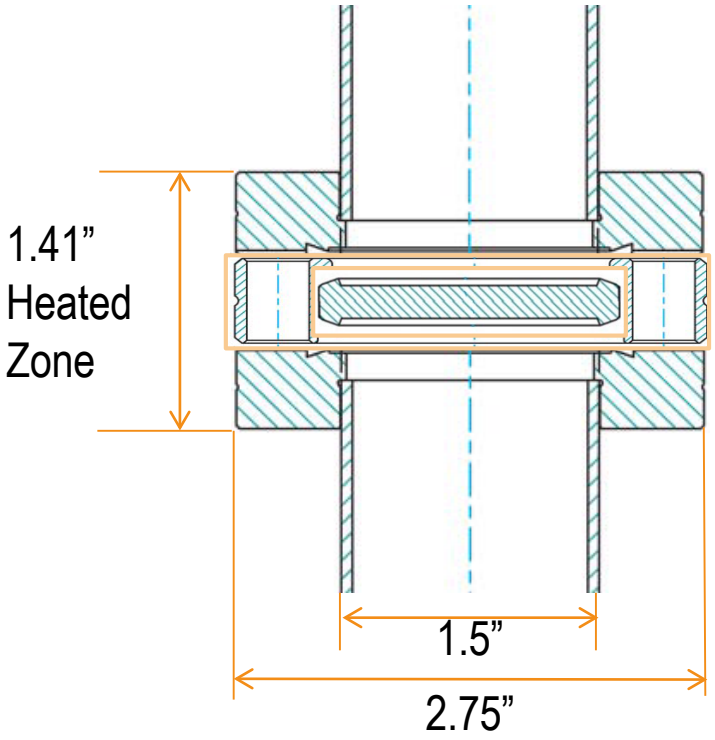
Arrhenius dependence requires accurate temperature control

$$\Phi=\Phi_0 e^{-E_a/RT}$$

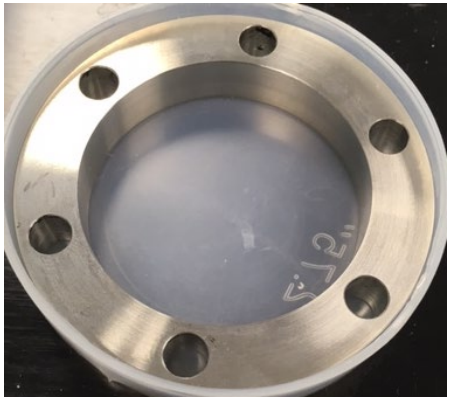




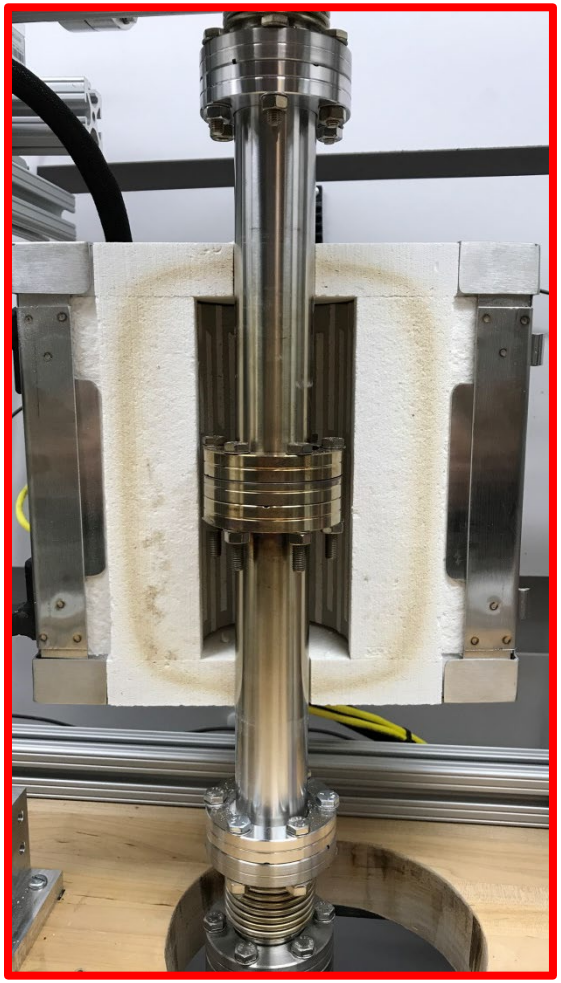
Sample Details



Centering Ring



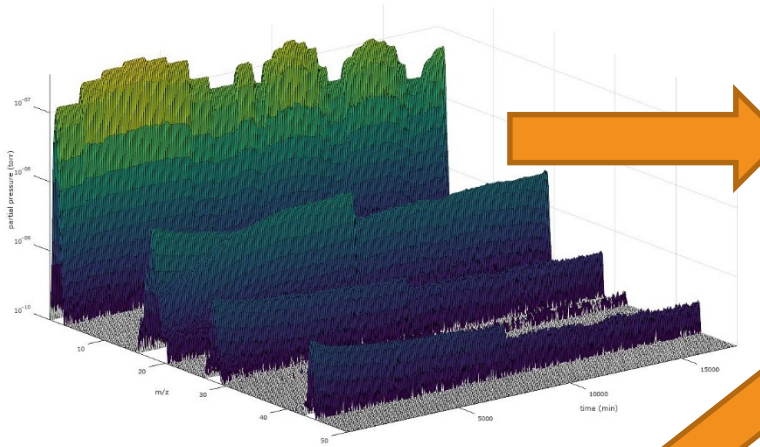
Sample with thinned region for permeation and twin knife edges for sealing to CF flanges

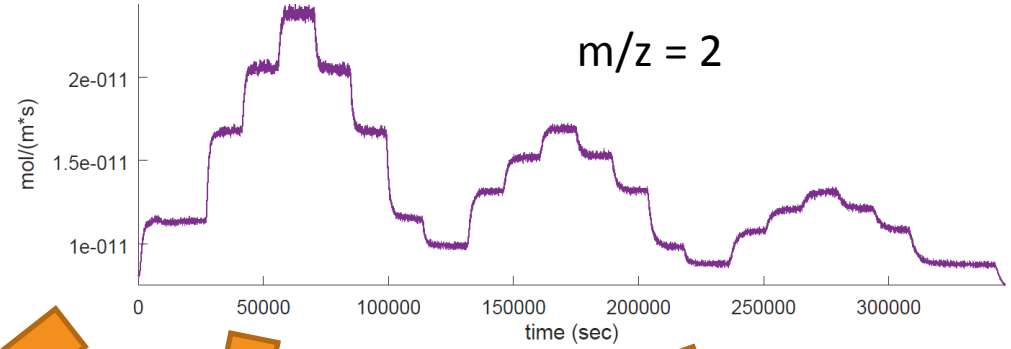


As printed membranes can be tested with minor surface grinding

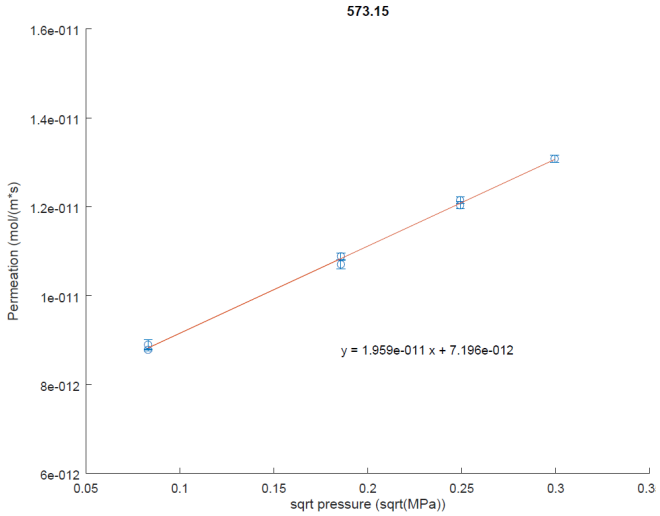
Variable thickness

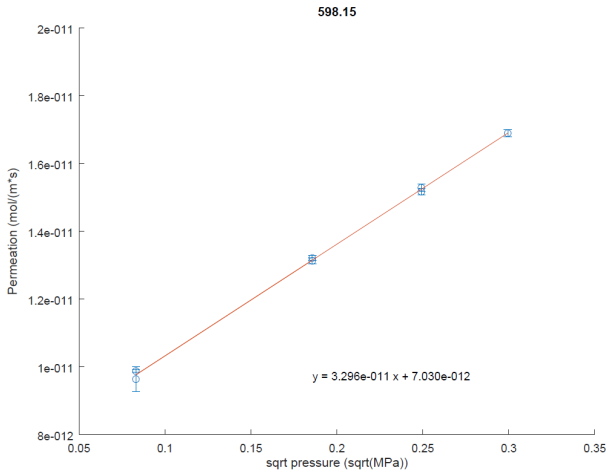
Data Analysis

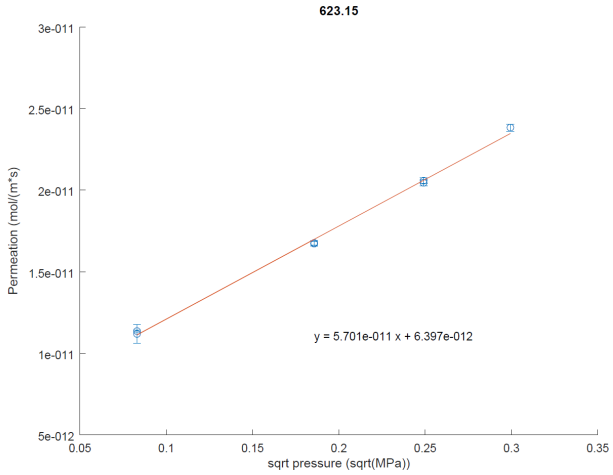




Mass spec current is converted to flow rate using a NIST traceable crimped capillary leak.







KCNSC samples

AM 304SS
As-Received

Conventional 304SS

Samples prepared using a Renishaw AM250 at the Kansas City National Security Campus (KCNSC)

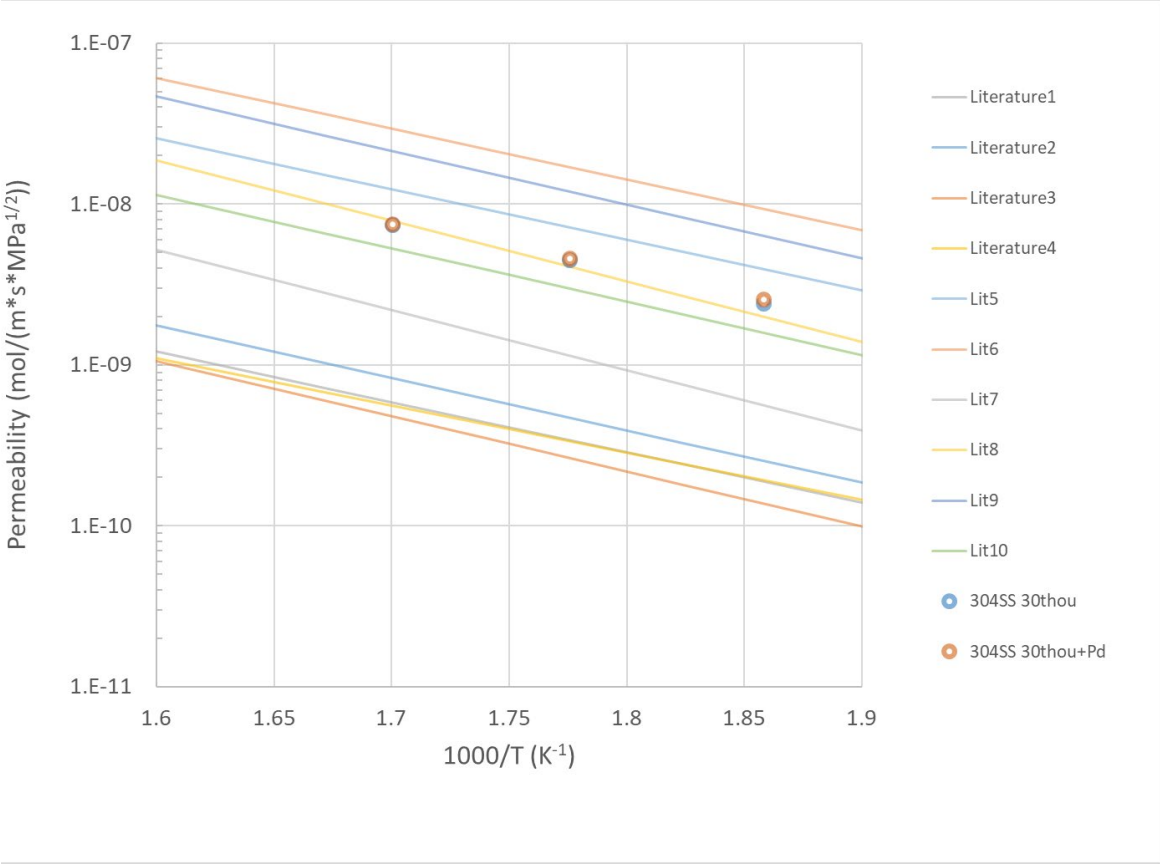
KCNSC samples

AM 304SS
Post-Grind

Conventional 304SS

As printed membranes can be tested with minor surface grinding

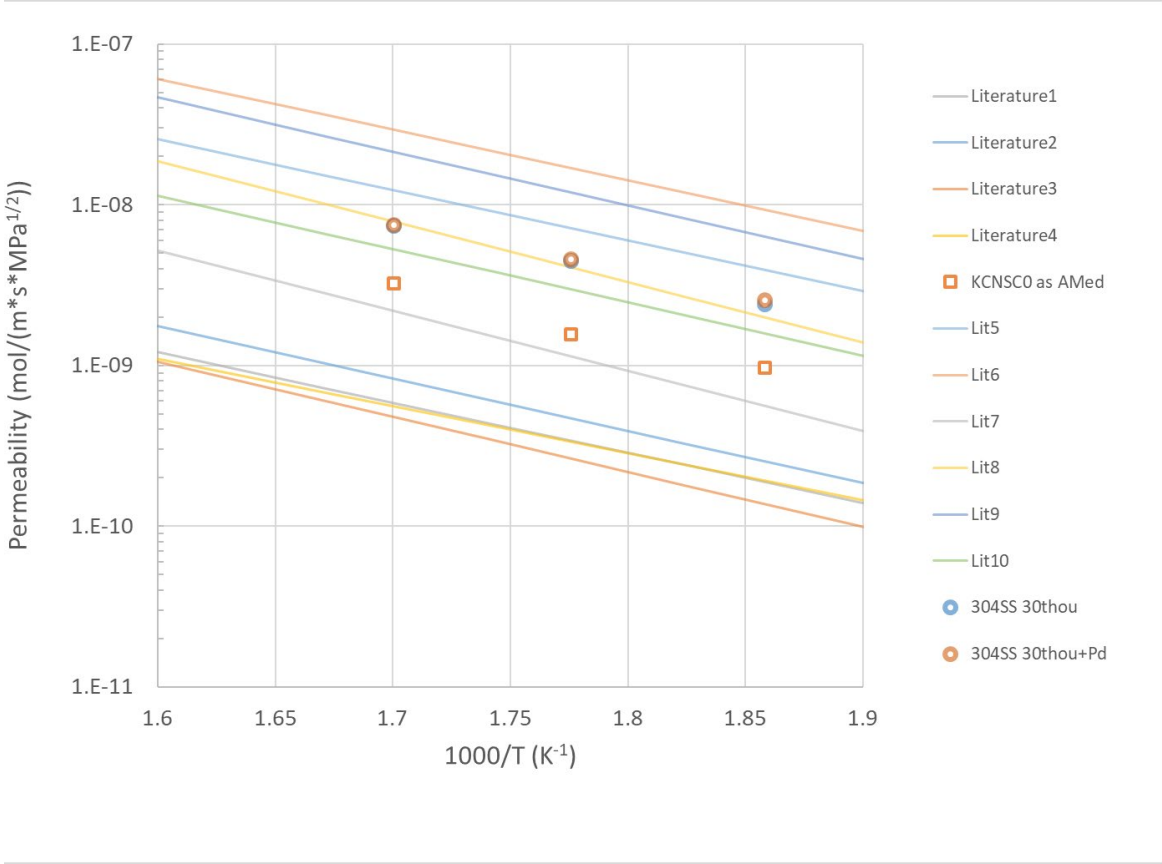
Permeability



- **Controls line up well with literature**

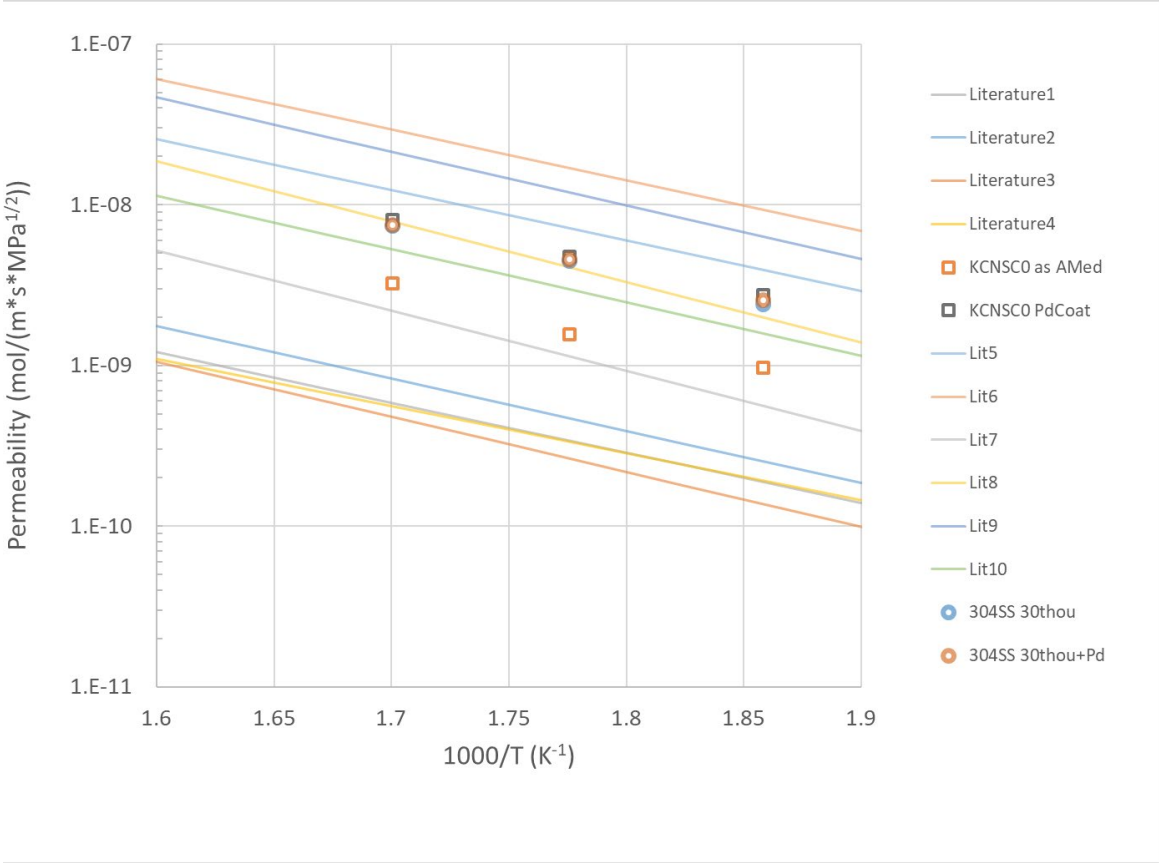
1. San Marchi, C., Somerday, B.P. and Robinson, S.L., 2007. International Journal of Hydrogen Energy, 32(1), pp.100-116.
2. Steward, S.A., 1983. Review of hydrogen isotope permeability through materials (No. UCRL--53441). Lawrence Livermore National Lab.(LLNL), Livermore, CA (United States).

Permeability



- **Controls line up well with literature**
- **As printed samples show lower permeability than conventional forged material**
  - Is the difference due to bulk permeability or a surface limiting process?

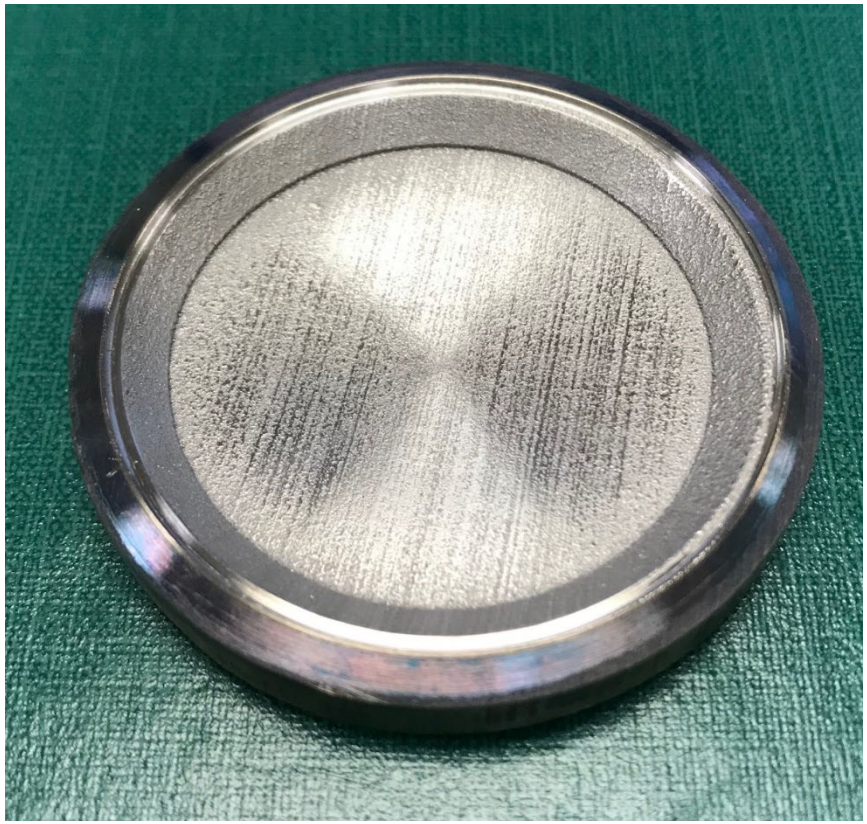
Permeability (Pd coated samples)



- **Controls line up well with literature**
- **As printed samples show lower permeability than conventional forged material**
- **After Pd coating permeability of AM samples is similar to conventional**
  - Suggests rate limiting surface step
  - Oxide on the surface?
  - Could it be surface area related?

Polished KCNSC samples

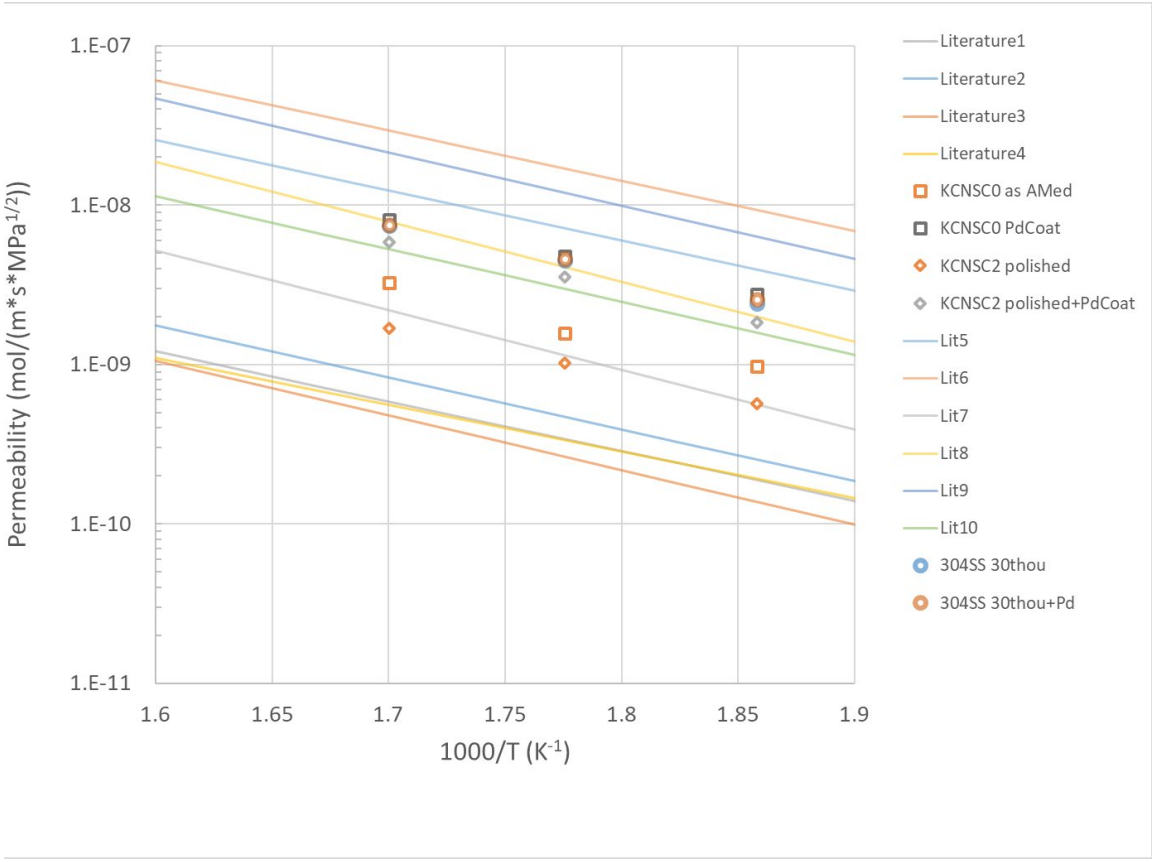
AM 304SS
Post-Grind



Polished 304SS

Printed surfaces of one sample were polished using a polishing cloth.

Permeability



- **Controls line up well with literature**
- **As printed samples show lower permeability than conventional forged material**
- **After Pd coating permeability of AM samples is similar to conventional**
  - Suggests rate limiting oxide on the surface
- **Polished sample shows lower permeability than as received**
  - Likely due to difference in surface area

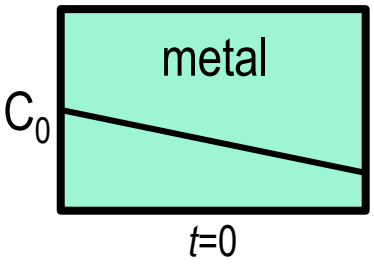
Hydrogen permeation (Diffusivity)

Fick's Second Law

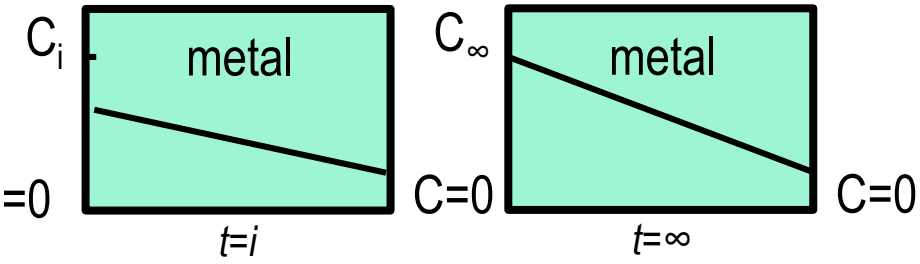
$$\frac{\partial \varphi}{\partial t} = D\frac{\partial^2 \varphi}{\partial x^2}$$

$$P = DK$$

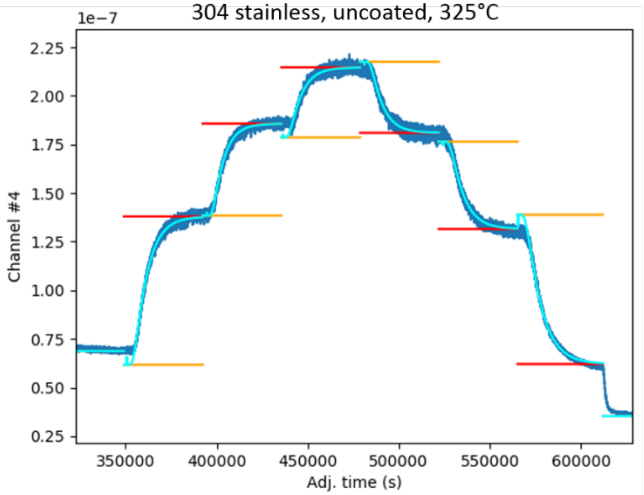
Initial conditions

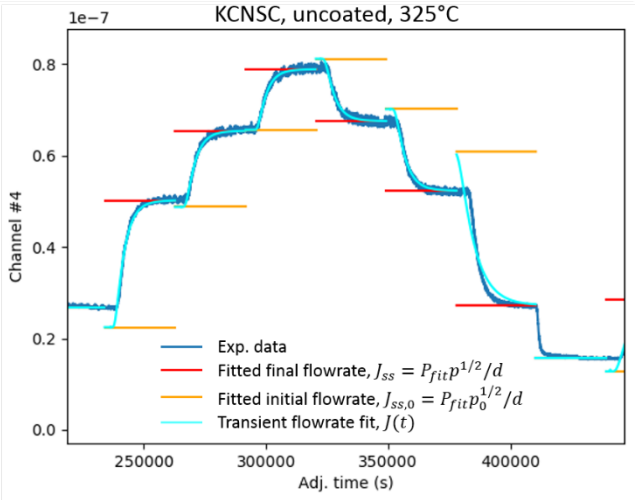


Boundary conditions



$$J(t) = \frac{Pp^{1/2}}{d}\left[1 - 2\left(\frac{p_0^{1/2}}{p^{1/2}} - 1\right)\sum_{n=1}^{\infty}(-1)^n \exp\left(-D\frac{\pi^2 n^2}{d^2}(t - t_0)\right)\right] \; for\, t > t_0$$



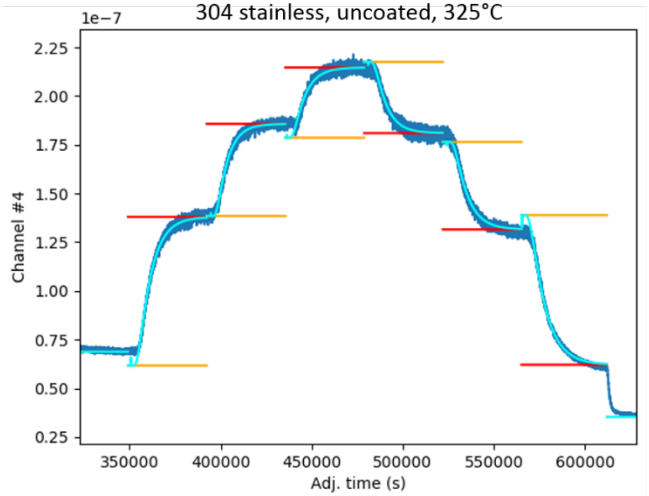


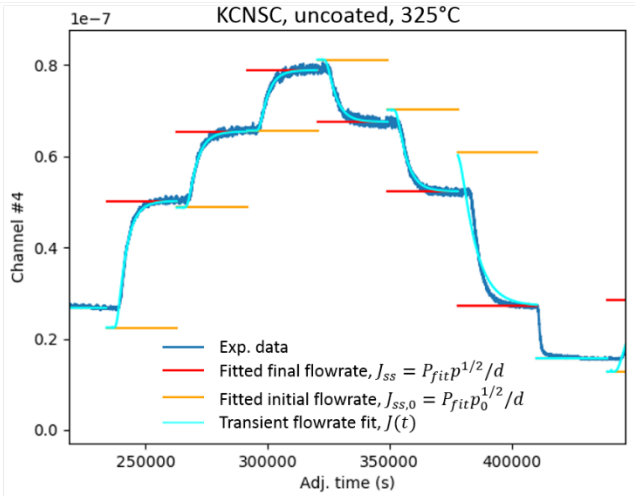
Hydrogen permeation (Diffusivity)

Use a python code to model the data

1. Fit P and D simultaneously
2. User defines number of terms to include in the series
3. Use pressure at previous step and P to get initial flow

Diffusivity of conventional steel can be well described using Fick's Law while the diffusivity AM material cannot



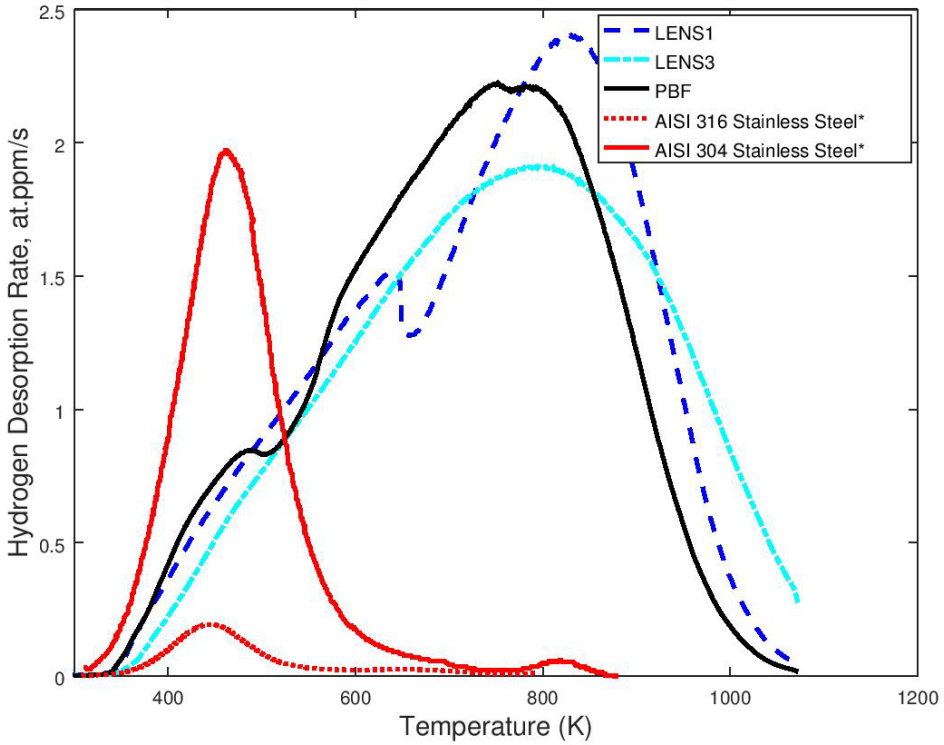


$$J(t) = \frac{Pp^{1/2}}{d}\left[1 - 2\left(\frac{p_0^{1/2}}{p^{1/2}} - 1\right)\sum_{n=1}^{\infty}(-1)^n \exp\left(-D\frac{\pi^2 n^2}{d^2}(t - t_0)\right)\right] \quad for\, t > t_0$$

Hydrogen permeation (Diffusivity-trap sites)

Diffusivity of conventional steel can be well described using Fick's Law while the diffusivity AM material cannot

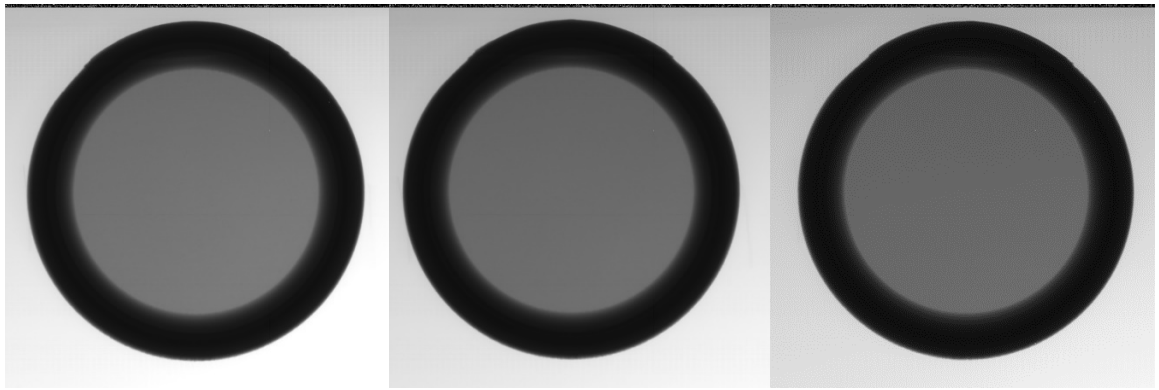
- We attribute the difference to hydrogen trap sites
- Likely due to structural defects



Karnesky et al. "HYDROGEN ISOTOPE PERMEATION AND TRAPPING IN ADDITIVELY MANUFACTURED STEELS" PVP2017-65857

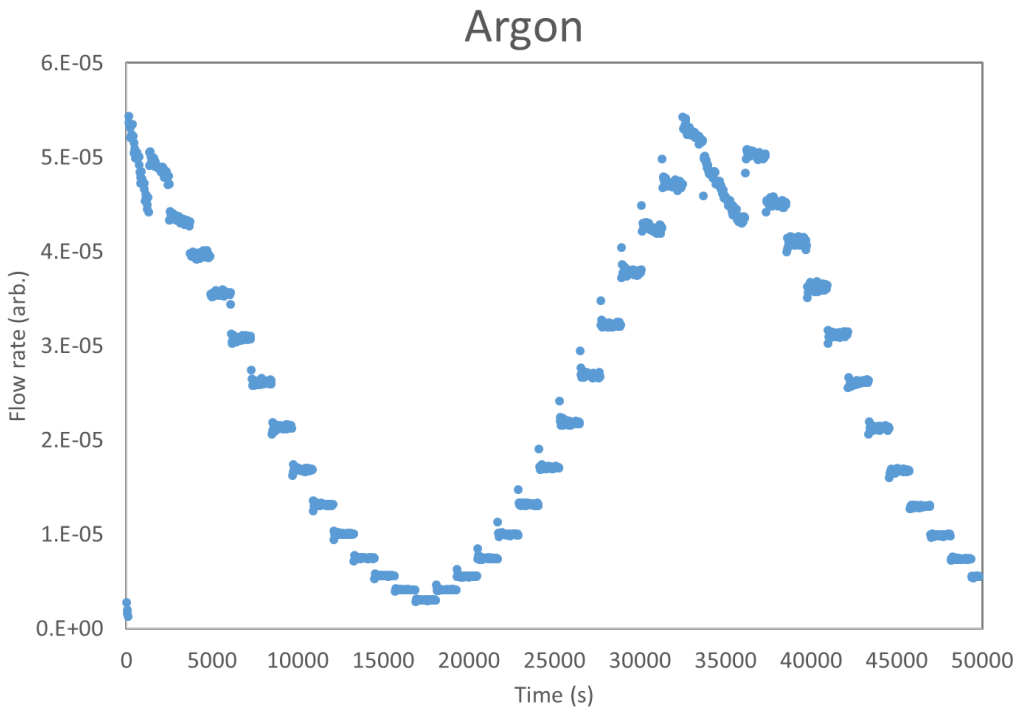
Printing defects

- Witness line (Planar defect)
- After machining the knife edge, it became clear that the defect seems to extend through the thickness.
- Faintly visible in digital radiography
- Likely due to a laser offset.



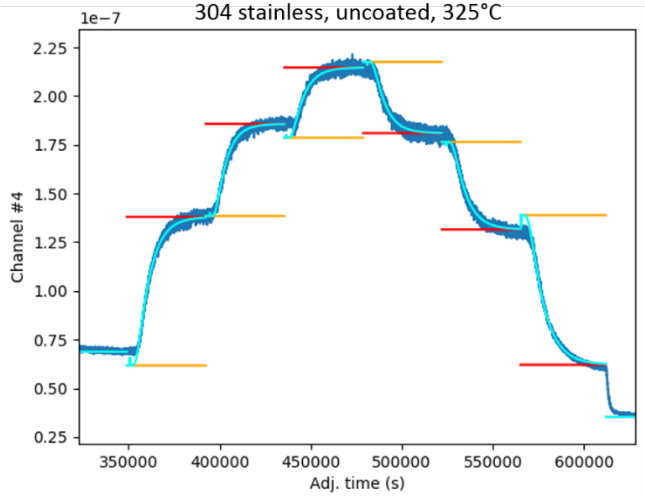
Printing defects

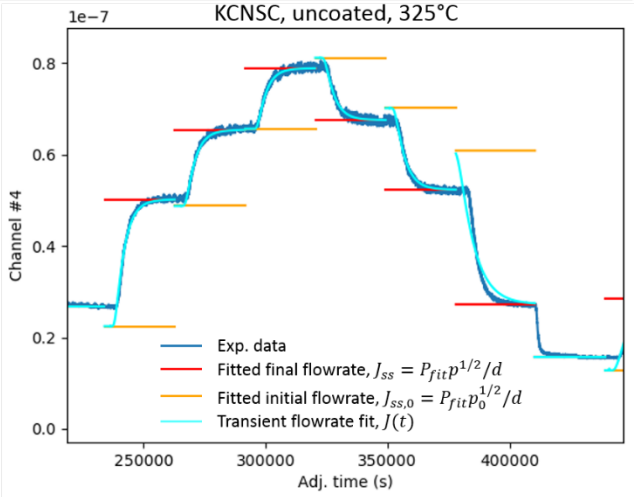
- Samples were not leak tight
- Permeability run performed with Ar as the test gas
- Pinhole in the planar defect
- Printing defects have significant effects on material performance



Conclusions

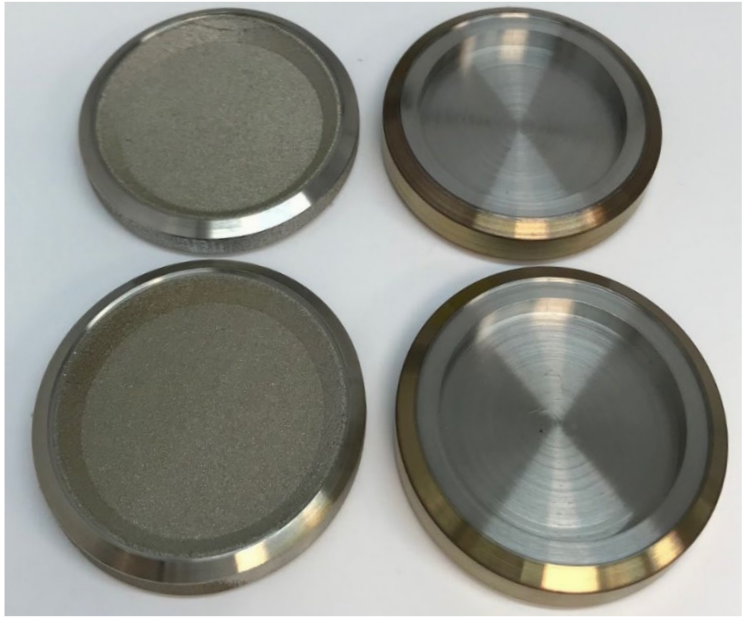
1. Bulk permeability of AM steel is similar to conventional
2. Printing defects lead to significant effects on material performance
3. Surface oxide may play a role in actual device performance
4. Unlike conventional material the transient portion of the permeation measurement for AM material cannot be well fit using Fick's law
5. We attribute the deviation to hydrogen trapping
6. Trapping is likely due to structural defects
7. The enhanced trapping is likely insignificant for hydrogen or deuterium service but could be critical for materials in tritium service.





Future work

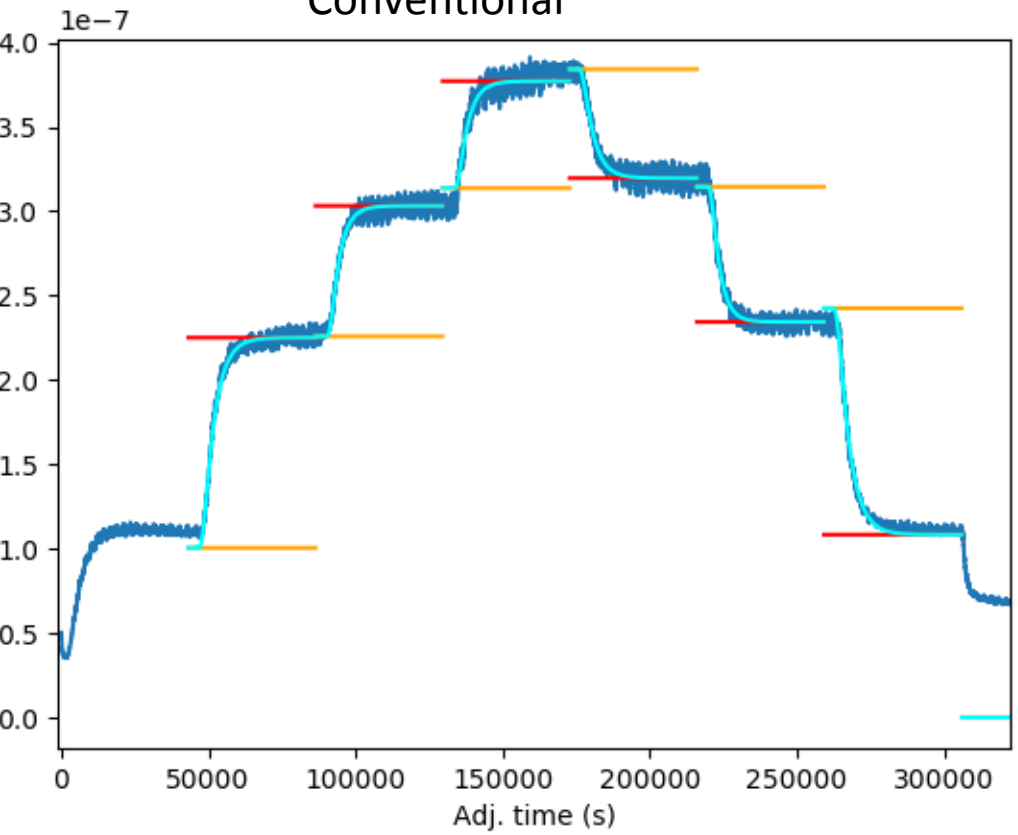
1. Thermal Desorption Spectroscopy to determine the nature of the traps
2. Complete surface effect study
3. Refine/Quantify model
4. Add Darcy's Law term to model



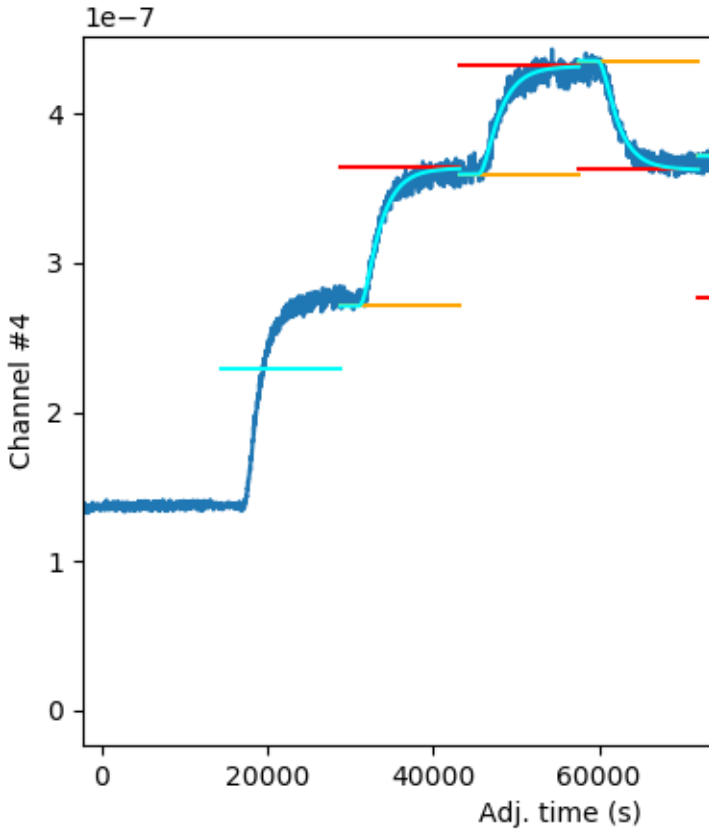
The bulk permeability of AM steel is similar to conventional, however the nature of the diffusion through the lattice appears different due to differences in trapping. The enhanced trapping is likely insignificant for hydrogen or deuterium service but could be critical for materials in tritium service.

Supporting Info

Conventional



AM



Fit machined LANL samples