

T R A N S A T O M I C

T H E L O S T M O D E R A T O R

T H E U S E O F Z I R C O N I U M H Y D R I D E I N R E A C T O R
A P P L I C A T I O N S

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INTRODUCTION

What is the significance of an additional functional moderator material from a core design perspective?

In order for nuclear reactors to achieve and maintain criticality it is necessary to minimize neutron absorption outside of the fuel. As a result, there exist a limited number of elements or isotopes, shown in Table 1, that can be used in the design of functional thermal/epithermal reactor cores. In recent decades, the field of core design has generally been confined to geometry manipulation, as many of the functional combinations of materials have already been explored. The addition of a new moderator material has the potential to open up an entirely new array of moderator fuel coolant combinations. With the potential for smaller, more power dense reactor cores, one of these combinations could hold the key to renewed economic competitiveness for nuclear in the global energy market. This paper addresses the feasibility of one such moderator, zirconium hydride, in reactor applications. Analysis into the allowable operational temperature ranges, expected hydrogen loss and neutronic considerations are discussed.

Table 1. Elements or isotopes which may be tolerable in thermal/epithermal high-temperature reactor fuels. [1]

Material	Neutron Absorption Cross Section (barns at 0.025 eV)	Material	Neutron Absorption Cross Section (barns at 0.025 eV)
¹⁵ N	0.000024	Zr	0.18
O	0.0002	P	0.21
² H	0.00057	Al	0.23
C	0.0033	H	0.33
F	0.009	Ca	0.43
Be	0.01	S	0.49
Bi	0.032	Na	0.53
⁷ Li	0.033	³⁷ Cl	0.56
¹¹ B	0.05	Sn	0.6
Mg	0.063	Ce	0.7
Si	0.13	Rb	0.7
Pb	0.17		

PRIOR REACTOR APPLICATIONS

How much experience is there for metal hydrides in reactor applications?

Metal hydrides are intriguing moderators because of their high hydrogen density and wide range of allowable operational temperatures. [2] They have been often looked at for applications in which the weight and volume of a reactor needs to be minimized. Zirconium-uranium hydride fuel was employed early on in the 1950s and 60s by both the System for Nuclear Auxiliary Power (SNAP) program [3] and General Atomics in their TRIGA research reactors. [4] Metal hydrides acting exclusively as moderators were examined in the 1960s through to the 80s in the Aircraft Nuclear Propulsion (ANP) program, the German compact sodium-cooled reactor project, and the Soviet Topaz II reactors, with ANP using yttrium hydride and the others zirconium hydride. [5] [6] [7]

MANUFACTURING AND FABRICATION

How is zirconium hydride manufactured?

Producing nuclear grade zirconium hydride requires high purity starting materials. As zirconium readily reacts with elements present in the atmosphere (oxygen, nitrogen, etc.) and forms alloys with other common metals, it must be electrochemically reduced prior to hydriding. One method for reducing zirconium comes through contacting the metal with alkaline earth hydrides such as calcium hydride, at elevated temperatures. [8] Once zirconium has been reduced, the most common method for producing the hydride is to subject the metal to a hydrogen atmosphere at elevated



temperatures, allowing the hydrogen to diffuse through the metal until an equilibrium concentration is reached. If special precautions are not taken, hydriding will almost always induce cracks in the material, as the density of the hydride is lower than the base metal. In order to eliminate or reduce cracking, the hydriding process can be dramatically slowed (i.e. 5 days for a 1" diameter rod), or alternatively, a small amount of carbon can be added to the metal (0.3 to 0.5 wt%). [5] Hydriding the metal without regard for cracking can be done if the resulting product is turned into a powder and then reformed through a sintering process, however, this method almost always yields inferior products with respect to hydrogen density, thermal conductivity, and strength. [5] [9]

The ease with which zirconium hydride can be machined is largely a function of the H/Zr ratio in question. When the H/Zr ratio is less than 1, the material can be turned on a lathe, cold-forged, ground, shaped, drilled, or tapped. If the ratio exceeds 1, the hydride becomes very brittle and much more difficult to machine. [5]

COST

What is the cost of manufacturing zirconium hydride?

Data from the German compact sodium cooled reactor project [6] indicated that delta phase zirconium hydride rods could be manufactured for 45 to 65 US\$ kg⁻¹ in 1964, accounting for inflation, an estimate of 350 to 500 US\$ kg⁻¹ is obtained. Although it is expected that the unit cost could be dramatically reduced when considering scaled production (i.e. thousands of rods per reactor), using the previous estimate indicates that the total cost of zirconium hydride for a commercial scale reactor core [10] is on the order of 20 Million US\$.

STRUCTURE

What is the structure of ZrH?

Zirconium hydride has four distinct phases (Figure 1 & 2). As hydrogen concentration increases, the crystal structure progresses towards that of a fluorite structure, cubic hydrogen contained within a face centered cubic (FCC) zirconium matrix. [10] Variations in lattice parameters between the four phases have the potential to induce cracking in the hydride if phase change occurs as a result of temperature gradient driven hydrogen migration.

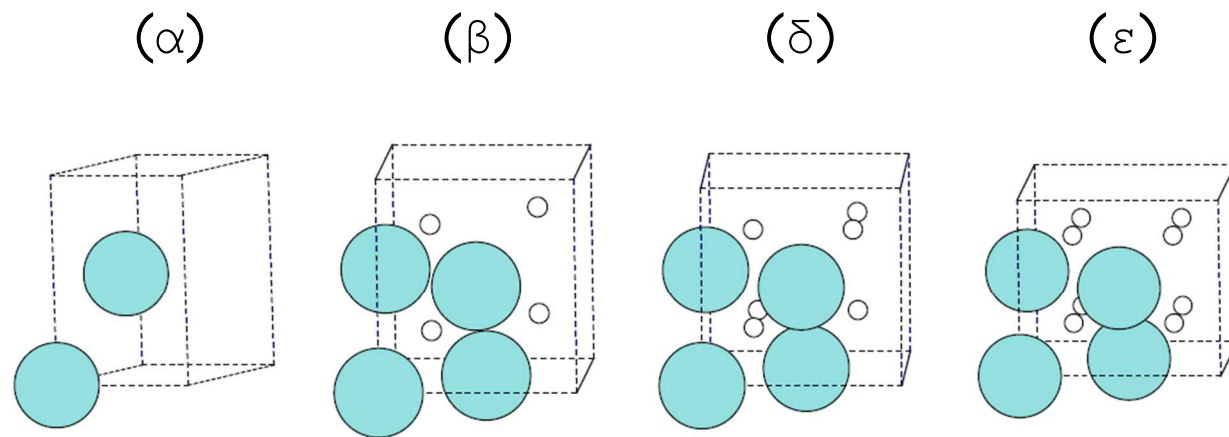


Figure 1. The crystal structures of the primary zirconium hydride phases. From left to right the corresponding phases are α , β , δ , and ϵ . [10]



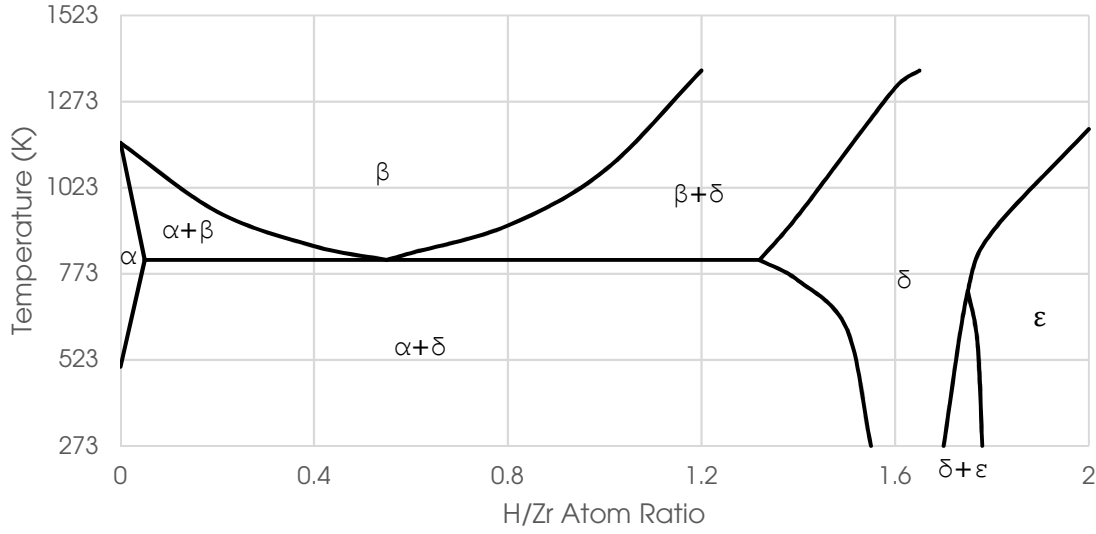


Figure 2. The Zirconium hydride phase diagram. [11]

PERFORMANCE

What are the feasible operational temperature ranges for zirconium hydride?

Hydrogen diffusion analysis was performed using the following methodology, adapted from Olander et al, 2005. [12]

One dimensional hydrogen diffusion for a constant heat of transport ($T_Q = 640 \text{ K}$) is expected to be governed by both the concentration (dC/dx) and temperature (dT/dx) gradients present within the hydride (Eq.1). Eq.1 also includes a term (ρ_{Zr}/M_{Zr}) to convert concentration (C) from the units of mol/cm^3 to H/Zr .

$$J = -D_s \left(\frac{\rho_{Zr}}{M_{Zr}} \right) \left(\frac{dC}{dx} + \frac{T_Q}{T} \frac{C}{T} \frac{dT}{dx} \right) \quad (\text{Eq.1})$$

At steady state, the flux (J) is zero, and therefore the concentration can be solved for as a function of temperature (T).

$$\frac{dC}{dx} = -\frac{T_Q}{T} \frac{C}{T} \frac{dT}{dx} \rightarrow C(x) = c_1 e^{\frac{T_Q}{T(x)}} \quad (\text{Eq.2})$$

The known average (initial) rod concentration (\bar{C}) can be used in order to find the constant c_1 . (This assumption will be addressed further in the later discussion surrounding hydrogen outgassing). Results depend on whether radial or axial diffusion is in question, shown respectively in Eq.3a and Eq.3b. For axial diffusion, the radial concentration is assumed to be constant in order to allow for the one-dimensional analysis to be valid.

$$\text{Radial:} \quad \bar{C} = \frac{\int_0^R 2\pi r \cdot C(r) dr}{\pi R^2} \rightarrow c_1 = \bar{C} R^2 \cdot \left[\sum_0^R e^{\frac{T_Q}{T(r)}} \cdot (r_n^2 - r_{n-1}^2) \right]^{-1} \quad (\text{Eq.3a})$$

$$\text{Axial :} \quad \bar{C} = \frac{\int_0^H C(z) dz}{H} \rightarrow c_1 = \bar{C} \cdot N \cdot \left[\sum_0^H e^{\frac{T_Q}{T(z)}} \right]^{-1} \text{ for } dz = H/N \quad (\text{Eq.3b})$$

To allow for the analysis to be design agnostic, temperature profiles within the hydride have been calculated using simplified sine and cosine functions, with the hottest (T_2) and coldest (T_1) parts of the profile being varied.

$$\text{Radial:} \quad T(r) = (T_2 - T_1) \cdot \cos(r) + T_1 \quad (\text{Eq.4a})$$



Axial:
$$T(z) = (T_2 - T_1) \cdot \sin(z) + T_1 \quad (\text{Eq.4b})$$

Despite its manufacturing challenges, delta phase zirconium hydride is often considered the most likely candidate for moderator applications, as it can accommodate a large hydrogen concentration over a wide temperature range. [2] In an operating reactor, phase change within the moderator could lead to cracking and reduced structural integrity. As a result, restricting phase change within the zirconium hydride was used as a means of assessing feasible operational temperature limits. Linear equations were used as estimates for the delta phase boundaries within the temperature range of 800 to 1200K (Figure 2), with the $\delta+\beta$ and ϵ borders being shown in Eq.5a and Eq.5b respectively.

$\delta+\beta$:
$$C = 0.0006 \cdot T + 1.2207 \quad (\text{Eq.5a})$$

ϵ :
$$C = 0.0005 \cdot T + 0.915 \quad (\text{Eq.5b})$$

The second factor limiting the feasible temperature ranges of zirconium hydride is the partial pressure of hydrogen at the moderator rod's surface. High pressures at the rod's surface increase hydrogen pressure in the rod cladding gap, resulting in higher hydrogen losses through the cladding and increased stress. As pressure limits are highly dependent on the cladding material and geometry, an arbitrary limit of 1 atm was chosen for this analysis, calculated using the following equation. [13]

$$\ln P = 2 \ln \left(\frac{C}{2 - C} \right) + 8.01 + 5.21C - \frac{2.0 \times 10^4}{T} \quad (\text{Eq.6})$$

Taking into account both the phase change and pressure limits, feasible operational temperature ranges for zirconium hydride were calculated for both the axial and radial directions, shown respectively in Figures 3 and 4.

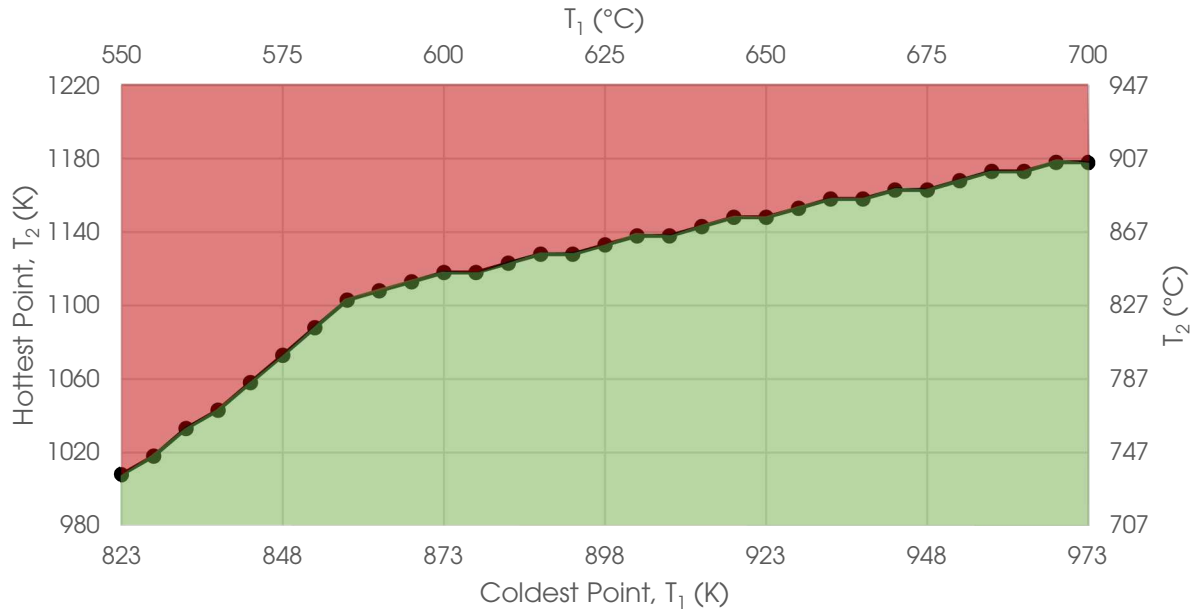


Figure 3. Feasible (green) and infeasible (red) radial temperature profiles for a zirconium hydride moderator rod. Feasible temperatures are defined as those that do not induce phase change while remaining below 1 atm of hydrogen partial pressure at the rod's surface.



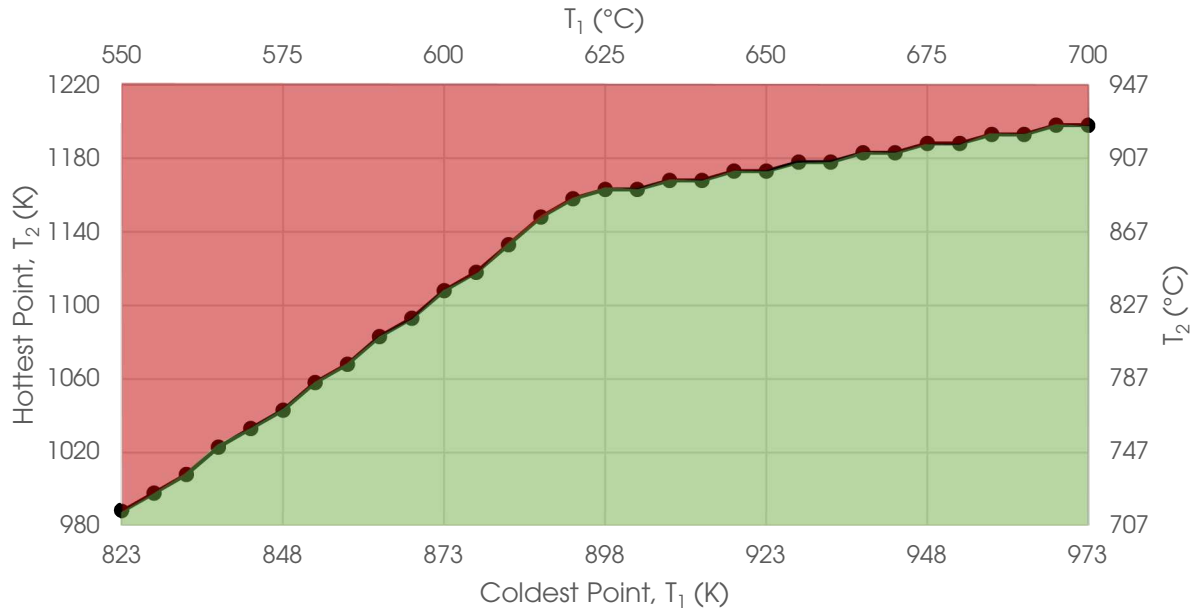


Figure 4. Feasible (green) and infeasible (red) axial temperature profiles for a zirconium hydride moderator rod. Feasible temperatures are defined as those that do not induce phase change while remaining below 1 atm of hydrogen partial pressure at the rod's surface.

How much hydrogen is lost through off-gassing?

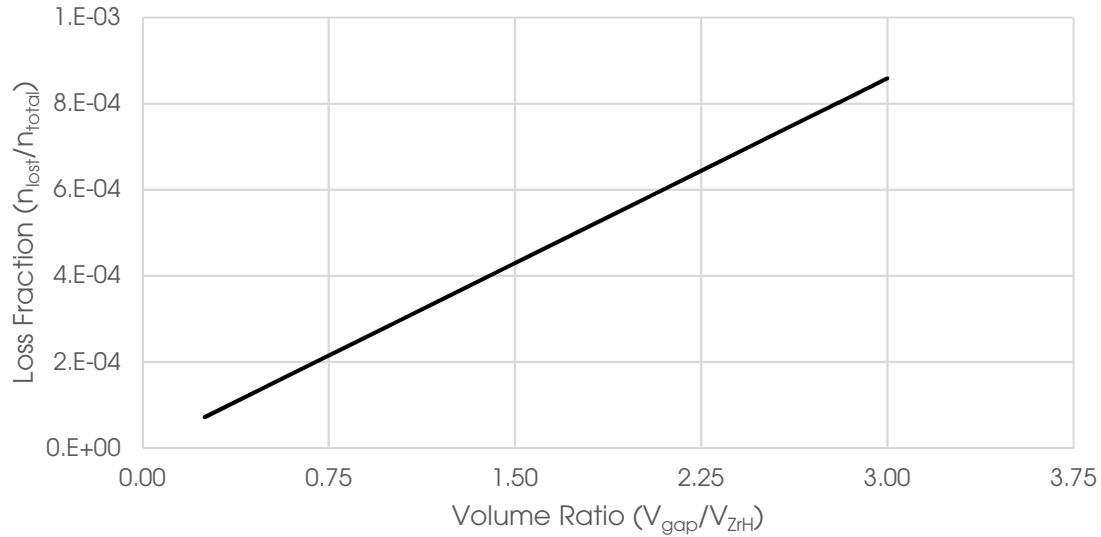


Figure 5. Hydrogen loss fraction as a function of gap moderator volume ratio for a temperature of 873 K. Plot is a visual representation of Eq.8.

Hydrogen uptake and release from the hydride is subject to the following equilibrium.



With the selection of a low hydrogen diffusion coefficient cladding material such as SiC, [14] minimal hydrogen loss through the cladding can be expected during normal operating conditions. It is therefore possible to assess hydrogen outgassing from the moderator using the ideal gas law, allowing equilibrium to be reached once the pressure of



hydrogen exterior to the rod (within the rod cladding gap) is equal to that of the surface. For an initial concentration (\bar{C}) of 1.6 H/Zr, and a surface partial pressure of 1 atm, the fraction of moles lost can be shown to be proportional to the volume of the rod/cladding gap (V_{gap}) and inversely proportional to the temperature of the surface (Eq.8). This indicates that in order to reach a loss fraction of 0.001 (0.1%) at an average surface temperature of 873K, the volume of the gap must be roughly 3.5 times that of the volume of the rod. As gap volumes are expected to be fractions of that of the moderator volume, the previous assumption used in the diffusion analysis that given an impermeable cladding, negligible hydrogen loss is expected, can be seen to be valid within reasonable operating conditions.

$$\frac{n_{lost}}{n_{total}} = \frac{\frac{2PV_{gap}}{RT_1}}{\frac{V_{ZrH}\rho_{ZrH}\bar{C}}{M_{ZrH}}} = 0.2499 \frac{V_{gap}}{V_{ZrH}} \frac{1}{T_1} \quad (\text{Eq.8})$$

What are the neutronic effects of hydrogen redistribution?

Radial redistribution of hydrogen for reasonable rod sizes is expected to have almost no influence on the neutronics of the system, however, axial redistribution may have an influence, as hydrogen accumulation at the ends of the rods shifts moderating power closer to the edges of the reactor core. In order to assess the extent of this negative feedback effect, the temperature profile from Figure 4 ($T_2 = 1163 \text{ K}$ & $T_1 = 898 \text{ K}$) that allowed for the most extreme hydrogen redistribution (Figure 6) was assessed using the Monte Carlo neutronics software Serpent 2. [15]

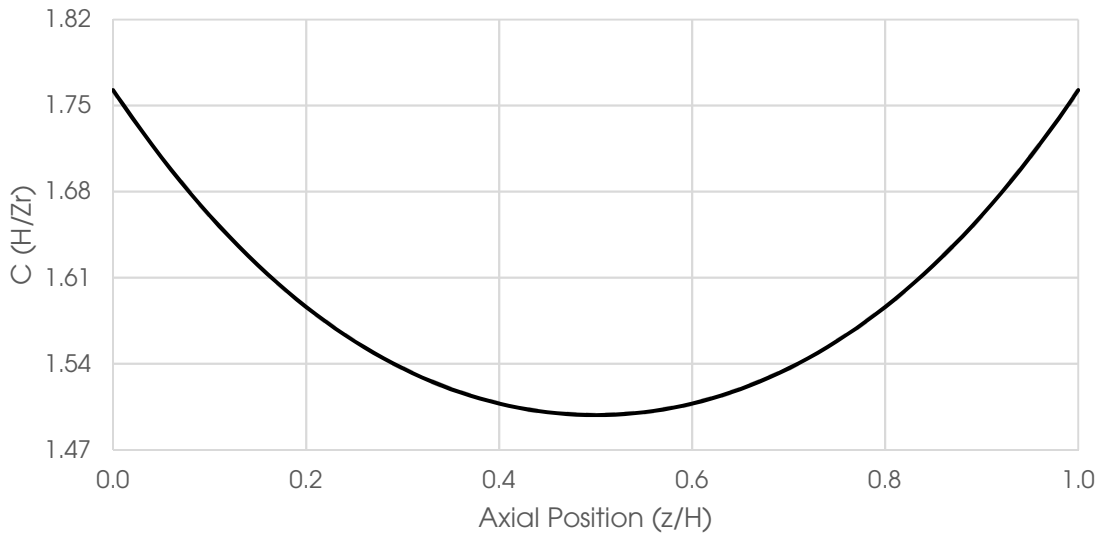


Figure 6. Equilibrium hydrogen concentration as a function of axial position for a temperature profile of $T_2 = 1163 \text{ K}$ and $T_1 = 898 \text{ K}$ (Eq.4b).

Using a short core of 1 m to exaggerate the potential effects of redistribution (large axial flux gradient), flux profiles for both the original 1.6 H/Zr homogenous rod and the redistributed rod (Figure 6) were calculated. As shown in Figure 7, the redistribution has a very minimal effect on the neutron flux profile, in part due to the inverse relationship that H/Zr holds with the density of Zirconium Hydride (Eq.9).

$$\rho_{\delta-ZrH} \left(\frac{g}{cm^3} \right) = -0.0939 \cdot C \left(\frac{H}{Zr} \right) + 5.8088 \quad (\text{Eq.9})$$

When comparing the reactivity change between the two calculations, a loss of 515 pcm can be seen to occur when progressing towards the migrated configuration. Although this is a benefit in terms of the safety of the reactor (negative feedback), the extent to which it will play a role in operations is expected to be minimal. The time scale for redistribution to reach 75% of equilibrium can be estimated with Eq.10. [12] Using an approximate diffusion



coefficient (D) of $10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 700°C [2] for hydrogen within δ -phase zirconium hydride and the previous core height of 1 m, it can be seen that roughly 75 years is expected for the time scale of redistribution.

$$\frac{Dt}{L^2} \approx 2 \quad (\text{Eq.10})$$

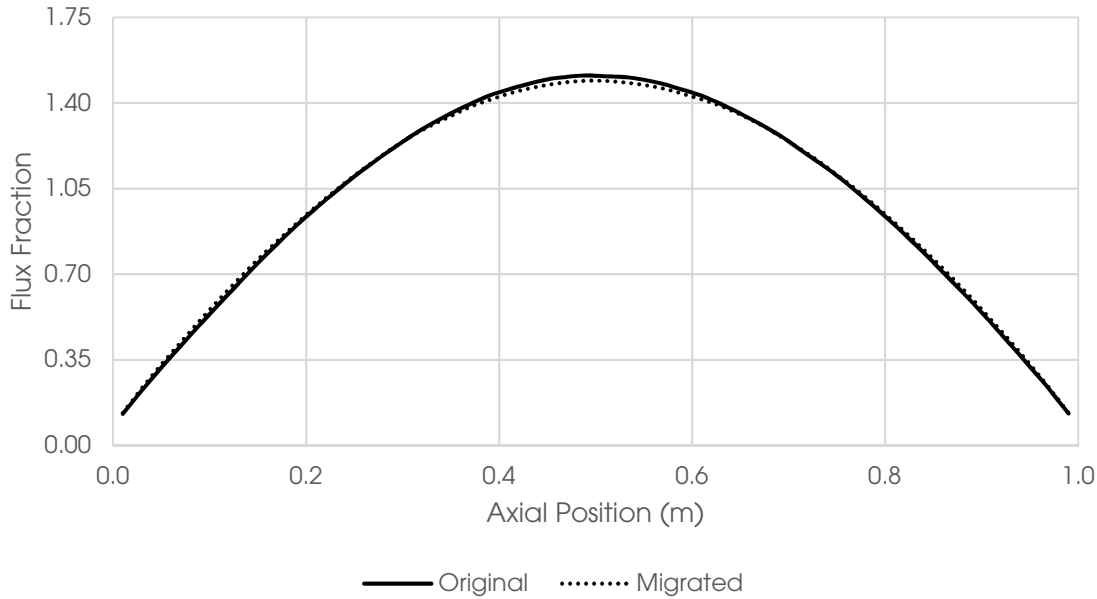


Figure 7. Neutron flux as a function of axial position for a homogenous 1.6 H/Zr rod (Original) and one with the H/Zr distribution indicated in Figure 6 (Migrated).

How does the moderator perform under irradiation?

Although extensive irradiation data exist for zirconium-uranium hydride fuel, there are limited experimental data for the use of a ZrH moderator on its own. In hydride fuels, swelling and void formation is thought to occur primarily as result of fission gas accumulation and radiation damage associated with escaping fission fragments. [12] As these two mechanisms will not exist in hydrides that are exclusively moderators, the swelling behavior of these materials is comparatively unknown. Experiments performed in conjunction with the compact sodium-cooled reactor (KNK-1) and Russian efforts showed that $\text{ZrH}_{1.85}$ samples that had been doped with 1 wt% niobium decreased in density by 0.6 and 5%, when subject to neutron irradiation on the order of $0.6 \cdot 10^{22}$ and $3.0 \cdot 10^{22} \text{ n cm}^{-2}$ ($> 0.1 \text{ MeV}$), respectively. [16] While other data indicated that without the presence of helium impurities, no pore formation was observed upon undergoing irradiation to the level of 23 dpa, [6] indicating that zirconium hydride moderators may not require replacement over the lifetime of a plant.

How does the neutronics performance compare to other moderators?

In comparison to other moderators, the main advantage of zirconium hydrides is its high hydrogen density, allowing for reduced moderator volumes. In the case of a LiF-UF_4 (0.725-0.275) molten salt reactor, graphite allows for a configuration with more excess reactivity, while ZrH can achieve criticality with much larger volumes of salt in the core (Figure 8). The ability to accommodate more salt volume in the core has the potential to reduce overall core size, refueling intervals, and the fraction of fuel salt that exists outside of the core. Coupling this to a wide range of achievable neutron spectrums (Figure 9) allows ZrH to facilitate fuel efficiency increases when compared to the current industry, [17] resulting in potential increases in economic performance.



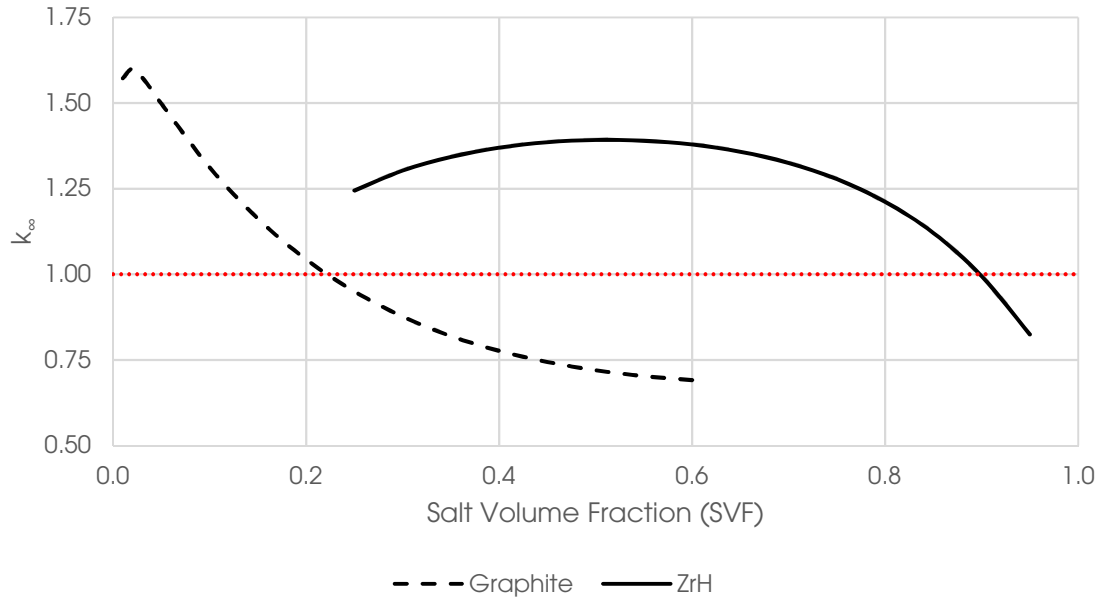


Figure 8. The infinite multiplication factor (k_{∞}) as a function of salt volume fraction for 5cm square pitch graphite moderated and zirconium hydride moderated unit cells. All calculations were performed using the Monte Carlo neutronics software Serpent 2. [15]

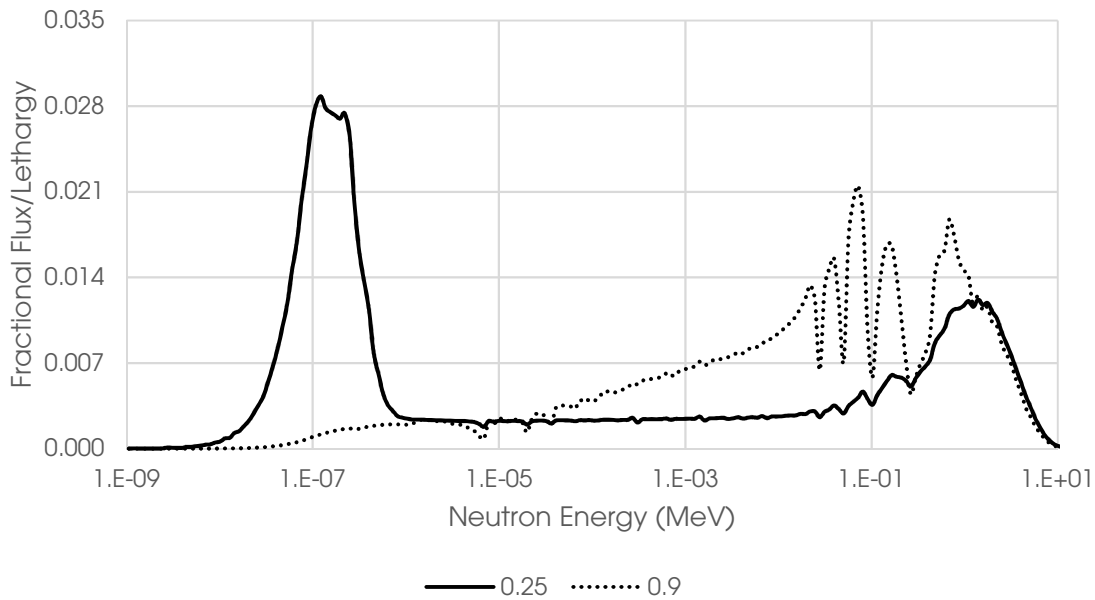


Figure 9. The neutron spectrum for the ZrH unit cells in that achieve criticality ($k_{\infty} > 1$) at the lowest (0.25) and highest (0.9) salt volume fractions. All calculations were performed using the Monte Carlo neutronics software Serpent 2 and were calculated for a uniform material temperature of 900 K. [15]

FUTURE DIRECTIONS & CONCLUSIONS

What additional work needs to be done?

The expanded design space that a new moderator material facilitates could hold the key to reactors with reduced waste profiles, increased economic performance and safety. Initial analysis shows that zirconium hydride has the potential to fulfill these objectives, and additional experimental research will provide further details surrounding its operating characteristics.

Experiments that can reduce the uncertainty surrounding the use of zirconium hydride revolve primarily around evaluating the performance of ZrH under irradiation. Although there are indications that swelling will be minimal at high fluence levels, [6] experiments should be repeated and validated in modern facilities. Assessing the influence of irradiation on hydrogen migration (ex. diffusion coefficient as a function of fluence) will also prove useful. Additional data with respect to scattering cross sections as a function of temperature will also prove useful for assessing to a higher degree of accuracy the neutronic performance of the moderator. Significant uncertainty still remains surrounding the cost of manufacturing, with larger scale production showing potential to dramatically reduce current estimates. Research into manufacturing hydrogen impermeable claddings suitable for reactor environments (such as SiC) will also prove necessary, as low levels of hydrogen outgassing is reliant on minimal losses through the cladding. Hydrogen redistribution analysis should also be repeated computationally, assessing coupled axial and radial diffusion as well as models that include heats of transport as a function of temperature.



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APPENDIX A: PHYSICAL PROPERTIES

Extensive work has already been conducted regarding the physicochemical properties of zirconium hydride, with Figures A1 – A5 summarizing some of the results. [18] [19]

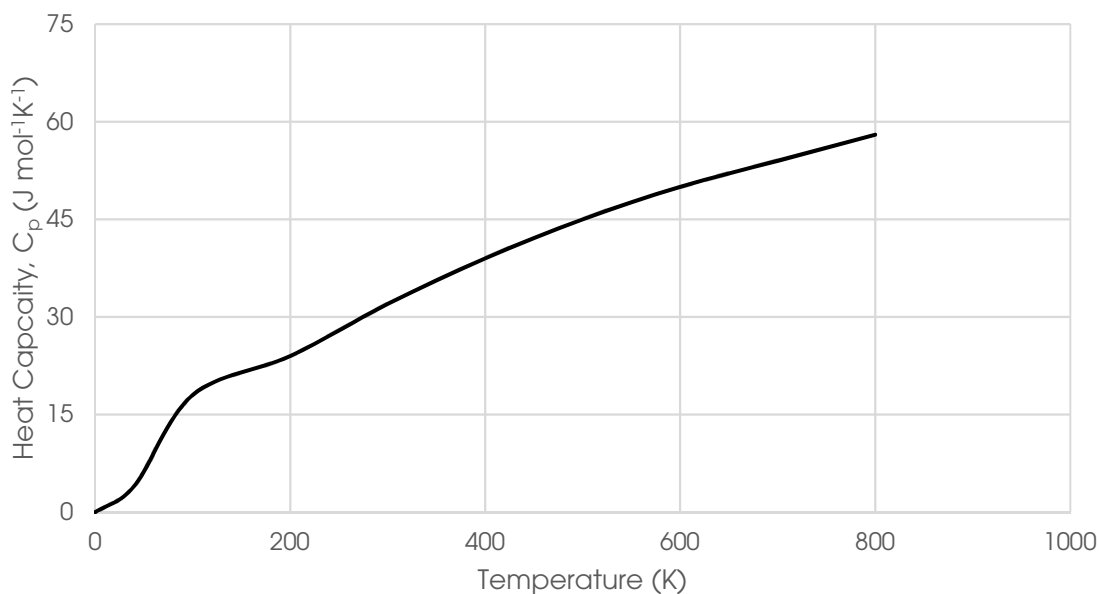


Figure A.1. Heat capacity (C_p) as a function of temperature for δ -phase zirconium hydride ($\text{H}/\text{Zr} = 1.66$). [18]

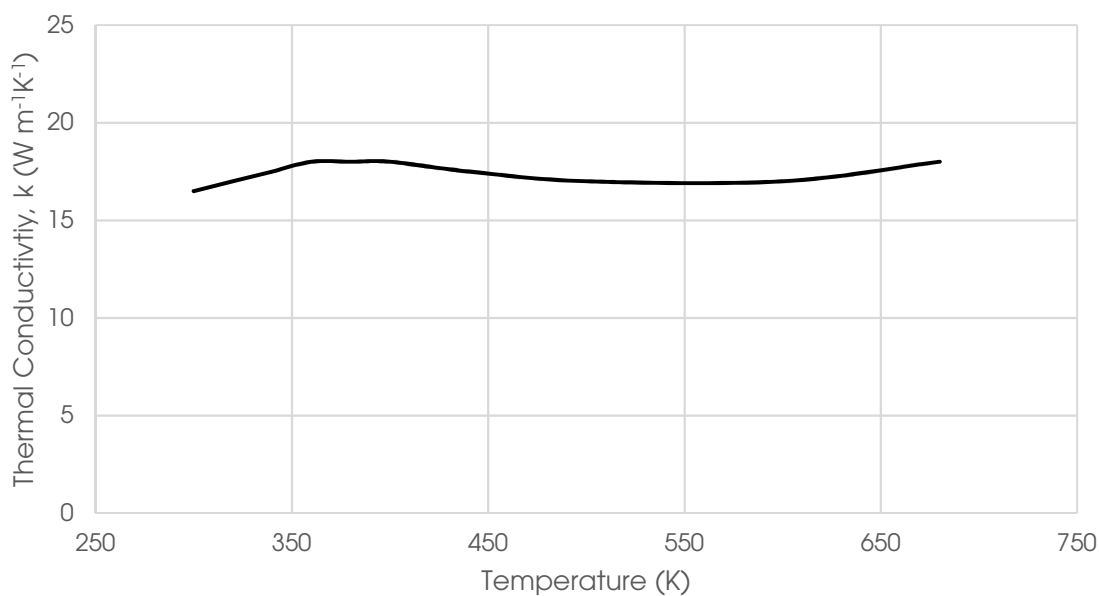


Figure A.2. Thermal conductivity (k) as a function of temperature for δ -phase zirconium hydride. [19]



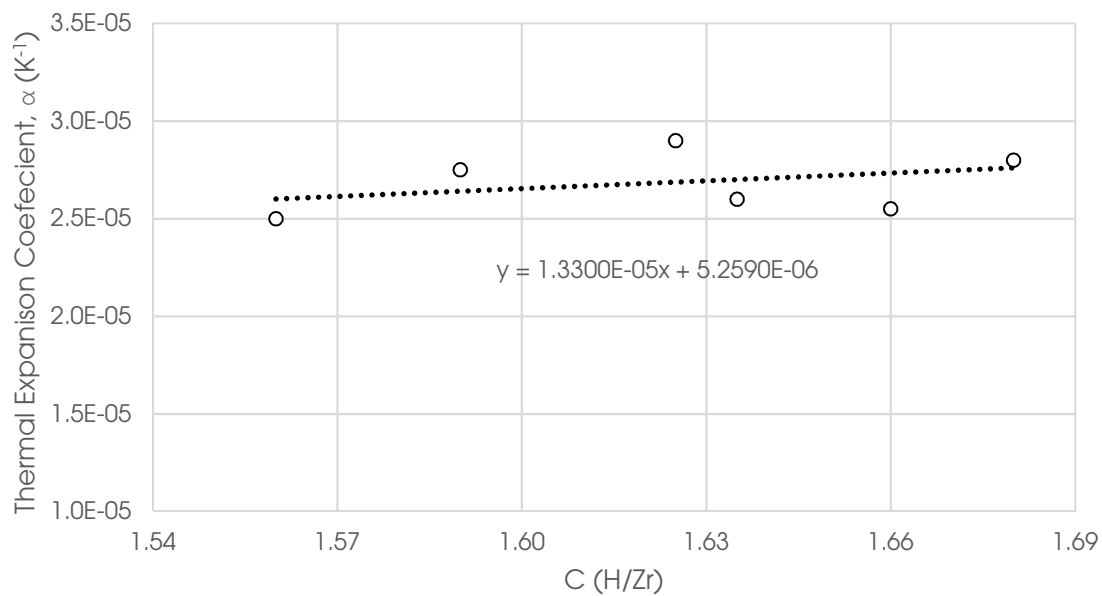


Figure A.3. δ -phase zirconium hydride's thermal expansion coefficient (α) as a function of hydrogen content. [18]

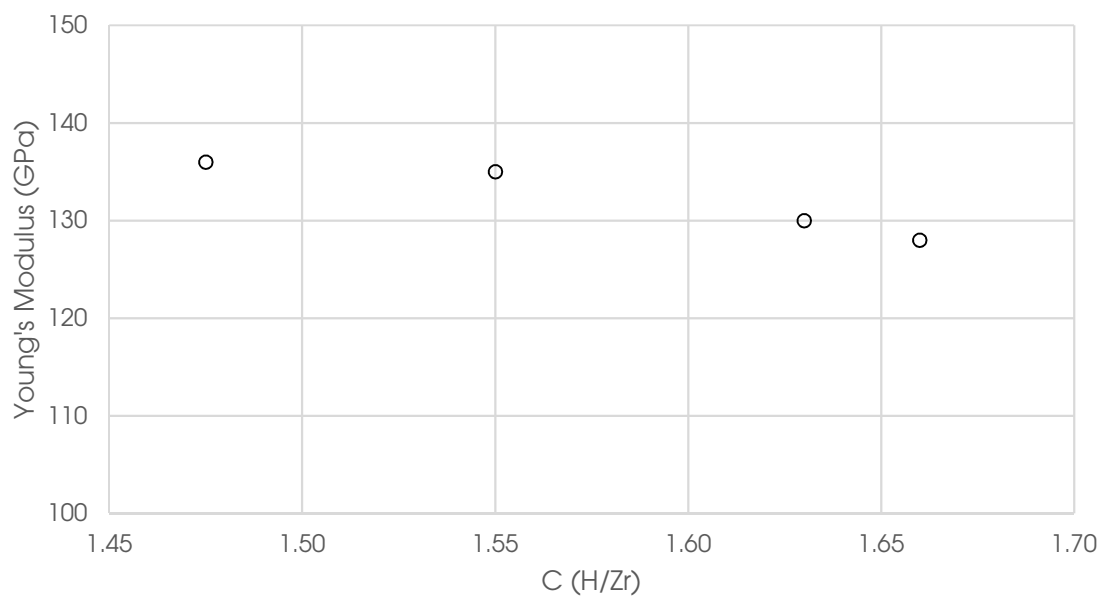


Figure A.4. δ -phase zirconium hydride's Young's modulus as a function of hydrogen content. [18]

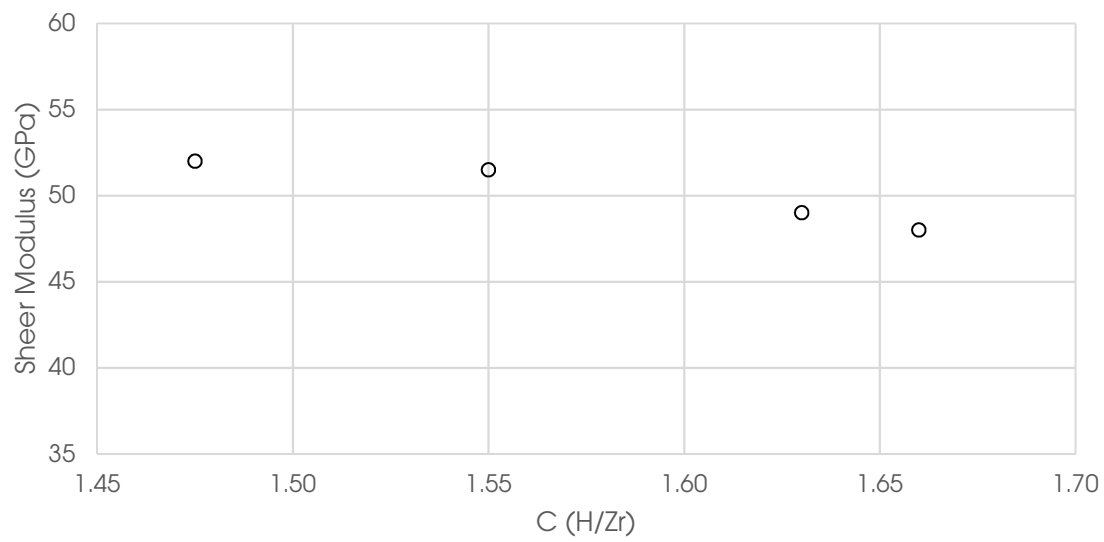


Figure A.5. δ -phase zirconium hydride's sheer modulus as a function of hydrogen content. [18]