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SNAP REACTOR,
SNAP PROGRAM
M-3679 (50th Ed.)

ANNEALING STUDIES ON IRRADIATED SNAP FUEL

(Title Unclassified)

By

F. C. SCHRAG

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ABSTRACT

The SNAP Annealing Program was conducted to determine the dimensional stability of zirconium hydride fuel, 90% Zr and 10% U, by heating irradiated fuel of burnup as high as 0.6 met. at. %. Annealing temperatures of 1400 to 1700°F were selected to evaluate the temperature sensitivity of the fuel in the expected range of fuel centerline temperatures required for SNAP programs.

The annealing program consisted of three major phases as follows:

1) Isothermal annealing at 1400 to 1700°F to determine temperature effects. These tests were conducted on fuel in various zirconium-hydride phases. Insignificant volume changes occurred in all phases with the exception of β phase. Beta hydride phase material swelled from 5 to 29%.

2) Hydriding and dehydriding annealing to simulate various reactor conditions with changes of H_2 content in the fuel. The results of this phase of the program indicated that fuel cracking was a problem when the fuel was dehydrided. Dimensional changes did not occur in the zirconium hydride until the β phase was obtained. Increases in volume as high as 14% were obtained by annealing fuel dehydrided to β phase.

3) Thermal gradient annealing obtained by placing a 100°F/in. gradient on the fuel sample, which would simulate an axial thermal gradient in the reactor. There was no appreciable fuel swelling with the above gradient and actual fuel temperatures of 1200 to 1600°F for as long as 1/2 hr. Volume changes were insignificant when the thermal gradient was reversed or cycled over a total of 4 hr.

In general, it appears that SNAP fuel irradiated to burnup as high as 0.6 met. at. % is dimensionally stable above the β phase; however, there is a relationship between fuel swelling and temperature for β-phase material.

I. INTRODUCTION

The objective of SNAP Annealing Program was to measure the dimensional changes in irradiated SNAP fuel with burnup ranging from 0.2 to 0.6 met. at. % when heated isothermally in the temperature range from 1400 to 1700°F. The experiments were also designed to study the possible dimensional changes caused by varying the hydrogen composition of fuel; that is, inducing phase changes in the fuel, axial thermal gradients on the fuel, and elevated short- and long-term thermal soaking of various zirconium hydride phase samples.

A. SOURCES OF MATERIAL

The irradiated fuel for the annealing studies was obtained from the S8ER reactor, the NAA 115-1 irradiation experiment, and the NAA 116-1 and -2 irradiation experiments. Samples were selected to yield burnup levels up to 0.6 met. at. %, carbon concentrations from 0 to 0.4 wt %, H/Zr* ratios from 0.8 to 1.85, and centerline operating temperatures of 500 to 1550°F. Unirradiated standards were run along with the irradiated material. The standards were obtained from production materials used for all SNAP experiments. The following is a brief description of the sources of the material.

1. SNAP 8 Experimental Reactor (S8ER) Core

The S8ER core[1] was 14 in. high and 9 in. in diameter and consisted of 211 fuel elements, approximately 0.560 in. in diameter. NaK-78 was used for primary coolant. The fuel elements contained hydrided 90 wt % Zr - 10 wt % U alloy clad in 0.010-in. -thick Hastelloy N. The uranium enrichment was 93.15%. The cladding was coated on the inside with a ceramic hydrogen retention barrier. A description of the fuel elements is presented in Table 1.

*H/Zr, in this report, indicates an "effective" hydrogen-to-zirconium ratio, calculated on the basis that the zirconium added to the fuel as ZrC does not hydride.

$$(H/Zr)_{eff} = \frac{90.496\,(\text{wt \% H})}{100 - 8.595(\text{wt \% C}) - (\text{wt \% U}) - (\text{wt \% H})}$$

The subscript is sometimes omitted from the $(H/Zr)_{eff}$ term for simplicity.

TABLE 1

S8ER DESIGN CRITERIA

Number Fuel Elements	211
Composition	Zr-U Alloy, Hydrided
Uranium Enrichment (at.% U^{235})	93.15
Fuel Alloy (wt % U in Zr)	10.01
Carbon (wt %)	0.49
Hydrogen Concentration (atoms/cc)	6×10^{22} [$\sim$1.76 $(H/Zr)_{eff}$]
Fuel Rod Diameter (in.)	0.532
Fuel Rod Length (in.)	14.00
Cladding Material	Hastelloy N
Hydrogen Leak Rate at 1400°F (cc/hr)	0.56
Fuel Element Radial Gap (in.)	0.0016

2. NAA 115-1 Irradiation Experiment

The NAA 115-1 Irradiation Experiment was designed to test and evaluate sublength S8ER fuel elements which contained zirconium-uranium hydrided fuel.[2] The experiment contained 12 sublength fuel rods, $\sim$0.532-in. diameter by 4 in. long. The composition of the fuel was 90 wt % Zr and 10 wt % U enriched to 93.1% U^{235}. Carbon contents were 0.02, 0.1, and 0.4 wt %, and the fuel was hydrided to 5.6, 5.8, 6.0, and 6.5×10^{22} hydrogen atoms/cc [$\sim$1.6 to 1.9 $(H/Zr)_{eff}$]. The cladding was 0.010-in.-thick Hastelloy N, with a continuous ceramic hydrogen barrier coating on the inside.

The NAA 115-1 experiment was designed for a nominal of 0.4 met. at. % burnup in $\sim$10,000 hr total irradiation time with operating centerline temperatures ranging from 1300 to 1600°F.

3. NAA 116 Irradiation Experiment

The NAA 116 Irradiation Experiment contained two capsules, each consisting of a fuel specimen train within a nickel flux depressor tube, which were irradiated at low temperature.[3] The two trains contained 10 fuel specimens each. Each fuel specimen contained 5 zirconium-uranium hydride fuel slugs encapsulated in a Type 304 stainless steel tube. The fuel diameter was 0.290 in., the 3 center

slugs were 3/4 in. long, while the 2 outer slugs were 0.3 in. long. Various fuel compositions were irradiated to 0.6 met. at. % burnup at 500°F centerline temperature. The uranium varied from 5 to 20 wt %, carbon varied from 0.2 to 0.45 wt %, and hydrogen varied from 1.2 to 1.8 wt % from slug to slug.

B. PURPOSE OF STUDY

Annealing studies on SNAP irradiated fuels were performed to examine the possibilities of a correlation between swelling induced by annealing irradiated fuel at temperatures in the range of 1400 to 1700°F and swelling which occurs in-pile. Fuel samples of varying burnup, H/Zr ratio, carbon additive, and operating temperatures were selected to examine the effect of these variables on dimensional stability. Data obtained in the postirradiation examination of the S8ER reactor showed volume changes of -5.8% to +5.8%[1] based on liquid density determinations. Also, the results of the postirradiation examination of the NAA 115-1[2] irradiation experiment showed fuel volume increases from 1.5 to 4.5%. The results from the NAA 116[3] postirradiation examination yielded volume increases of 1.1 to 5.0% based on density measurements.

Volume changes in uranium-zirconium hydride fuel reflect a combination of hydrogen loss and fuel swelling. The two effects oppose one another: hydrogen loss causes a volume decrease, and irradiation effect on the fuel causes swelling. It is theorized that the fission products generated in the fuel can be agglomerated in zirconium hydride when it undergoes diffusional phase change during operation. Phase changes can be caused by loss of hydrogen through permeation through the cladding, redistribution of hydrogen in the fuel caused by temperature gradients in the fuel, or thermal cycling of the fuel from a low temperature to a high temperature.

It should be understood that only the zirconium in the fuel is hydrided and not the uranium. As the zirconium-uranium alloy is hydrided, the uranium is precipitated out of solution; thus, the zirconium-hydrogen phase diagram is applicable.

Phase change phenomena can be demonstrated on the phase diagram seen in Figures 1 and 2 by the following.

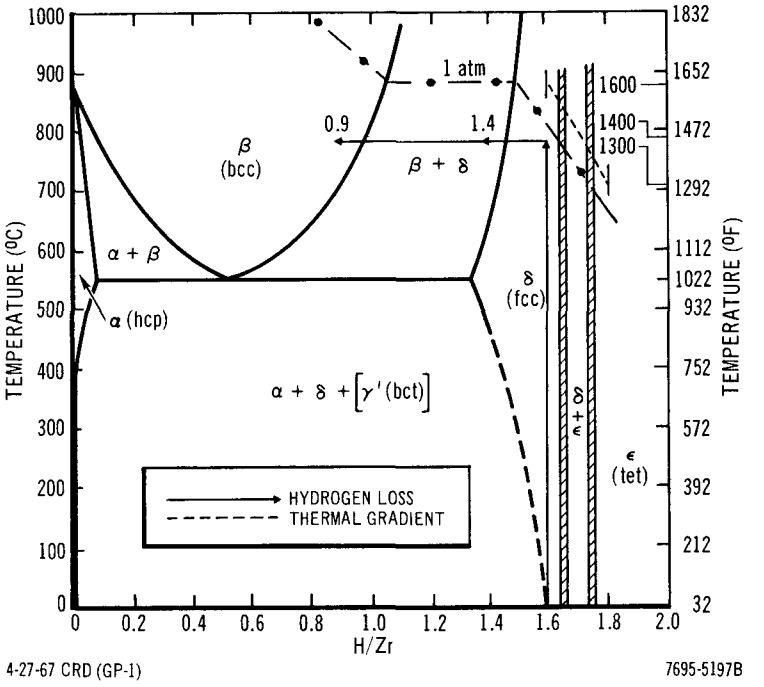


Figure 1. Zirconium-Hydrogen Phase Diagram Depicting Hydrogen Loss and Thermal Gradient in Annealing

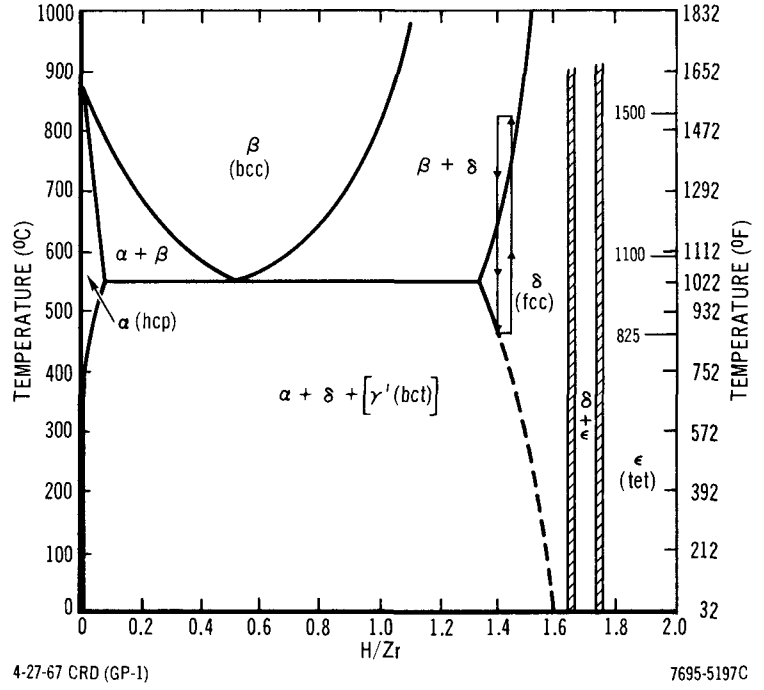


Figure 2. Zirconium-Hydrogen Phase Diagram Depicting a Thermal Cycle Anneal

Fuel of 1.6 H/Zr at 1400°F isothermal will go from δ phase to (β + δ) phase at 1.4 H/Zr, and into pure β phase at ~0.9 H/Zr ratio. Phase changes induced by gross hydrogen loss could be obtained in fuel with defective cladding. Fuel with 1.7 H/Zr ratio and a temperature gradient between 1300 and 1600°F will generate ~1 atm of hydrogen, and the H/Zr gradient will range from 1.6 to 1.8 and structure gradient from δ to ε, as shown by constant pressure lines on the phase diagram. A thermal cycle from 1500 to 1100°F on zirconium-uranium hydrided fuel of H/Zr ratio of 1.4 will change the material from 90% δ and 10% β to pure δ phase; and if the material were cooled to less than 875°F, it would be in a mixed phase of δ + α. When H/Zr changes are experienced in the zirconium hydride, it should be remembered that the lever arm principles apply in mixed phase regions.[4] That is, a material can change from 90% δ and 10% β to 80% δ and 20% β, which means 10% of the material has changed structure.

C. PHASES OF PROGRAM

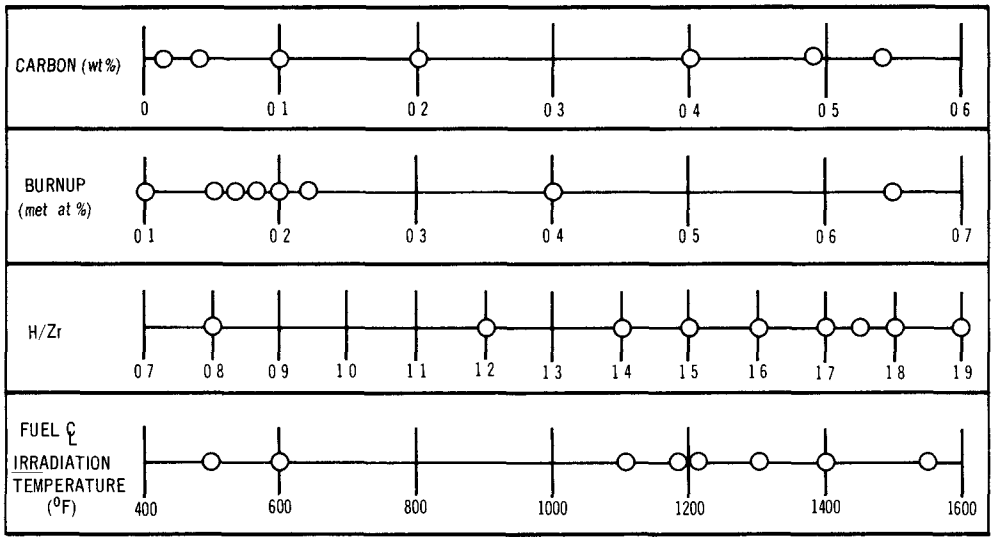
The Annealing Program on irradiated SNAP fuel was conducted in three basic phases.

1. Isothermal Annealing

These tests simulated long-term steady-state reactor conditions with negligible hydrogen loss. Samples with carbon additives ranging from 0.01 to 0.54 wt % were annealed. Samples of fuel with an H/Zr ratio ranging from 0.8 H/Zr (pure β material at temperature) to 1.88 H/Zr (pure ε material) covering a burnup range of 0.1 to 0.65 met. at. % were annealed. Samples were also selected that were operated in the reactor at fuel centerline temperatures ranging from 500 to 1550°F. Figure 3 shows these parameters and locations for the samples selected for this phase of the program. Unirradiated control samples (not shown in Figure 3) were also annealed to determine whether irradiation had any effect on the dimensional changes in the fuel.

2. Hydride and Dehydride Annealing

This test simulated steady-state reactor conditions with gross hydrogen changes caused by hydrogen leakage or hydrogen redistribution. Table 2 shows the parameters of samples selected for this phase of the program. Here, also, samples varied in wt % carbon ranging from 0.12 to 0.54; H/Zr ratios ranged



ISOTHERMAL ANNEALING SAMPLE PARAMETERS AND LOCATIONS
○ (INDICATES SAMPLE LOCATIONS)

4 27 67 CRD (GP 1)

7695 51157

Figure 3. Isothermal Annealing Test Parameters

TABLE 2

HYDRIDE AND DEHYDRIDE ANNEALING TEST PARAMETERS

Preannealing History				Test Objectives	
Additive (wt %)	Temperature (°F)	$(H/Zr)_{eff}$	Burnup (met. at. %)	Hydride → Dehydride (1600°F)	Dehydride → Rehydride (1600°F)
0.12	1400/1550	1.45/1.55	0.4	X	
0.54	1380/1400	1.49/1.55	0.2	X	
0.49	1390/1400	1.55/1.60	0.2		X
0.48	1380/1400	1.35/1.40	0.2	X	
0.54	1390/1400	1.50/1.60	0.2		X
0.25	1100/1400	1.78	0		X
0.25	1100/1400	0.92	0	X	
0.17	-	1.73	0	X	X
0.30	-	1.77	0		X

from 0.9 to 1.7 and burnups of 0.2 and 0.4 met. at. %. The irradiated fuel used for this phase had previously been operated in the reactor between the temperatures of 1100 and 1550° F. Unirradiated fuel of similar composition was also tested.

3. Thermal Gradient Annealing

Thermal gradient annealing tests were run to simulate the axial thermal gradient obtained in a reactor. These tests were run with a thermal gradient of 100° F/in. of fuel. Table 3 shows the parameters of the samples selected for this phase of the program. Carbon additives between 0.1 to 0.5 wt % were used. The H/Zr ratio varied from 1.4 to 1.7, burnup varied from 0.1 to 0.2 met at. %, and the fuel operating centerline temperature ran from 1270 to 1410° F. One unirradiated sample was tested using the same techniques as used for irradiated samples. The gradients were held 1/2 hr and were reversed several times during a total of 4 hr.

TABLE 3

THERMAL GRADIENT ANNEALING PARAMETERS

Preannealing History				Test Objectives	
Additive (wt %)	Temperature (° F)	$(H/Zr)_{eff}$	Burnup (met. at. %)	100° F/in. Gradient	Reverse Gradient
0.50	1360/1410	1.41/1.56	0.14/0.2	X	X
0.37	1320/1390	1.52/1.6	0.1/0.2	X	X
0.37	1360/1400	1.57/1.65	0.2	X	X
0.48	1270/1390	1.5/1.6	0.15/0.2	X	X
0.01	1390/1410	1.6/1.7	0.15/0.2	X	X
0.05	-	1.7	0	X	X

II. EQUIPMENT AND TEST PROCEDURE

A. ENCAPSULATION

All samples were sealed in quartz tubes shown in Figure 4. The sample was placed inside the tube along with a quartz platform spacer. The large end of the tube was sealed in air atmosphere. After the large end was closed, the cylinder was evacuated to <50 torr and backfilled with helium. Helium was partially evacuated and the tube was remotely sealed at the restriction with 75 to 200 torr of helium remaining in the tube (Figure 5). All sealed quartz tubes were leak tested with a helium mass spectrometer type leak tester. Figure 6 shows a typical group of sealed containers. Figure 7 shows a group of samples after annealing.

B. VOLUME MEASUREMENTS

Volume changes for irradiated and unirradiated U-ZrH_x fuel were measured by recording diameter measurements and liquid displacement densities using monobromobenzene and a 200 gm remotely[1] operated Mettler balance. The density technique proved to be more accurate than the dimensional technique because of the irregular shape of the irradiated samples, such as ovality and

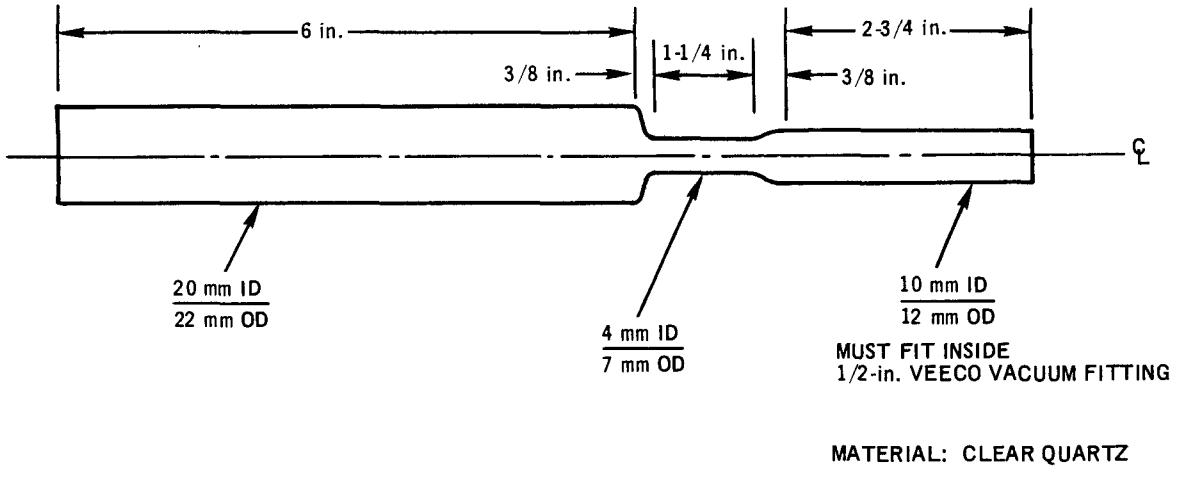


Figure 4. SNAP Annealing Vessel

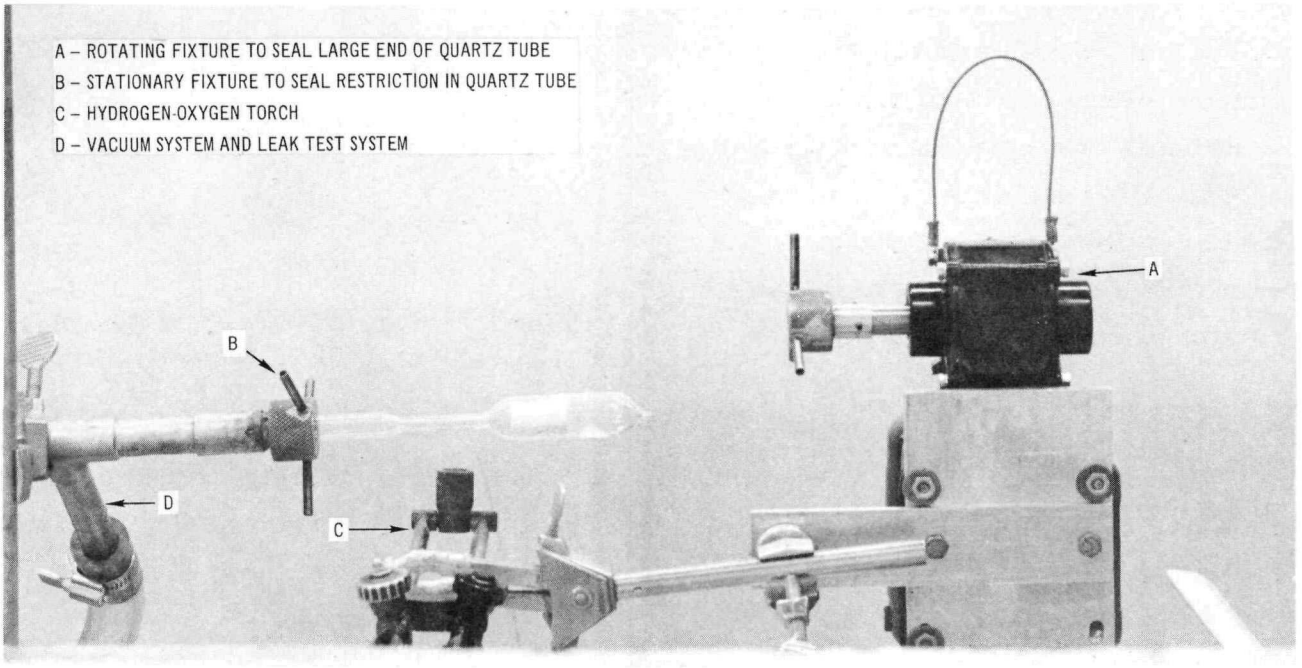


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Figure 5. Quartz Seal-Off Fixture

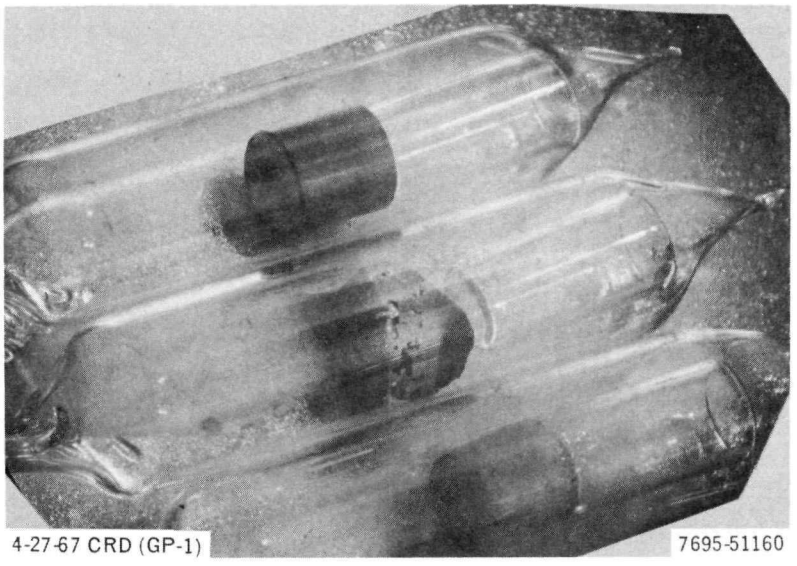

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Figure 6. Typical Group of Sealed Irradiated Samples

irregular cut surfaces. The average percent error for density measurements was ±0.06% and the average percent error for the diameter measurements of a uniform sample was ±0.4%. Because of the greater accuracy of the density technique, the diameter measurements were discontinued during the program.

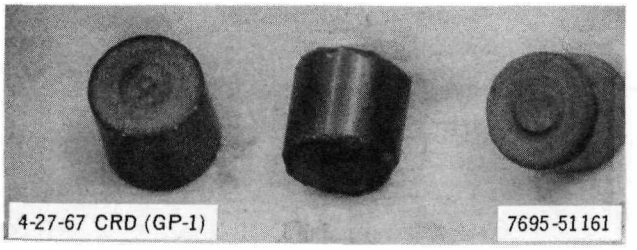


Figure 7. Typical Group of Samples After 1500°F Anneal

C. FURNACES

Electrical resistance-type furnaces were used for annealing, and the temperature control was accurate to within ±25% at 1400°F. The majority of testing was conducted at 1400 to 1700°F.

D. TEST OF QUARTZ TUBING

Unirradiated hydrided fuel samples sealed in 1-mm wall quartz were permeation tested at 1600°F to evaluate the hydrogen permeation characteristics of the quartz sample containers. The average leak rate was 0.53 cc/hr. Figure 8 shows the change in hydrogen composition for a 1.6 wt % H_2 sample. Tests on 3-mm wall tubing were conducted at both 1600 and 1700°F. The average leak rates were 0.50 cc/hr at 1600°F and 0.85 cc/hr at 1700°F, Figure 9. Both tests were conducted using unirradiated SNAP fuel of H/Zr = 1.6.

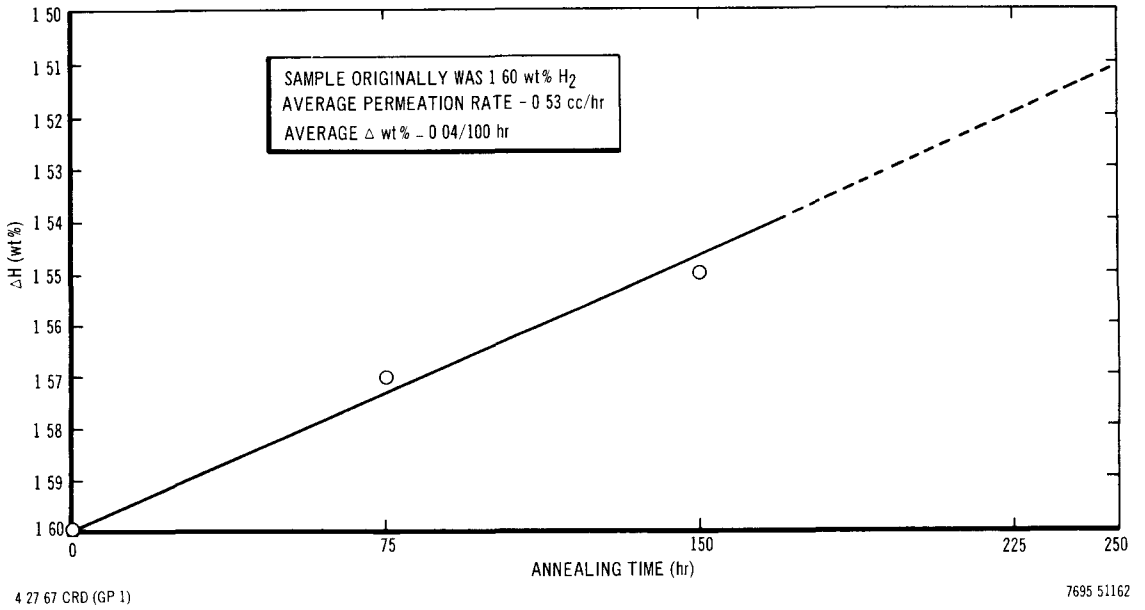


Figure 8. Change in Hydrogen Weight Percent for a Sample Annealed at 1600°F in 1-mm-Wall Quartz Tubing

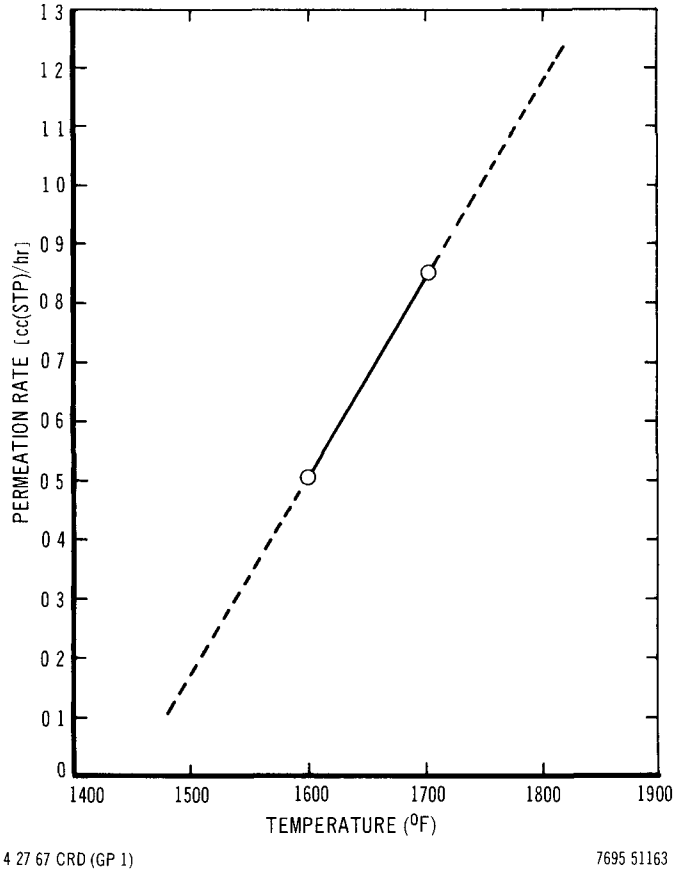


Figure 9. Leak Rate Through 3-mm-Wall Quartz at 1600 and 1700°F

TABLE 4

RESULTS OF SNAP ANNEALING TESTS, H/Zr VARIABLE

H/Zr	Phase	Thermal Data				
		Annealing Temperature (°F)	Annealing Time (hr)	ρ_2 (gm/cc)	$\Delta\rho$ (gm/cc)	$\frac{\Delta\rho}{\rho_2}$ (%)
1.72	ϵ	-	0	5.9683	-	-
(1.6)*		1400	75	5.9739	+0.0056	+0.093
		1500	75	5.9739	0.0000	0.000
		1600	75	5.9730	-0.0009	-0.015
		1700	75	5.9720	-0.0007	-0.012
1.81	ϵ	-	0	6.0016	-	-
		1400	75	5.9829	-0.0187	-0.31
		-	0	5.9274	-	-
		1700	75	5.9589	+0.0315	+0.53
1.48	δ	-	0	5.8943	-	-
		1400	75	5.9276	+0.0333	+0.56
		1500	75	5.9352	+0.0076	+0.13
		1600	75	5.9537	+0.0185	+0.31
		1700	75	5.9670	+0.0133	+0.22
1.57	γ	-	0	5.9265	-	-
		1400	75	5.9353	+0.0088	+0.15
		1500	75	5.9411	+0.0058	+0.098
		1600	75	5.9464	+0.0053	+0.089
		1700	75	5.9603	+0.0139	+0.23
1.62	$\gamma + \epsilon$	-	0	5.8637	-	-
(1.5)*		1400	75	5.8631	-0.0006	-0.010
		1500	75	5.8671	+0.0040	+0.068
		1600	75	5.8769	+0.0098	+0.17
		1700	75	5.8986	+0.0217	+0.37
~1.75	ϵ	-	0	6.0832	-	-
		1500	75	6.0869	+0.0037	+0.061
		1600	75	6.0885	+0.0016	+0.026
1.58	γ	-	0	5.8869	-	-
		1400	75	5.8870	+0.0001	+0.0016
		1500	75	5.8897	+0.0027	+0.046
		1600	75	5.8923	+0.0026	+0.044
		1700	75	5.9050	+0.0127	+0.22

*Hydrogen analysis after completion of annealing by vacuum extraction.

III. ISOTHERMAL ANNEALING

A. POSTIRRADIATION H/Zr RATIOS

The results of annealing irradiated fuel of various postirradiated H/Zr ratios are shown in Table 4. A positive $\Delta\rho/\rho_2$ indicates a volume decrease caused by hydrogen loss, whereas a negative $\Delta\rho/\rho_2$ indicates an increase in volume or swelling.

No significant volume increases were observed from isothermal annealing of δ- or ϵ-phase fuel at 1400, 1500, 1600, or 1700°F. The physical appearance of the fuel was unchanged when annealed at 1400 and 1500°F (Figure 7), but fuel spalling on the circumference of the fuel specimens was observed after annealing the fuel at 1600 and 1700°F. In all cases, the spalled fuel had indications of microcracking and slight dehydriding of the outer surface as shown on photomicrographs after irradiation.[1] Fuel which did not indicate microcracks or dehydrided skin did not spall.

Two irradiated samples were analyzed for hydrogen by vacuum extraction technique after annealing. The hydrogen loss during annealing was in the range of 0.6 to 0.14%.

B. BURNUPS

Samples of (δ+ϵ) and ϵ SNAP fuel varying in burnup from 0.1 to 0.2 met. at. % were annealed at 1400, 1500, 1600, and 1700°F. The results are shown in Table 5. No significant volume increases were observed. The physical appearance of all samples was unchanged with the following exceptions: slight fuel spalling was observed on samples annealed for 75 hr at 1600 and 1700°F; and in all cases, the spalled sample exhibited microcracking before annealing.

C. CARBON CONCENTRATIONS IN FUEL

No significant volume changes were obtained when samples of irradiated (δ + ϵ) and ϵ SNAP fuel containing varying percentages of carbon from 0.01 to 0.5 wt % were annealed for 75 hr at 1400, 1500, 1600, and 1700°F. The results are shown in Table 6. In general, slight volume decreases were obtained as shown by the positive density changes. One sample was analyzed for hydrogen by vacuum extraction and showed a 0.07% change in hydrogen during annealing.

TABLE 5

RESULTS OF SNAP FUEL ANNEALING TESTS, BURNUP VARIABLE
[($\delta + \epsilon$) and ϵ Phase Fuel]

Burnup (met. at. %)	Thermal Data				
	Annealing Temperature (°F)	Annealing Time (hr)	ρ_2 (gm/cc)	$\Delta\rho$ (gm/cc)	$\frac{\Delta\rho}{\rho_2}$ (%)
0.15	-	0	5.9683		
	1400	75	5.9739	+0.0056	+0.094
	1500	75	5.9739	0.0000	0.000
	1600	75	5.9730	-0.0009	-0.015
	1700	75	5.9720	-0.0010	-0.017
0.1	-	0	6.0016	-	-
	1400	75	5.9829	-0.0187	-0.31
	1500	75	fractured		
0.15	-	0	5.9274	-	-
	1700	75	5.9589	+0.0315	+0.53
0.2	-	0	5.8869	-	-
	1400	75	5.8870	+0.0001	+0.0016
	1500	75	5.8897	+0.0027	+0.046
	1600	75	5.8923	+0.0026	+0.044
	1700	75	5.9050	+0.0127	+0.22
0.08	-	0	6.0191	-	-
	1400	75	6.0188	-0.0003	-0.0049
	1500	75	6.0128	-0.0060	-0.010
	1600	75	6.0132	+0.0004	+0.0067
0.21	-	0	5.9776	-	-
	1400	0	5.9814	+0.0038	+0.064
	1500	0	5.9799	-0.0015	-0.025
	1600	0	5.9807	+0.0008	+0.013
0.15	-	0	5.8943	-	-
	1400	75	5.9276	+0.0333	+0.56
	1500	75	5.9352	+0.0076	+0.13
	1600	75	5.9537	+0.0185	+0.31
	1700	75	5.9670	+0.0133	+0.22
0.17	-	0	5.8637	-	-
	1400	75	5.8631	-0.0006	-0.010
	1500	75	5.8671	+0.0040	+0.068
	1600	75	5.8769	+0.0098	+0.17
	1700	75	5.8986	+0.0217	+0.37

TABLE 6

RESULTS OF SNAP FUEL ANNEALING TESTS, CARBON VARIABLE
[($\delta + \epsilon$) and ϵ Phase Fuel]

Carbon (wt %)	Thermal Data				
	Annealing Temperature (°F)	Annealing Time (hr)	ρ_2 (gm/cc)	$\Delta\rho$ (gm/cc)	$\frac{\Delta\rho}{\rho_2}$ (%)
0.40	-	0	5.8873	-	-
	1500	75	5.8908	+0.0035	+0.059
	1600	75	5.8957	+0.0049	+0.083
	1700	75	5.8984	+0.0027	+0.046
0.40	-	0	5.8232	-	-
	1500	75	5.8289	+0.0057	+0.098
	1600	75	5.8324	+0.0035	+0.060
	1700	75	5.8408	+0.0084	+0.14
0.10	-	0	5.9698	-	-
	1500	75	5.9668	-0.0030	-0.050
	1600	75	5.9702	+0.0034	+0.057
	1700	75	5.9750	+0.0048	+0.080
0.01	-	0	6.0103	-	-
	1400	75	6.0135	+0.0032	+0.053
	1500	75	6.0193	+0.0058	+0.096
	1600	75	6.0245	+0.0052	+0.086
	1700	75	6.0286	+0.0041	+0.068
0.01	-	0	5.9683	-	-
	1400	75	5.9739	+0.0056	+0.094
	1500	75	5.9739	0.0000	0.000
	1600	75	5.9730	-0.0009	-0.015
	1700	75	5.9720	-0.0010	-0.017
0.01	-	0	6.0016	-	-
	1400	75	5.9829	-0.0187	-0.31
	1500	75	fracture	-	-
0.54	-	0	5.9274	-	-
	1700	75	5.9589	+0.0315	+0.53
0.54	-	0	5.8869	-	-
	1400	75	5.8870	+0.0001	+0.0016
	1500	75	5.8897	+0.0027	+0.046
	1600	75	5.8923	+0.0026	+0.044
	1700	75	5.9050	+0.0127	+0.22
0.49	-	0	5.9756	-	-
	1500	75	5.9732	-0.0024	-0.040
	1600	75	5.9721	-0.0011	-0.018
	1700	75	5.9741	+0.0020	+0.033
0.17	-	0	5.9798	-	-
	1500	75	6.0066	+0.0268	+0.45
	1600	75	6.0075	+0.0009	+0.015
	1700	75	6.0277	+0.0202	+0.34
0.17	-	0	5.9641	-	-
	1500	75	5.9735	+0.0094	+0.16
	1600	75	5.9773	+0.0038	+0.064
	1700	75	5.9871	+0.0098	+0.16

Fuel spalling was observed after annealing irradiated samples at 1600 and 1700°F. In all cases, the spalled samples exhibited microcracks on photomicrography before annealing.

D. OPERATING TEMPERATURES

No significant volume changes were obtained by annealing irradiated ($\delta + \epsilon$) and ϵ phase SNAP fuel operated in the reactor with centerline temperatures between 1100 and 1400°F. The annealing results for annealing temperatures of 1400, 1500, 1600, and 1700°F are presented in Table 7. The appearance of the fuel

TABLE 7

RESULTS OF SNAP FUEL ANNEALING TESTS, IRRADIATING OPERATING TEMPERATURE VARIABLE
[($\delta+\epsilon$) and ϵ Phase Fuel]

Operating Temperature (°F)	Thermal Data				
	Annealing Temperature (°F)	Annealing Time (hr)	ρ_2 (gm/cc)	$\Delta\rho$ (gm/cc)	$\frac{\Delta\rho}{\rho_2}$ (%)
1300	-	0	6.0056	-	-
	1500	75	5.9398	-0.0658	-1.11
	1600	75	5.9372	-0.0026	-0.044
	1700	75	5.9052	-0.0320	-0.54
1100-1400	-	0	6.0832	-	-
	1500	75	6.0869	+0.0037	+0.061
	1600	75	6.0885	+0.0016	+0.026
1300	-	0	5.9683	-	-
	1400	75	5.9739	+0.0056	+0.094
	1500	75	5.9739	0.0000	0.000
	1600	75	5.9730	-0.0009	-0.015
	1700	75	5.9720	-0.0010	-0.017
1200	-	0	6.0191	-	-
	1400	75	6.0188	-0.0003	-0.0049
	1500	75	6.0128	-0.0060	-0.010
	1600	75	6.0132	+0.0004	+0.0067
1400	-	0	5.8943	-	-
	1400	75	5.9276	+0.0333	+0.56
	1500	75	5.9352	+0.0076	+0.13
	1600	75	5.9537	+0.0185	+0.31
	1700	75	5.9670	+0.0133	+0.22
1400	-	0	5.8637	-	-
	1400	75	6.8631	-0.0006	-0.0087
	1500	75	5.8671	+0.0040	+0.068
	1600	75	5.8769	+0.0098	+0.17
	1700	75	5.8986	+0.0217	+0.37

was unchanged after the 1400 and 1500°F annealing, but was slightly spalled after 1600 and 1700°F. In all cases, the spalled fuel exhibited microcracking on photomicrographs before annealing.

E. SAMPLES WITH 0.65 met. at. % BURNUP

SNAP fuel samples irradiated to a burnup of 0.65 met. at. % at 500 to 600°F centerline temperature were annealed at 1500, 1600, and 1700°F. The $(H/Zr)_{eff}$ of the material during irradiation was 1.15 [$(\alpha + \beta)$ phase], 1.68 [$(\delta + \epsilon)$ phase], and 1.80 (ϵ phase) at room temperature. These samples were selected for annealing because, at annealing temperatures, a sample of H/Zr of 1.15 would change from $\alpha + \beta$ to essentially pure β; the samples of H/Zr 1.68 or $(\delta + \epsilon)$ phase would remain $\delta + \epsilon$ or change to pure δ phase; and ϵ material, H/Zr 1.8, would remain in single-phase ϵ as seen in the phase diagram, Figure 1.

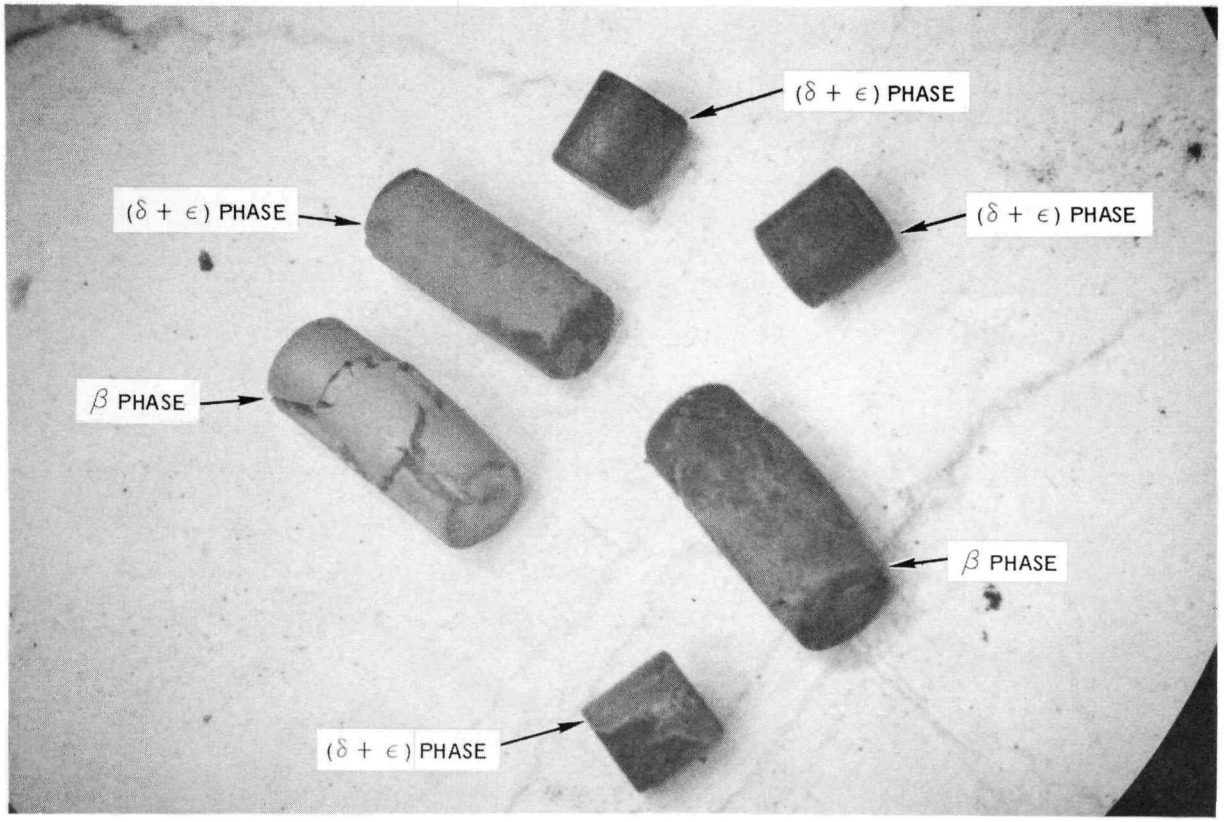
1. β-Phase Material

Volume increases were large for β-phase material, ranging from 7.24 to 29.4%, and appear to be temperature or phase-content dependent. Two β-phase samples are shown in Figure 10 after annealing, and exhibit obvious swelling. A tabulation of the annealing results for β-phase samples is presented in Table 8. Microstructure of β-phase material before and after annealing is shown in Figure 11. The annealed sample shows large cracks and voids, verifying swelling data obtained from density measurements.

It is apparent there is a relationship between annealing temperature and volume change for irradiated β-phase material as seen in Figure 12. The swelling or volume change increases as the annealing temperature is increased; however, a phase-content effect may also be present since this parameter varied slightly.

2. $(\delta + \epsilon)$- and ϵ-Phase Material

Volume changes for irradiated $(\delta + \epsilon)$ material were minor, ranging from +1.4 to -0.40%, and volume changes for pure ϵ material were small, ranging from +0.66 to -0.22%. The data are presented in Table 9. These changes correspond to volume changes observed for lower burnup samples.



5-16-67 CRD (GP-1) 116-2-15

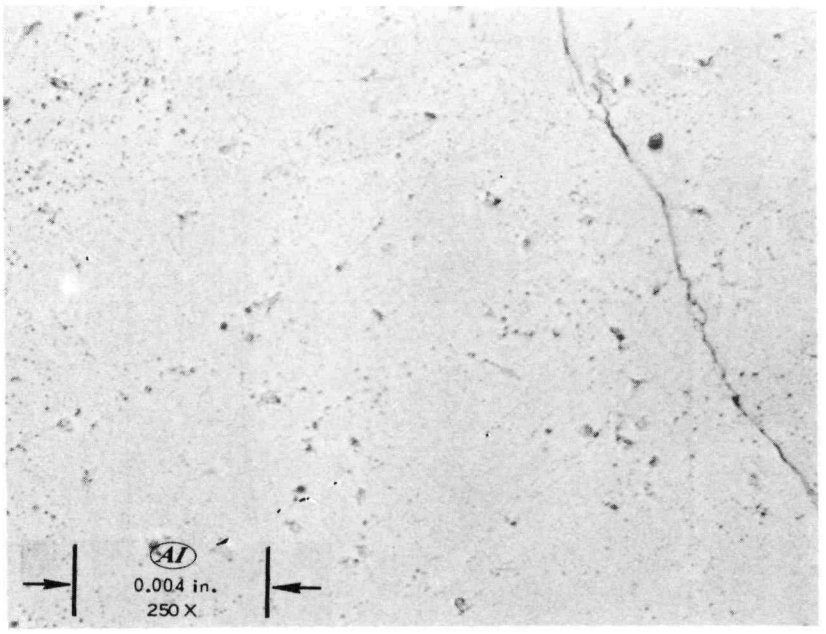
Figure 10. 0.65 met. at. % Burnup Samples After 1600°F Annealing

TABLE 8

ANNEALING DATA FOR β-PHASE MATERIAL
(0.65 met. at. % Burnup)

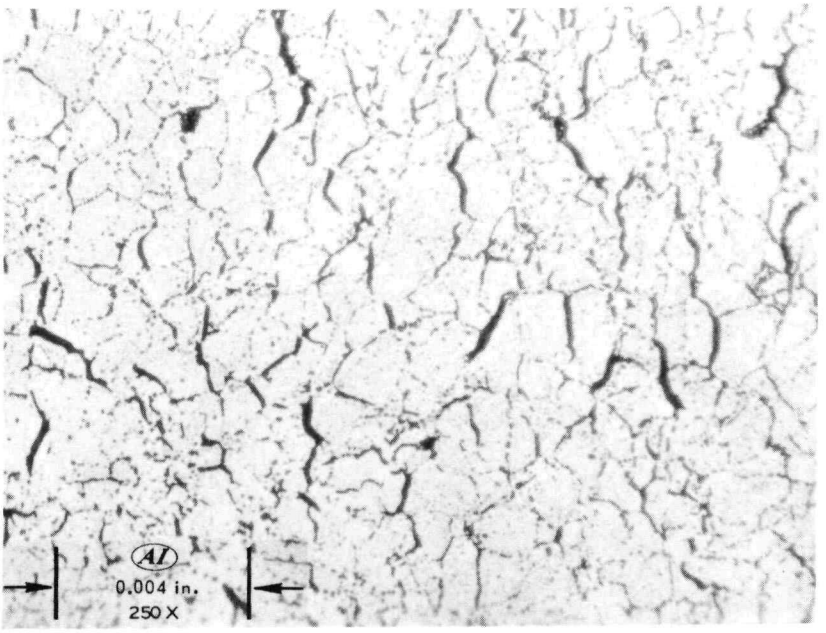
Sample No.	Post-irradiation Hydrogen (wt %)	Phase	Annealing Temperature (°F)	Annealing Time (hr)	ρ_1 (gm/cc)	ρ_2 (gm/cc)	$\frac{\Delta\rho}{\rho_2}$ (%)
14-2*	1.16	β	1300	90	6.209	6.238	+0.47
25-1	1.12	β	1600	75	6.1763	4.7724	-29.41
				150	6.1763	4.6929	-31.60
25-3	1.12	β	1600	75	6.1651	5.1639	-19.38
27-3	1.15	β	1600	75	6.1497	5.1733	-18.87
27-1	1.15	β	1500	75	6.5601	6.1172	-7.24

*Sample annealed during earlier examination[4]



CRD (GP-1) 66-6-1

a. Before Annealing: 10.04 wt % U, 0.12 wt % C, 1.15 wt % H



CRD (GP-1) 66-5-1

b. After Annealing at 1600°F: 10.11 wt % U, 0.15 wt % C, 1.12 wt % H

Figure 11. Microstructure of β-Phase Irradiated Fuel, Before and After Annealing

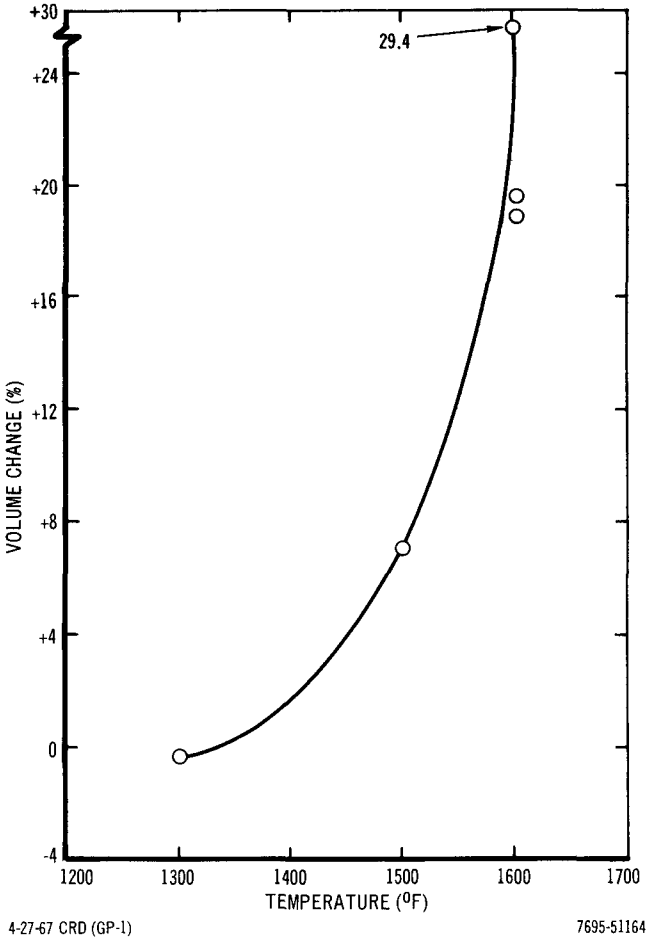


Figure 12. Volume Change vs Annealing Temperature for β-Phase SNAP Fuel

TABLE 9

ANNEALING RESULTS, ϵ- AND $(\delta+\epsilon)$-PHASE MATERIAL
(0.65 met. at. % Burnup)

Postirradiation Hydrogen (wt %)	Phase	Annealing Temperature (°F)	Annealing Time (hr)	ρ_1 (gm/cc)	ρ_2 (gm/cc)	$\frac{\Delta\rho}{\rho_2}$ (%)
1.68	$\delta+\epsilon$	1600	75	5.8333	5.8539	+0.35
		1600	75	5.8539	5.8756	+0.37
		1700	75	5.8756	5.7932	-1.42
1.64	$\delta+\epsilon$	1600	75	5.8601	5.8833	+0.40
		1600	75	5.8833	5.8761	-0.13
1.84	ϵ	1600	75	5.8116	5.8147	+0.05
		1600	75	5.8147	5.8273	+0.22
1.88	ϵ	1600	75	5.8902	5.8515	-0.66
				5.8515	5.8463	-0.089

TABLE 10

RESULTS OF CHANGING H/Zr AND PHASES
(at 1600°F for 75 hr)

Sample No.	$(H/Zr)_{eff}$ and Phase	$\Delta\rho$ (gm)	$\frac{\Delta\rho}{\rho_2}$ (%)	Burnup (met. at. %)
1	1.66 → 1.69 δ δ + ϵ	-0.0029	-0.05	0.2
	1.69 → 1.3 δ + ϵ β + δ	+0.0795	+1.34	
2	1.76 → 1.42 ϵ β + δ	+0.0747	+1.26	0.2
	1.42 → 1.49 β+ δ δ	-0.0281	-0.47	
3	1.63 → 1.28 δ β + δ	+0.1066	+1.82	0.2
	1.28 → 1.39 β + δ β + δ	-0.0207	-0.35	
4	1.50 → 1.58 β + δ δ	-0.0076	-0.13	0.2
	1.58 → 1.28 δ β + δ	+0.1835	+3.17	
5	1.50 → 1.56 β + δ δ	-0.0213	-0.35	0.4
	1.56 → 1.35 δ β + δ	+0.0991	+1.65	
A	0.92 → 1.17 β β + δ	-0.1207	-1.85	0
	1.17 → 0.96 β + δ β	+0.1347	+2.11	
B	1.75 → 1.63 ϵ δ	+0.0434	+0.71	0
	1.65 → 1.64 δ δ	-0.0086	-0.14	
C	1.73 → 1.37 δ + ϵ β + δ	+0.0987	+1.62	0
	1.37 → 1.46 β + δ β + δ	-0.0461	-0.72	
D	1.73 → 1.85 δ + ϵ ϵ	-0.0055	-0.09	0
	1.85 → 1.21 ϵ β + δ	+0.1973	+3.24	
E	1.77 → 1.40 ϵ β + δ	+0.1150	+1.89	0
	1.40 → 1.50 β + δ δ	-0.0536	-0.88	

IV. HYDRIDE AND DEHYDRIDE ANNEALING

Irradiated and unirradiated SNAP fuel was hydrided and dehydrided at 1600°F. A known quantity of zirconium metal, along with the fuel sample, was sealed in a quartz tube and heated to dehydride the sample. A known weight of zirconium hydride was sealed in a quartz tube along with the fuel sample to hydride the sample. The postannealing hydrogen content of the fuel sample was calculated on the basis of equilibrium hydrogen redistribution between the sample and the zirconium or zirconium hydride. Weight change of the fuel sample was used as an experimental check on the calculations; also, selected samples were analyzed for hydrogen content after completion of annealing.

Five irradiated and five unirradiated SNAP fuel samples were hydrided and dehydrided across phase boundaries at 1600°F. Samples were held at temperature for 75 hr. The data are tabulated in Table 10. Variability in density change for irradiated samples compares well with unirradiated samples. In all cases, the samples were cracked during dehydriding. Density variability was a problem because the liquid did not completely fill the cracks.

This technique of dehydriding and rehydriding did yield hydrogen transfer, but the rate of hydrogen transfer was uncontrollable. Hydriding or dehydriding operations require precise controls as experienced in the fuel development efforts.

A comparison of the hydrided and dehydrided data in Table 10, when compared to the isothermal annealing data for 0.65 met. at. % burnup fuel shown in Table 8, demonstrates that gross swelling did not occur on irradiated SNAP fuel during hydriding or dehydriding annealing at the times studied.

One irradiated SNAP fuel sample containing 0.12 wt % carbon and 0.37 met. at. % burnup was heated at 1600°F for a total of 409 hr to evaluate the influence of time on dimensional stability of the fuel. The sample was cooled periodically and fuel density measured. A tabulation of the data is presented in Table 11.

The sample began to expand after 250 hr as shown by negative $\Delta\rho/\rho_2$ (Figure 13). Assuming a uniform leak rate of hydrogen through the quartz, Figure 9, the sample would have an H/Zr of 1.5. At 1600°F, the $\beta \rightleftarrows (\beta + \delta)$ phase boundary is at 1.50 H/Zr. It appears that, as the sample approached the phase

TABLE 11

LONG-TERM ANNEAL AT 1600°F

Time (hr)	ρ_2 (gm/cc)	$\Delta\rho$ (gm/cc)	$\frac{\Delta\rho}{\rho_2}$ (%)
0	5.9695		
5	5.9710	+0.0015	+0.03
15	5.9837	+0.0127	+0.21
40	5.9710	-0.0127	-0.21
84	5.9708	-0.0002	-0.003
134	5.9833	+0.0125	+0.20
159	6.0046	+0.0213	+0.35
184	6.0127	+0.0081	+0.13
259	6.0186	+0.0059	+0.098
334	5.9959	-0.0227	-0.38
409	5.9610	-0.0349	-0.58

Sample History:
0.12 wt % Additive
1200°F Operating Temperature
1.6 H/Zr
$\beta + \delta$ Phase
0.37 met. at. % Burnup

boundary and went into the mixed $(\beta + \delta)$ phase, swelling started. The change in H/Zr ratio was a very slow process as compared to the technique used for phase change annealing. A further examination of the permeation rate shows the H/Zr ratio should be about 1.44 after 400 hr. The sample was analyzed for hydrogen and had an average H/Zr of ~1.3 after annealing, which agrees well with the calculated value.

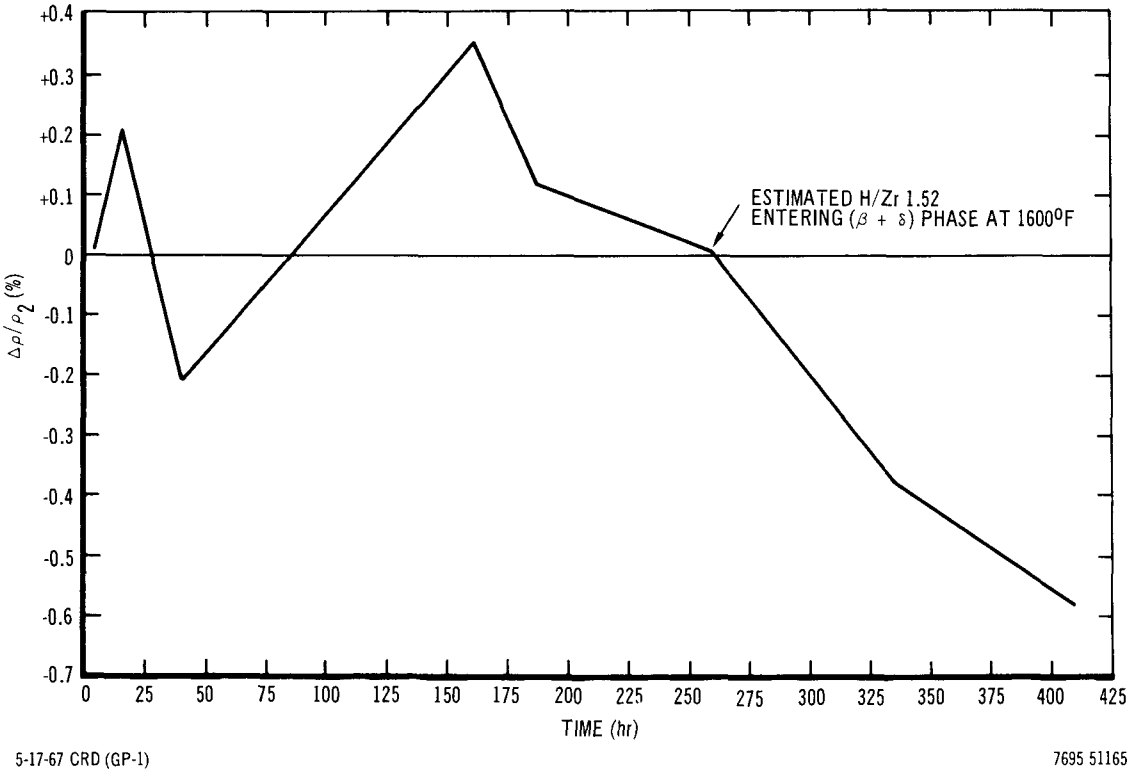


Figure 13. Long-Term Annealing, $\Delta\rho/\rho_2$ vs time at 1600°F

TABLE 12

RESULTS OF THERMAL GRADIENT ANNEALING

Post-irradiation H/Zr	Additive (wt %)	Burnup (met. at. %)	Density Pre-Anneal (gm/cc)	Density After 4 Cycles (gm/cc)	$\Delta\rho/\rho_2$ After 4 Cycles (%)	Density After 8 Cycles (gm/cc)	$\Delta\rho/\rho_2$ After 8 Cycles (%)
1.58	0.48	0.18	6.0452	6.0414	-0.046	6.0368	-0.076
1.74	0.01	0.15	6.0020	5.9891	-0.21	5.9985	+0.16
1.72	0.05	-	6.0466	6.0403	-0.10	6.0453	+0.083
1.52	0.37	0.15	5.8936	5.8999	+0.11	5.9014	+0.025
1.57	0.37	0.20	5.9331	5.9352	+0.033	5.9395	+0.07
1.45	0.50	0.18	5.9620	5.9662	+0.070	5.9702	+0.07

V. THERMAL GRADIENT ANNEALING

SNAP fuel samples were thermal cycled in an electrical thermal gradient furnace. The furnace was designed to yield a temperature gradient of 100°F/in. with a 1400°F midpoint furnace temperature.

Fuel samples from 2 to 4 in. long were sealed in individual quartz tubes. The tubes were leak tested with a mass spectrometer type helium leak detector and placed in a wire rack with thermocouples spaced every inch along the length of the quartz tube. The sample and rack were placed in the preheated furnace at 800 to 1000°F, and the furnace was heated to yield a nominal 1400°F in the center of the fuel sample. To reverse the gradient and thermal cycle the fuel, the center of the sample was allowed to cool to 1000°F, the sample tube was inverted, and again the center of the sample was heated to 1400°F nominal for 1/2 hr.

After each series of four thermal cycles, the sample was removed from the quartz tube, and density measurements were taken. Each sample was cycled eight times and two density measurements were made. A sample of nominal 1.6 H/Zr ratio should obtain a temperature spread of 1200 to 1600°F in 4 in. of length and have an H/Zr spread of 1.35 to 1.75 as shown in Figure 1.

The data for five irradiated SNAP fuel samples and one unirradiated standard sample are presented in Table 12. The volume changes, as indicated by changes in density, were very small. The changes for five irradiated samples varied from -0.21 to +0.16%; this compared to changes of -0.10 to +0.08% for the unirradiated standard sample. A variation of burnup, additive, or H/Zr ratio yields no apparent relationship to changes in density of the fuel sample. It must be noted that a total of 4 hr (8 x 1/2 hr) at 1400°F was experienced, and these results may merely show a too-short time at temperature.

VI. DEHYDRIDING INTO β PHASE

Two irradiated SNAP fuel samples were dehydrided at 1600° F from δ-hydride phase, 1.5 to 1.60 $(H/Zr)_{eff}$, to β-hydride phase, 0.7 to 0.8 $(H/Zr)_{eff}$. Both samples reduced in volume from hydrogen loss. Both the samples were then annealed at 1600° F for 75 to 85 hr. One sample was badly cracked, but both samples had only small volume changes. The uncracked sample was then annealed at 1700° F for 78 hr and swelled 13.8% with large cracks, as seen in Figure 14. A summary of the data is presented in Table 13.

Both samples were analyzed for hydrogen by vacuum extraction technique,[1] after completion of annealing. One sample changed from 1.6 $(H/Zr)_{eff}$ to 0.8 $(H/Zr)_{eff}$, and the other sample went from 1.5 to 0.7 $(H/Zr)_{eff}$. These hydrogen analysis results agree well with the calculated target $(H/Zr)_{eff}$ for the dehydriding operation.

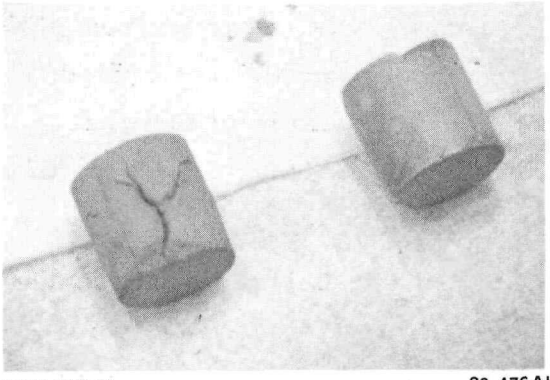


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Figure 14. β-Phase Sample After Annealing Compared to an Unirradiated Standard Sample After Annealing

TABLE 13

SNAP FUEL DEHYDRIDED TO β PHASE

Irradiation Data H/Zr	Annealing Temperature (°F)	Time (hr)	ρ_2 (gm/cc)	$\Delta\rho$ (gm/cc)	$\frac{\Delta\rho}{\rho_2}$ (%)
1.6	-	0	6.0021	-	-
Dehydrided to 0.8	1600	75	6.2966	+0.2945	+4.67
	1600	75	6.2946	-0.0020	-0.032
	1700	75	5.5317	-0.7629 (cracked)	-13.79
1.5	-	0	5.9506	-	-
Dehydrided to 0.7	1600	85	6.2870	+0.3364	+5.35
	1600	78.5	6.2956	+0.0086 (cracks)	+0.137

VII. CONCLUSIONS

A. ISOTHERMAL

Irradiated fuel of H/Zr from 1.5 to 1.8 appears to be dimensionally stable at temperatures up to 1700°F when annealed for 75-hr periods in the absence of a neutron flux. Volume changes, based on changes in density of the fuel, ranged between +0.6 to -0.6% after isothermal annealing, whereas volume changes in the S8ER reactor ranged from -5 to +5% for temperatures of irradiation up to 1450°F for 6000 hr and volume changes in the NAA 115-1 irradiation experiment changed from -1.5 to +4.3% on temperatures of up to 1500°F for 10,000 hr. In general, the volume changes observed after annealing were negative as shown by an increase in density. This is attributed to the loss of hydrogen from the sample as demonstrated by a comparison of hydrogen analysis before and after annealing. In all cases, the samples tested for hydrogen after annealing lost hydrogen by permeation through the quartz tubing.

B. β-PHASE HYDRIDE

It is apparent that the irradiated 90% Zr and 10% U hydrided fuel tends to swell as β-hydride phase increases in the fuel. All the annealed samples of 1.1 H/Zr and 0.65 met. at. % burnup swelled at 1500 to 1600°F, from 7 to 29%. The long-term annealing sample (0.37 met. at. % burnup) annealed for a total of 409 hr at 1600°F started to swell after 250 hr as the fuel increased in β phase. This sample ultimately increased in volume by 0.58% after 409 hr and had an H/Zr ratio of 1.3, which is well within the $(\delta + \beta)$ mixed phase. The irradiated sample dehydrided to 0.8 H/Zr and annealed at 1600 and 1700°F for 75 hr swelled by 13.8%.

There is a relationship of fuel swelling and temperature for β-phase irradiated hydrided SNAP 8 fuel. The samples of H/Zr 1.1 increased in volume as the temperature was changed from 1300 to 1500 to 1600°F. This temperature dependence was shown by dehydriding an S8ER sample from 1.6 to 0.8 H/Zr ratio and annealing for 75 hr at both 1600 and 1700°F. The volume increased 0.03% at 1600°F and 13.79% at 1700°F.

C. LOW IRRADIATION TEMPERATURE ($\delta + \epsilon$) HYDRIDE

It appears that there is a slight swelling during annealing in the ($\delta + \epsilon$)-hydride phase when the fuel is irradiated at low temperature to burnup in the range of 0.65 met. at. %. The fuel samples from the 0.65 met. at. % burnup experiment annealed at 1600 and 1700°F for 75 hr (Table 9) had a volume change from -0.4 to +1.4% based on density change.

D. PHASE SWEEP

There appears to be no appreciable fuel swelling caused by dehydriding or rehydriding 90% Zr and 10% U irradiated fuel of burnup up to 0.4 met. at. % as long as the material is not in the β phase. It is obvious from results of dehydriding that irradiated fuel will grossly swell when dehydrided into β phase. Samples dehydrided to 0.8 H/Zr swelled in excess of 13% (Table 13) and were visually deformed (Figure 14). The variability of density changes for irradiated samples is similar to variability of unirradiated samples when the H/Zr is changed in the range of H/Zr 1.5 to 1.85 (Table 4).

The dehydriding technique used in these annealing experiments produced cracks both in unirradiated and irradiated fuel because of the rapid transfer of hydrogen at 1600°F. Cracked fuel caused problems in density measurements because the liquid did not always fill the voids in the fuel completely, thus adding to the variability of the data. It is apparent a slower dehydriding and rehydriding technique similar to the production hydriding process should be used.

E. THERMAL GRADIENT

There appears to be no gross swelling caused by annealing irradiated 90% Zr - 10% U hydrided to H/Zr in the range of 1.4 to 1.7 for about 4 hr under a temperature gradient of 100°F/in. at temperatures from 1200 to 1600°F. Five irradiated (Table 12) S8ER samples heated with a temperature gradient which was reversed eight times in 1/2-hr dwells had volume changes in the range of +0.21 to -0.16% as compared to an unirradiated sample subjected to the same test with volume change of +0.1 to -0.08%. Even though the maximum volume range for irradiated fuel appears to be 2X, the range for the single unirradiated sample, the average volume change for all tested samples is very similar, being +0.06 to -0.08%.

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