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ABSTRACT

SNAP 8 fuel materials have been studied by low-level irradiations, followed by a variety of annealing treatments. From these tests, it is concluded that the ϵ - δ phase transition does not promote gas release. Other transitions can cause massive gas release, and the importance of these phase transitions is burnup dependent. The gas release obtained from this material indicates that it will perform satisfactorily at reference reactor temperatures under circumstances where hydrogen loss does not promote phase transitions. Where phase transitions do occur, sudden fission gas release can be anticipated for any reasonable burnup levels. This suggests a swelling region at high burnup levels.

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I. INTRODUCTION

The relative volume stabilities of potential SNAP 8 fuel materials have been investigated by the technique of postirradiation annealing of lightly irradiated materials. This volume stability interest arises because one-quarter to one-third of the fission products are the rare gas atoms, xenon and krypton, which can greatly increase their volume when they form a gaseous phase. The fission products, including these rare gases, are initially distributed in a rather random fashion in microscopically homogeneous alloys. Accordingly, they must migrate, or diffuse, in order to form the macroscopic bubbles that can affect fuel volume stability.

In studies such as this one, the release of a specific rare gas atom, xenon-133, is monitored. This isotope has a convenient fission yield (6.62%) and a tolerable half-life (5.27 days). This atomic species is assumed to be characteristic of all rare gas atoms. In view of the comparable sizes and similar unreactiveness of xenon and krypton, this appears to be a reasonable assumption.

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II. BACKGROUND

Theory and experimentation on other fuel systems suggested that:

- 1) Within a single-phase region, changes in composition at constant temperature would not be a source of gas release.
- 2) Shear transformations of the δ - ϵ variety would not promote phase changes.
- 3) The α - β or β - δ phase transformation could provide copious gas release.
- 4) More rapid gas release would be obtained at higher temperatures than at lower temperatures.
- 5) Related to Item 4, the gas release during phase transformation could be annealing-history dependent or burnup dependent. If the limit of gas mobility with trapping is attained, no further gas release need be observed during subsequent transformation.
- 6) Cooling time of the 5.27-day xenon would alter measurement sensitivity, but would not change material response at low burnups if adequate time for the decay of the iodine-133 precursor were allowed (> 3 days).

Two additional concepts which are unique to this hydride system need evaluation:

- 1) The lattice may contain small Zr^{++} ions and large H^- ions, in which event the hydrogen mobility can influence the mobility of the large rare gas atoms.
- 2) Transient effects could occur if the loss of hydrogen from the surface is rapid, relative to the hydrogen mobility within the solid, because a thermodynamically stable β surface layer could be formed. Once formed, it could be stable; because the dissociation pressures of β and δ phases are equal in the two-phase region of the equilibrium diagram.

III. EXPERIMENTAL

A. APPROACHES

The experimental approach used in this program was to heat the materials to successively higher temperatures for extended time periods, and finally to vent or add hydrogen to the system to evaluate the significance of phase transformations in inducing gas release. Since the level of dehydriding was limited by vacuum considerations, some Zr-U samples were hydrided during annealing at temperatures above and below the eutectoid temperature.

Burnup was varied, in order to examine the kinetic arguments that are advanced in Appendix I. The test sequence at the higher dose levels was oriented toward proving or disproving existing fuel swelling concepts. It was also oriented toward providing test data, independent of fuel burnup, at the lower dose levels.

B. MATERIALS

A phase diagram for the Zr-H binary system⁽¹⁾ is presented in Figure 1. At elevated temperatures, the dissociation pressure of uranium hydride is considerably higher than that of zirconium hydride; and, accordingly, the Zr-U-H system contains free, unhydrided, finely dispersed uranium metal. The size scale of the dispersion is such that, although the mass is heterogeneously fissionable, it is homogeneously damaged by fission processes.

The δ - ϵ phase transformation is unique, in that it involves only a duplex shear transformation, although it is said to possess a miscibility gap.⁽²⁾ Such a transformation is not unique to this system, and arises due to a slight tetragonality of the transformed phase.⁽³⁾

The compositions explored in these tests are presented in Table 1. Sample lot designations are described in terms of internal records. The uranium was nominally 93% enriched. The modifier was added carbon, which served as a grain refiner during hydriding. The unmodified material contained normally existing carbon impurities.

The composition at annealing temperature during heating was deduced from the pressure-temperature isochores developed by Raymond,⁽⁴⁾ and his results are presented in Figure 2. Only minor importance was placed on evaluating the

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Figure 1. Modified Zirconium-Hydrogen
 Phase Diagram
 (Figure Unclassified)

TABLE 1
 DESCRIPTION OF TESTED MATERIALS

Sample	Designation	Uranium (%)	Carbon Modifier (%)	H/Zr
623	C-2	10	0.02	1.03
623	C-1	10	0.02	1.75
624	D-1	10	0.10	1.34
624	D-2	10	0.10	1.58
626	C-3	10	0.40	1.81
530	C-3	10	Unmodified	1.69

Figure 2. Isochores of Zirconium Hydride (Figure Unclassified)

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effect of the carbon additive, since errors introduced could easily have been within measurement sensitivity. Bourdon gauges and transducers were used to measure pressures.

C. EXPERIMENTAL TECHNIQUES

The experimental techniques parallel those previously reported by Savage.⁽⁵⁾ Xenon-133, which has the decay scheme that is presented in Figure 3, is used as a monitor of the gas release because it has an appreciable fission yield (6.62%), a convenient and nearly unique photon energy (81 kev), and an attractive half life (5.27 days).

Deviations from the procedures described in Reference 11 included the use of:

- 1) Zircofrax containers in place of quartz, because of their impermeability to hydrogen
- 2) A steel collection tube, as a consequence of the need for pressure containment
- 3) The SNAP Shield Test Irradiation Reactor at the Santa Susana facility of Atomics International, which increased activity measurement levels as a result of reduced shipping time
- 4) Activated charcoal in the counting tube (collection tube) to concentrate the released gases.

The net result is approximately two orders of magnitude gain in measurement sensitivity, particularly as a result of Item 4.

To review the improvements in test procedure⁽⁵⁾ briefly, the sample was placed in a hot tube furnace with the counting tube inserted into a thallium-activated, sodium iodide scintillation crystal, as shown in Figure 4. The sample was suitably distant from the crystal to provide low background count rates of the xenon released from the heated sample. From 90 to 96% of the gas was absorbed on the activated charcoal in an evacuated system or a system that contained high hydrogen pressures.

The presence of high gas pressures interferes with the transport rate, but not the efficiency of the charcoal, as was demonstrated by the control experiment that is presented in Figure 5. In this experiment, xenon-133 was introduced

Figure 3. Nuclear Properties of Xe¹³³
 (Figure Unclassified)

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Figure 4. Annealing System in the Annealing Position
 (Figure Unclassified)

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Figure 5. Temperature-Dependence of Xenon Desorption From Activated Charcoal
 (Figure Unclassified)

into a standard system that contained activated charcoal in the heated zone. The percentage released was measured at various charcoal temperatures for several reference hydrogen pressures.

All tests incorporated insertion of the charcoal-containing counting tube in liquid nitrogen and counting the total absorbed activity after such complete absorption. Ninety-five percent or more of the activity released from the charcoal contained within the hot oven was collected on the charcoal that was held at room temperature in the counting tube.

A single-channel pulse height analyzer was used to discriminate the 81-kev gamma peak of xenon-133. A 100-channel analyzer was used to ensure that only this isotope was measured in the counter. The system was calibrated on the basis of standardized Tm¹⁷⁰ or Cd¹⁰⁹ sources.

In order to maintain the H/Zr ratio in the 0.004-in. thick by 0.25-in. diameter irradiated specimens that were contained within an 80-cc system volume, the samples were sandwiched vertically between two massive pieces of unirradiated material which had been obtained from the same source material. These massive pieces will henceforth be called "buffer slugs," in that they provide hydrogen but no fission gases to the 80-cc volume, and thereby minimize the loss of hydrogen from the irradiated specimen. This procedure obviated the need for complicated programming of temperature and hydrogen pressure. The composition was evaluated by means of the measured dissociation pressure, and chemical analysis was used to substantiate these measurements.

The samples were contained within a molybdenum boat into which the monitoring thermocouple penetrated, as shown in Figure 6. Initial vacuums were nominally 10^{-6} torr; and, in several experiments, the test device was backfilled with argon or ultra-high-purity hydrogen.

The irradiation procedure has been described in Reference 10. Initial 20-hr exposures at 10^{12} nv, which were necessary because the activated charcoal technique had not yet materialized, were ultimately reduced to 2-min exposures. Thus, a range of burnup levels have been explored. Irradiations were conducted at ambient temperatures.

Chemical analyses have shown that hydrogen losses during postirradiation annealing were minimal, an expected result based on hydrogen permeation testing of the Zircofrax tubes prior to experimentation.

Figure 6. Annealing System, Disassembled
(Figure Unclassified)

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Figure 7. Dissolution Apparatus
(Figure Unclassified)

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Tests have been conducted to explore specifically the consequences of surface cold work during polishing of the specimen to the required thickness, and no effect was observed.

Neutron dose was evaluated through the use of Co-Al flux monitors and evaluation of total fission gas formed by dissolution of annealed and unannealed samples. The device is shown in Figure 7 and includes, from right to left, a helium flow over the $\text{HNO}_3 + \text{HF}$ dissolver, two drying tubes which also remove iodine (it is formed in the proper oxidation state for absorption), two xenon collection traps which are cooled to dry-ice-acetone temperature, and finally, an oil bubbler to assist helium flow regulation. At higher dose levels, the fuel materials were not sandwiched between comparable fuel materials, and half of the fission products generated within the $6.4\text{-}\mu$ recoil range were transported to the surrounding aluminum foils. Analyses of these foils, the fuel samples, and the Co-Al flux monitors ensured 1 to 5% precision in exposure measurements.

a. Containing 0.0 wt % Carbon Additive

b. Containing 0.11 wt % Carbon Additive

c. Containing 0.40 wt % Carbon Additive

Figure 8. Fractional Gas Release From Zr-U-H_x

IV. RESULTS

Addition of hydrogen to or removal from the system within the δ -phase field or in the δ - ϵ phase transformation region does not promote gas release. Some minimal amount of gas release does occur on heating to successively higher temperatures. The gas that is released is a small fraction of the total present, $<1\%$ in an irradiated fuel sample.

At higher burnup levels (10^{17} fissions/cc), no difference in gas release characteristics can be attributed to differences in carbon content. At this burnup level, homogeneous nucleation (Xe-Xe interactions) probably dominates over the heterogeneous, trapping mechanisms.

At lower burnup levels (1×10^{15} to 6×10^{15} fissions/cc), the 0.11% carbon additive material releases less gas than either the 0.0 or 0.40% additive level. These data are summarized in Figure 8. These are the most pertinent test data obtained with reference to SNAP 8 operation. The units of gas release (fd/w) represent a normalization of gas release per unit area, or fraction released (f) per unit weight (w) per unit thickness (d) (with a constant sample density being assumed). The fractional release and surface area are the basic quantities. The fractional release is determined chemically; and the surface area is computed from sample weight, thickness, and density.

At the 1×10^{15} fissions/cc level, successive annealing treatments provided no gas release at progressively higher annealing temperatures, no gas release during δ - β transformations, no difference among additive levels, and no gas release on quenching from the β phase. Conversely, at higher dose levels, additional gas release was obtained on successively higher temperature anneals and in response to the δ - β transition, but never any gas release during the ϵ - δ transition, and a variable response on quenching. These results are summarized in Table 2.

Diffusion coefficients cannot be obtained in the hydrogen atmosphere, because the delay times between the release and the measurement of collected xenon are long.

The δ - β phase transformation is a source of copious gas release during temperature cycling through this region at the higher burnup levels (2 to 10 hr exposure).

Figure 9. Influence of Hydriding Zr-U Alloy at Temperature on Fission Gas Release (Figure Unclassified)

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TABLE 2
RESPONSE TO TREATMENTS AS A FUNCTION OF DOSE

Dosage (fissions/cc)	Gas Release at Each Successive Temperature	Gas Release on $\delta - \beta$ Transformation	Gas Release on $\epsilon - \delta$ Transformation	Gas Release Differing Between Additive Levels	Gas Release on Quench From β - Phase or $\beta - \delta$ Equilibrium
1×10^{15}	No	No	No	No	No
2×10^{15}	Yes	-	No	-	No
6×10^{15}	Yes	Yes	No	Yes	Yes for 0.40%
2×10^{17}	Yes	Yes	No	Yes	?

Hundredfold increases in gas release rate can be achieved by cycling through this phase transformation.

A specific experiment, designed to evaluate the importance of the $\delta - \beta$ transformation, was conducted. With the system volume utilized, there is a loss of hydrogen from the fuel on heating to test temperature. A sample, held at temperature in the δ - phase field for several days, released only nominal amounts of fission gas. The sample temperature was then increased 2 to 4°C to enter the $\beta + \delta$ phase field, and a 10-fold increase in gas release was obtained in a very short time period.

The $\delta - \beta$ phase transformation does not consistently cause gas release at the 10^{14} fissions/cc exposure level.

Hydriding Zr-U alloy into the two-phase region ($\alpha + \beta$ or $\alpha + \delta$) causes gas release (Figure 9). Rapid quenching of samples is not a source of massive gas release, where residual hydrogen pressures are low.

As is shown in Figure 9, the hydriding of material containing no initial hydrogen does result in massive gas release when the α to $\alpha + \beta$ two-phase region is obtained. The employed temperature is above the range of UH_3 stability, which has also been shown to be a source of gas release. Interestingly, the power failures which caused sample cooling, and probably transformation to the $\alpha + \delta$ region, did not cause additional gas release. The massive gas release occurred on entering the two-phase ($\alpha + \beta$) region.

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While no direct statement can be made concerning trapping density and nucleation density, the observed gas release appears to fall within the ranges of gas release that are obtained from nondispersed uranium fuels. The particle or additive density does, therefore, approach the number and size scale that would be expected to stabilize existing fuels within the limits of available fuel technology.

No correlation exists, at the higher burnup levels, among samples taken from the edge and center regions of reference fuel rods (no similar test was conducted at the lower burnup levels). Grain size and orientation does not, however, appear to be a major factor in fission gas release.

The quantity of gas released on annealing is temperature dependent (Figure 8).

On heating in vacuum, the partial pressure of hydrogen is insufficient to cause uranium hydriding and fission gas release. On quenching at high hydrogen pressures, sufficient residual pressures exist to cause uranium hydriding and gas release. This observation is not germane to SNAP 8 fuel stability during reactor operation. It has been shown that uranium metal has exactly this response.

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V. DISCUSSION

In principle, the evaluation procedure assumes that a substitutional diffusion process of some form describes the behavior of the mobile rare gas atoms which occupy forced substitutional positions⁽⁶⁾ in the parent lattice. Diffusion equations have been developed that describe the cumulative release of the gas from solids.⁽⁷⁾

Certain aspects of these theoretical considerations are not fulfilled. In general, deviations from ideal behavior are not considered. One problem arises as a consequence of an "initial burst" or an initial rapid rate of gas release. Two interpretations exist; either the initially high rate of gas release is due to some unidentified surface effect, or it is the only region that describes true diffusion. A second problem area arises because only small fractions of the contained gases are released during annealing, although simple theory suggests the release of all of the contained rare gas.

The conflict between simple theory and experiment can be resolved if internal defects exist which trap the migrating gas atoms. The rapid reduction in gas release and early saturation of cumulative release would then be anticipated. With this assumption, the fractional release is a measure of average migration volume of a gas atom and the corresponding bubble density. It can be used to compare various fuel materials with respect to anticipated swelling resistance.

Recent observations on the motion of bubble clusters⁽⁸⁾ and experimental results that suggest rare gas solubility at high ambient rare gas pressures^(9,10) and their release on subsequent heating cause some concern about data interpretation, as well as theoretical discontent. However, the low-level annealing technique has been applied quite successfully in the design of swelling-resistant uranium alloys.⁽¹¹⁾ Further aspects of fuel stability are briefly reviewed in Appendix I.

The test results consistently demonstrate that the δ - ϵ phase boundary crossing does not cause gas release at any burnup level studied. The δ - β , α - β , and α - δ phase transitions promote gas release at the higher burnup levels; but, at the lowest burnup levels, the situation is not so clear. A similar phenomenon has been observed by the writers during the α - β and β - γ transformations in uranium.

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A plausible interpretation of the variation in mode of gas release can center about the form of the trapped gas atoms. Gas atoms trapped at macroscopic impurities may behave differently from binary and ternary, homogeneously and mutually trapped, gas atoms, based purely on the size scale of the trapping sites and their interactions with the transformation surfaces. Under such conditions, transformation rates may play a dominant role, and no effort has been expended in this program to control these rates. Referring to the kinetic arguments included in Appendix I, the low burnup levels may encompass only heterogeneous trapping.

The successive release of additional gas at progressively higher annealing temperatures at low burnup could be the consequence either of gas re-solution or of migration of small gas bubbles. This technical point was not pursued, because the studied burnup levels will be attained early in the life of SNAP 8 fuel materials. The significance of such studies could then be of only marginal importance to the program objectives.

This work suggests that the evaluation of fuel materials by postirradiation annealing of lightly irradiated materials is useful only at the lower levels of irradiation. The reason for this is that the xenon and krypton gas atoms are currently assumed to be chemically inert and, accordingly, insoluble. When they are distributed throughout the lattice in forced substitutional positions, their mutual interactions can overshadow the heterogeneous trapping tendencies of dispersed phases. Bubbles have been observed to migrate; and these extraneous migration phenomena, while important to fuel technology, must be independently evaluated to define basic bubble stability concepts. This second phenomenon, bubble migration, can only be studied at the higher dose levels.

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VI. CONCLUSIONS

The $\delta - \epsilon$ phase transformation poses no limitations on SNAP 8 fuel operation. Loss of hydrogen to reach the $\delta - \beta$ two-phase region could cause catastrophic gas release. Thermal cycles which do not provide phase transformations of the $\delta - \beta$ variety are probably unimportant to fuel stability.

The stability of this fuel system is remarkably independent of hydrogen content, so long as diffusion-limited phase transformations are not encountered. If transformations other than the shear variety (i. e., $\delta - \epsilon$) are encountered, copious gas release must result.

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APPENDIX I FUEL STABILITY CRITERIA

A. FUEL STABILITY CONCEPTS

The ideal gas law states that

$$PV = NRT \quad , \quad \dots(1)$$

where:

P = pressure constraints

V = gas volume

N = moles of gas

R = a constant

T = absolute temperature.

Where the gas bubble density, N, is described in terms of the gas bubbles per cubic centimeter of initial matrix volume, this equation can be written as*

$$P \frac{\alpha}{1 - \alpha} = \frac{BRT}{3V_m} \quad , \quad \dots(2)$$

where:

V_m = molar volume of the fuel

B = fractional fuel burnup

α = volume of gas per unit metal volume.

Since fuel burnup, temperature, and other factors are, in a sense, predetermined, then the size of α is intimately related to $1/P$. The interesting point is that the constraining pressure due to matrix strength is adequately related to the geometric considerations of bubble radius to matrix thickness for elastic, plastic, or thin wall pressure vessel constraints. This fact arises from dispersion fuel technology, wherein it is shown that

*The constant, 3 or 4, depends upon flux level, depending upon whether Xe^{135} decays to Cs^{135} or proceeds to Xe^{136} by neutron capture.

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$$\frac{t}{r} = \left(\frac{\pi}{3\sqrt{2}} \alpha \right)^{1/3} - 1, \quad \dots (3)$$

where:

t = thickness of boundary matrix about a bubble of radius (r)

and both the elastic and plastic stress solutions incorporate only t/r as a variable parameter.

Under such conditions, it can be shown that the bubble density is the most important parameter for a solid that possesses surface tension but no mechanical strength⁽¹²⁾ and a wide variety of bubble sizes. For a constant bubble density, orders of magnitude variations in bubble size distribution do not result in significant increase in fuel swelling. The central point of this analysis can be demonstrated by citing that matrix force constraints are of the order of

$$P = \frac{2t\sigma}{r}, \quad \dots (4)$$

where:

σ = matrix strength

for elastic and plastic matrix constraints and are of the order of

$$P = \frac{2\tau}{r}, \quad \dots (5)$$

where:

τ = surface energy

and surface tension forces predominate.

Equation 4 has the geometric relationship that was cited in Equation 3. The volume increase is dependent upon α . Equation 5 has a $1/r$ responsibility. The strength of metals might vary by a factor of three. The bubble radius might be controlled within a factor of 10 or more.

B. KINETIC CONSIDERATIONS

The previous paragraphs suggest that the bubble density is an important fuel stability criterion. They also suggest that more numerous bubbles are conducive to fuel stability. Assumption that the rare gas atoms are chemically inert or insoluble at reactor operating temperatures permits the deduction that

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a collision between two rare gas atoms within the solid leads to a stable bubble nucleus. Then, any procedure that leads to a high degree of gas atom supersaturation prior to nucleation (reduction in gas mobility) or fine size scale trapping of the rare gas atoms will promote fuel stability.

Brinkman⁽¹³⁾ has suggested the introduction of small or large atoms into the host lattice to reduce gas mobility, or the introduction of a dispersed phase to trap the migrating rare gas atoms on a fine size scale. This concept has been evaluated for metal fuels by Johnston with promising results.⁽¹¹⁾ Kinetic equations have been written for the binary trapping case which indicate that such procedures will result in fuel material stabilization.^(14,15) The entire problem has not yet been resolved, but all technological developments indicate that low-level irradiation studies which are followed by high-temperature annealing can be fruitful measures of potential fuel volume stability.

The recent experiments that have demonstrated that small gas bubbles do move in high thermal gradients,⁽³⁾ of the order of 10,000°C/in., are beyond the realm of practical fuel element thermal gradients.

At any rate, if the rare gas atoms can move large distances, then large bubbles can form. Their mechanism of movement can be substitutional diffusion or phase boundary induced migration. The question of whether one fuel type is superior to another depends upon the evaluation of these possible reactions.

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APPENDIX II

SIGNIFICANCE OF THE LACK OF GAS RELEASE ON ANNEALING

With the current state of gas mobility and heterogeneous trapping theory, no detailed calculation of trapping is justifiable. An estimate of the significance of the lack of gas release from annealed samples is, however, interesting and it will be presented.

A gas atom must pass the solid-gas interface to be released, and its probability of being outside the fuel volume $[P(E)]$, after it has migrated a distance (r) , is given by

$$P(E) = \frac{V}{\frac{2\pi r^3}{3}} = \frac{\int_{-r}^{-r+a} \pi y^2 dx}{\frac{2\pi r^3}{3}} = \frac{3}{2} \left(\frac{a^2}{r^2} \right) - \frac{1}{2} \left(\frac{a^3}{r^3} \right) , \quad \dots (6)$$

where (a) is the distance between the fuel surface and the maximum gas migration distance (r) . One tacitly assumes, for simplicity, that the gas atoms have equal probabilities of being anywhere within the spherical volume defined by the radius (r) . This assumption is not too conservative where maximum gas release is being evaluated, because either each atom migrates this distance eventually or it has been trapped internally prior to migrating this distance.

The average probability of escape $[P(E)]$ is given by

$$P(E) = \frac{\int_0^r P(E) da}{\int_0^r da} = \frac{1}{2} - \frac{1}{6} = \frac{1}{3} , \quad \dots (7)$$

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and the mean migration distance is then

$$3 \times \text{Fraction Escaping} \times \text{Sample Thickness};$$

for, if all of the gas within the assumed trapping distance (r) had escaped, the release rate would have been three times greater. Since the fractional release is inversely dependent upon sample thickness, the cited migration distance is independent of sample thickness. Thus, for a 0.004 in. (0.01 cm) sample thickness and only 0.002 fractional release at 800°C, the migration distance is of the order of

$$3 \times 2 \times 10^{-3} \times 1 \times 10^{-2} = 6 \times 10^{-5} \text{ cm} ,$$

and nearly 1.38×10^{14} bubbles/cc exist. This merit number is higher for zirconium-uranium hydride than it is for untreated uranium metal.

Simple transport theory, which considers mean free paths that are large relative to the size scale of absorbers, suggests an e^{-x} form for the migration radius; and one might anticipate a lower absorption rate in the case of migrating atoms. Admittedly, some difficulty arises in defining this spatial relationship. It still seems reasonable to assume that a maximum migration radius does exist; otherwise, with increased annealing time, additional gas would be released. Such is not the case; and assumptions, other than those selected, would provide still smaller migration volumes.

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