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THE EFFECT OF WATER VAPOR ON THE RELEASE OF FISSION GAS FROM THE FUEL ELEMENTS OF HIGH TEMPERATURE, GAS-COOLED REACTORS:

A PRELIMINARY ASSESSMENT OF EXPERIMENTS HRB-17, HFR-B1, HFR-K6 AND KORA

B. F. Myers

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Metals and Ceramics Division

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THE EFFECT OF WATER VAPOR ON THE RELEASE OF FISSION GAS FROM THE FUEL ELEMENTS OF HIGH TEMPERATURE, GAS-COOLED REACTORS

B. F. Myers

ABSTRACT

The effect of water vapor on the release of fission gas from the fuel elements of high temperature, gas-cooled reactors has been measured in different laboratories under both irradiation and post irradiation conditions. The data from experiments HRB-17, HFR-B1, HFR-K6, and in the KORA facility are compared to assess their consistency and complimentarity. The experiments are consistent under comparable experimental conditions and reveal two general mechanisms involving exposed fuel kernels embedded in carbonaceous materials. One is manifest as a strong dependence of fission gas release on the partial pressure of water vapor below 1 kPa and the other, as a weak dependence above 1 kPa.

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1. INTRODUCTION

The effect of water vapor on the release of fission gas from the fuel elements of high temperature, gas-cooled reactors has been investigated by injection of water vapor into carbonaceous systems containing particles with exposed fuel kernels. Such experiments have led to an understanding of the mechanisms of fission gas release in the presence of water vapor and of the dependence of the quantity released and the duration of release on the partial pressure of water vapor, the fission gas inventory and the temperature.

The interaction of water vapor with particles having exposed fuel kernels has been investigated both during and after irradiation. Although these types of experiments differ severally, they are complementary. The complementarity reveals two general mechanisms. One is manifest as a strong dependence of fission gas release on the partial pressure of water vapor below 1 kPa and the other as a weak dependence above 1 kPa.

2. EXPERIMENTAL APPROACH

2.1 DURING IRRADIATION

Three irradiation experiments, HRB-17/18[1], HFR-K6[2], and HFR-B1[3,4], one in the ORNL high

flux isotope reactor, HFIR, and the latter two in the Petten high flux reactor, HFR, have been conducted. In experiments HRB-17/18 and HFR-B1, the fuel element consisted of a cylindrical fuel compact, containing coated fuel particles dispersed in carbonaceous matrix material and surrounded by graphite. A selected number of particles had only a thin coating of pyrocarbon which failed, as designed, shortly after irradiation began. Consequently, a known number of exposed kernels and a known source of fission products were established. The exposed kernels initially consisted of 80% UO_2 and 20% UC_2. During irradiation, the UC_2 content declined to 13%, before exposure to water vapor, as a result of fissioning and reaction with oxygen from UO_2 fissioning, and then to 0% after exposure to water vapor ($\approx$ 0.2 kPa).[5] In experiment HFR-K6, the fuel element consisted of four fuel spheres containing coated UO_2 particles dispersed in A3-3 matrix graphite. During irradiation, two of the normally configured particles failed in a manner that exposed the kernels.

The experiments were conducted by injecting water vapor into capsules containing fuel compacts with exposed kernels at partial pressures $\leq$ 1 kPa, and into a capsule containing fuel spheres with exposed kernels at partial pressures $\leq$ 2.4 kPa. In experiment HRB-17, the water vapor passed over the surface of the fuel compacts, in experiment HFR-B1, over the surface of a graphite cylinder containing fuel compacts, and in experiment HFR-K6, over the graphitic surface of the fuel sphere. Reaction and adsorption of water vapor with and on the carbonaceous material occurred to varying degrees. The released fission gas was monitored for the quantity of several or all of the isotopes ^{85m}Kr, ^{87}Kr, ^{88}Kr, ^{133}Xe, ^{135}Xe and ^{138}Xe.

2.2 POST IRRADIATION

The post irradiation experiments were conducted[6] in the KFA corrosion apparatus "KORA." This apparatus can accept, as samples, fuel particles, fuel compacts and spherical fuel elements equally well. Samples can be heated to a maximum temperature of 1600°C in a helium stream containing water vapor or air. The partial pressures of water vapor achievable, as large as $\approx$ 80 kPa, exceed those reached in the irradiation experiments. However, only the long-lived isotope, ^{85}Kr, was monitored in experiments as the shorter-lived isotopes had already decayed before experimentation. For ^{85}Kr no steady value of the production-loss ratio can be established; only an inventory-normalized release rate, R/N, can be given.

Experiments were conducted with fuel compacts and spherical fuel elements, with embedded, exposed fuel kernels, and with bare kernels. The experiments are characterized, as indicated in Table 1, by selected fuel sample properties and by the irradiation conditions to which the samples were exposed before insertion in the KORA apparatus. Note especially that the acronym UCO is indicative only of the initial, elemental composition of the corresponding kernel. The acronym represents a mixture of UO_2 and UC_2. At the time of insertion into KORA, the HFR-B1 samples had a much reduced carbon content for the reasons given in Section 2.1. For the compact sample from capsule 3, no UC_2 remained; for the compact sample from capsule 2 and the kernel samples from capsule 3, the compositions were, respectively, 93.5% UO_2 and 6.5% UC_2 and 92.4% UO_2 and 7.6% UC_2, with an error of the order of 10% in the UC_2 content.

Table 1. Properties and irradiation history of fuel samples used in the water-vapor injection tests in KORA

				Irradiation Conditions		
Fuel Samples (a), (b)	Type of Sample	Ker-nel	Defect Particles (%)	Burnup (% FIMA)	Fast Fluence $E+25/m^2$ $E>.1$ MeV	Irrad. Temp. (°C)
AVR 89/30	Sphere	UO_2	< 2E-4	9.0	2.6	max. surface temp.
AVR 92/8	Sphere	UO_2	< 2E-4	9.0	2.6	
AVR 92/7	Sphere	UO_2	< 2E-4	9.2	2.7	
AVR 73/8	Kernels	UO_2	100	4.7	0.8	1000-1280
AVR 92/29	Kernels	UO_2	100	9.2	2.7	
HFRB1,2.2.1+2	Compacts	UCO	9	21.6	6.6	880-1230
HFRB1,3.2.1+2	Compacts	UCO	9	19.6	5.1	820-1050
HFRB1, tr. 3-7a	Kernels	UCO	100	19.6	5.1	820-1050
HFRB1, tr. 3-7b	Kernels	UCO	100	19.6	5.1	820-1050

(a) AVR, the Arbeitsgemeinschaft Versuchs-Reaktor of the Forschungszentrum Jülich
(b) HFR, the High Flux Reactor at the Joint Research Centre, Petten, The Netherlands
HFRB1,x.y.z + z′ ≡ experiment, capsule, fuel hole, compacts at stack locations z + z′
tr. 3-7a,b ≡ tray 3-7, containing unbonded, intact fuel particals; a, b ≡ sets of particles

3. EXPERIMENTAL RESULTS

3.1 RESPONSE OF EMBEDDED, EXPOSED KERNELS TO WATER VAPOR

During irradiation, the general sequential response of the embedded, exposed fuel kernels to the injection of water vapor, as shown in Fig. 1, consists of three stages: (1) a rapid transient release of fission gas with a concomitant increase in the steady-state release, (2) a period of constant steady-state release, and, upon cessation of water vapor injection, (3) a decline in the release to prehydrolysis values.

During post irradiation testing, the general sequential response of the exposed fuel kernels is similar to that observed during irradiation. This is shown in Fig. 2. The stages, in post

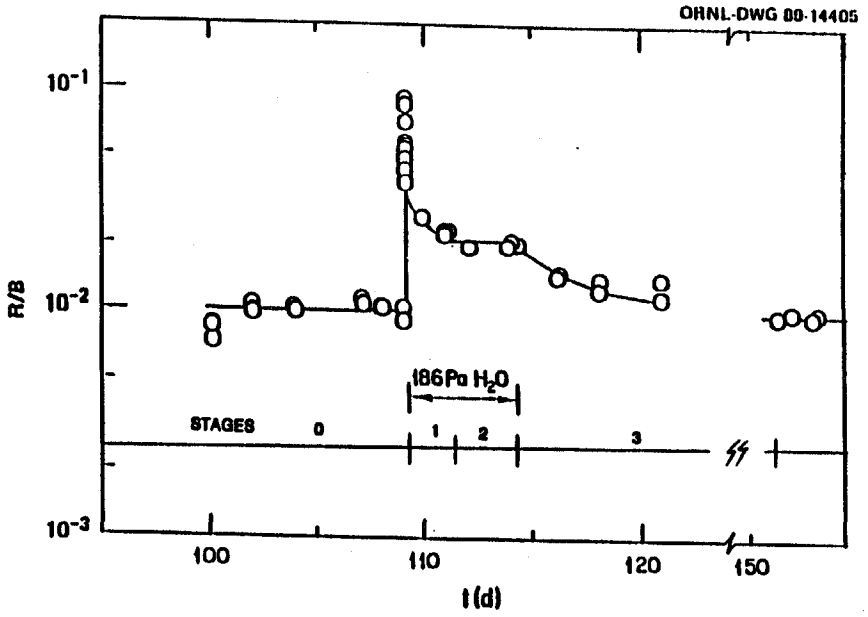

Fig. 1 R/B-time profile for ^{85m}Kr before, during and after a water vapor injection test under irradiation conditions.[1] The temperature and water vapor pressure were 775°C and and 186 Pa, respectively.

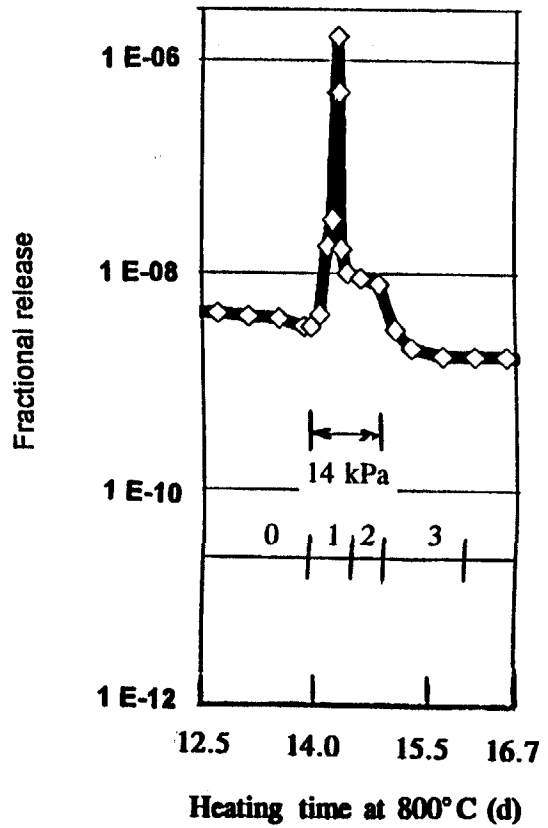

Fig. 2 R/N-time profile for ^{85}Kr before, during and after a water vapor injection test under post irradiation conditions.[7] The temperature and water vapor pressure were 800°C and 14 kPa, respectively. Source Forschungszentrum Jülich GmbH

irradiation testing consist of (1) a rapid transient release of fission gas with a concomitant increase in steady-state release, (2) a period of declining release, and, upon cessation of water vapor injection, (3) a decline in the release to prehydrolysis values. The decline in release of stage 2 and of the pre- and post-hydrolysis periods is a consequence of the declining inventory of the ^{85}Kr. The decline in release after the cessation of water vapor injection occurs much more rapidly under post irradiation than under irradiation conditions.

3.2 STAGE 1

3.2.1 During Irradiation

During stage 1, the primary and secondary sources of released fission gas are, respectively, collectives (gas bubbles) and interstitial gas atoms[1,5]. The identification of the sources is derived from the quantity λ^{-n} on which the fractional release, R/B, depends; here n is a constant and λ is the isotopic decay constant. The value of n may be viewed as a measure of the relative concentrations of the isotopes of a given element in a gas sample; thus high values of n correspond to a preponderance of long-lived isotopes. Fission gas collectives have n values in the range ~1 to ~1.5 and diffusively released fission gas has n values in the range ~0.2 to ~0.5. The profiles of n for the monitored Kr and Xe isotopes are show in Fig. 3 on an expanded time scale for stages 0, 1 and 2 where stage 0 is the pre-injection period. The n values are essentially the same in stages 0 and 2 and correspond to diffusive release of fission gas. In stage 1, the high n values indicate a major contribution from fission gas collectives; for further analysis see Refs. 1 and 5.

By separating the contributions of the sources for the fission gas released in stage 1, the dependencies of the transient release and of the steady state release of fission gas on the partial pressure of water vapor and on temperature were determined[1,4] for pressures $\leq$ 1 kPa. A preliminary analysis[4] indicated a dependence of the transient release of ^{85m}Kr on a power of the partial pressure of water vapor. Thus:

$$f = kP_{H2O}^{\alpha} \qquad (1)$$

where

f = the fraction of the inventory released by the transient mechanism,
k = a constant ($1/Pa^{\alpha}$),
P_{H2O} = the partial pressure of water vapor (Pa)
α = a constant

At 767°C the constant α is 1.9 for $P_{H2O} < 1$ kPa. A further analysis indicates that α is temperature dependent.

In experiment HRB-17,[1] the fractional transient release of gas from collectives was shown to be the same for all isotopes of a given element and the same for the elements Kr and Xe provided the contribution of the Xe precursor, ^{133}I, was taken into account. In this experiment, the range of water-vapor pressures was only one order of magnitude, i.e., ~20 to

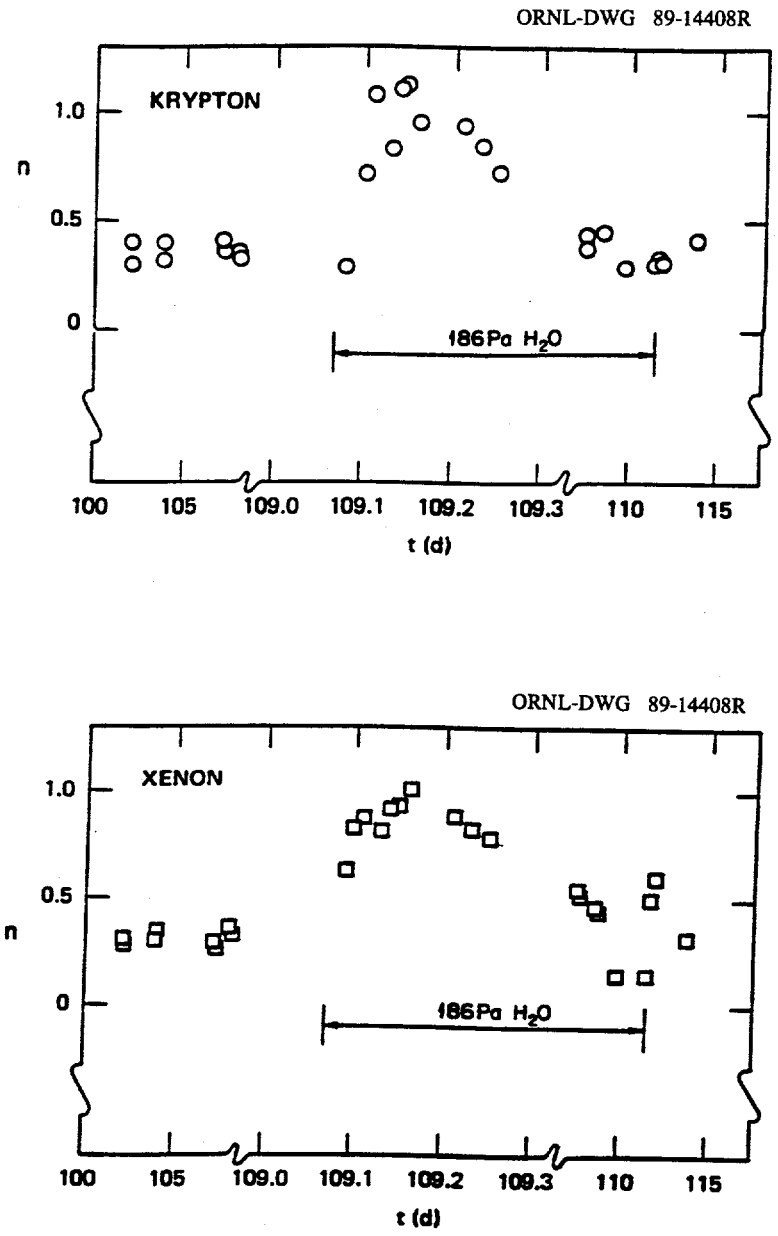

Fig. 3 A measure of the relative concentrations of the isotopes of Kr and Xe before and during water vapor injection. The temperature and water vapor pressure[1] were 755°C and 186 Pa, respectively.

~200 Pa. Nevertheless, the common, fractional, transient release for all isotopes is strong evidence for the release of fission gas atoms in collectives and would be expected also at pressures outside the forementioned range.

The temperature dependence of the transient release of fission gas contained in collectives expressed as an activation energy, was determined[4] to be 393 kJ/mol in the preliminary analysis of experiment HFR-B1.

The fractional transient release is independent of the fission gas inventory[1] and also of the fuel structural changes occurring during accumulation of a specific burnup ($\leq$ 22 % FIMA) for embedded, exposed kernels. This release is thus independent of the burnup at least for isotopes with half-lives $\leq$ 5.3 d.[1] The absolute transient release of long-lived isotopes such as ^{85}Kr, for which the inventory and the burnup approach proportionality, could be dependent on the burnup for embedded, exposed kernels. Further consideration of the effects of burnup on fission gas release are presented in Section 3.5.

Experiment HFR-K6[2,7] provides additional information about the effect of water vapor on fission gas release. A detailed analysis of the experiment and comparison with the results of experiments HRB-17 and HFR-B1 are summarized in Section 3.2.3. The results provide a bridge between the irradiation and post irradiation results and will be introduced into the text only after discussion of the post irradiation release profiles in Stage 1.

3.2.2 Post Irradiation

The response of embedded, exposed kernels to water vapor under post irradiation conditions can be similar to that under irradiation conditions provided account is taken of the post-irradiative, continually-declining inventory (see Section 3.1 and Figs. 1 and 2). However, following certain water vapor injections, profile peaks have occurred in stage 2, i.e., in the period following completion of the first transient release. This is shown in Fig. 4 by profiles from KORA tests with HFR-B1 compacts from capsule 3 during intermittent water-vapor injection.[6,8,9,10] At the beginning of these tests the temperature was raised to 800°C.

As Fig. 4 shows, the departures from the profile in Fig. 2 (also appearing in Fig. 4), consists of peaks in both stages 1 and 2, as presently defined. Further, a pattern is suggested when an injection at a specific partial pressure is repeated (in Fig. 4 once or twice) or follows the temperature ramp at the start. The temperature ramp or the first injection yields a profile having the form of the profile of Fig. 2. Additional injections yield profiles with peaks in both stages 1 and 2. This pattern is repeated when the partial pressure is changed. Thus the pattern of Fig. 2 occurs with the temperature ramp at 1 kPa, with the first injections at 14 and 45 kPa and, arguably, at 50 kPa (see Section 3.3.1). The peak dominated profiles occur on the additional injections which are at partial pressures of 14 and 50 kPa. Strangely, this repetitive pattern occurs also at 1 kPa but with profiles of the second and third intermittent injections being flat and distinctively lower than the fractional release expected in the absence of water vapor.

Also to be noted is the dependence of the profile on the time span of the water-vapor

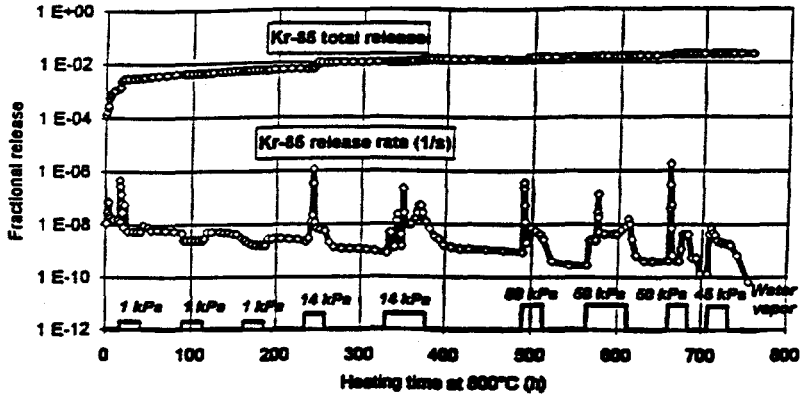

Fig. 4 ^{85}Kr release from compacts under intermittent water vapor injections in KORA. Compacts 3.2.1 and 3.2.2 from experiment HFR-B1 used. Source: Forschungszentrum Jülich GmbH

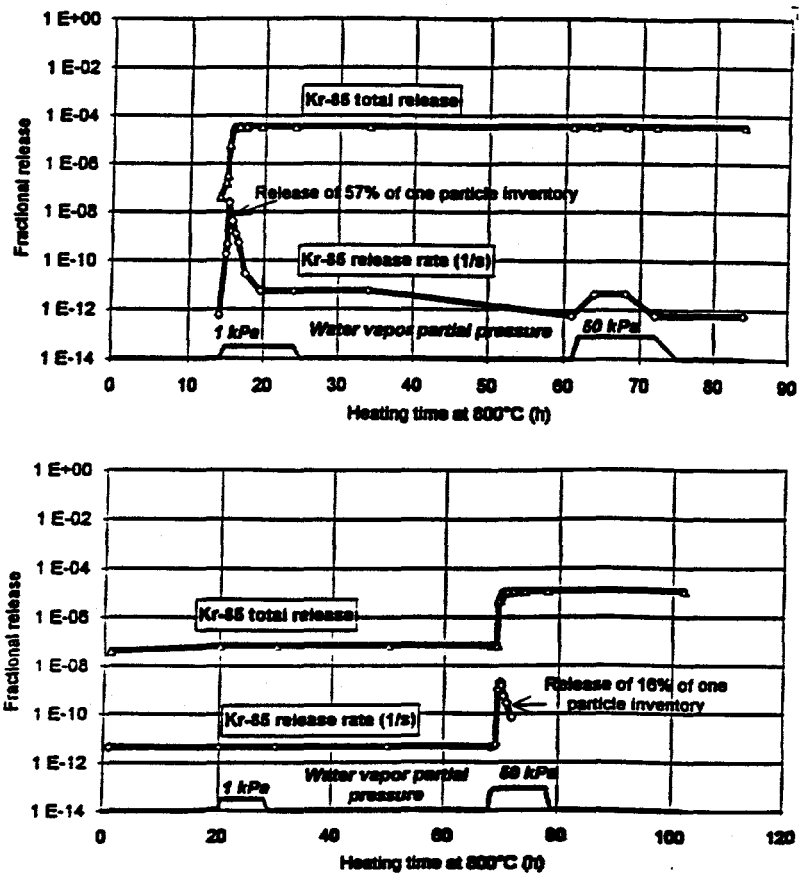

Fig. 5 ^{85}Kr release from fuel spheres under intermittent water vapor injections in KORA. Data shown are for fuel spheres AVR GLE-3, 89/30 (upper graph) and AVR GLE-3, 92/7 (lower graph). Source: Forschungszentrum Jülich GmbH

injection. A clear peak in a clearly established stage 2 occurs only for injection durations of 48 h and not for those of 24 h. (The case of the third injection at 50 kPa is problematic.) Furthermore, following the 48 h injections, the fractional release remains elevated above the values corresponding to the fractional release profile in the absence of water vapor. These patterns and dependencies in post irradiation tests remain to be elucidated. In that task, the difficulty of maintaining high pressures of water vapor and the possibility of fluctuations in the pressure should be addressed.

Similar tests with capsule 2 yielded only a very small release upon water-vapor injection presumably due to the low inventory of ^{85}Kr.[6]

The results of KORA tests with AVR GLE-3 fuel spheres during intermittent water vapor injection are shown in Fig. 5.[6,9,10] For the data from AVR GLE-3, 89/30, the assumption has been made[9,10] that three defective particles are releasing ^{85}Kr.

3.2.3 Comparison of Irradiation and Post Irradiation Data

In stage 1, the comparison of irradiation and post irradiation data is based on the fractional release of fission gas located in collectives. The analysis of the release profile conducted[1,4,5] for stage 1 is clear and definitive for irradiation conditions. The result[1,4] yields the fractional release of gas from collectives as a function of the partial pressure of water vapor, the fractional release being the ratio of the quantity of fission gas released from collectives to the total quantity of fission gas. For post irradiation conditions, there is yet no analysis which can identify the quantity of fission gas release from collectives. Rather the analysis[6,8] is based on the total quantity of released gas (atom collectives and interstitial atoms) minus release in the absence of water vapor. A general assessment of Fig. 4 does not rule out the possibility that the release from collectives dominates and that the release of interstitial atoms is marginally important. In this assessment, all profile peaks are assumed to represent release from collectives. To proceed with the comparison requires acceptance of the general assessment; therefore the assumption, that the reported fractional releases under post irradiation conditions can be regarded as representing release of fission gas from collectives, is adopted.

The data for release of fission gas from collectives as a function of the partial pressure of water vapor at 800°C is shown in Fig. 6. The numerical data are taken from Table 6 of Appendix A. The experimental data and their normalization to a common temperature of 800°C are treated in Appendix A. The derivation of the data from experiment HFR-K6[2,7] is presented in Appendix B. In regard to the partial pressures of water vapor, the irradiation data lie within the range 0.003 to 2.4 kPa and the post irradiation data within the range 1 to 50 kPa.

Consider first, the data on tests with HFR-B1 compacts under irradiation[4] and AVR GLE-3 fuel spheres under post irradiation conditions.[6,8,9,10] They form two distinct groups according to the water-vapor pressure. All those data at pressures < 1 kPa form one group and those above 1 kPa, another. The dependence of the fractional release on the partial pressure of water vapor is given by Eq. (1) ($f = kP_{H2O}{}^{\alpha}$; see Section 3.2.1). At 800°C, $\alpha = 1.7$ below 1 kPa and $\alpha = 0.07$ above 1 kPa. That the α values of the two groups differ for mechanistic reasons and not because of methodology or experimental conditions is supported by two

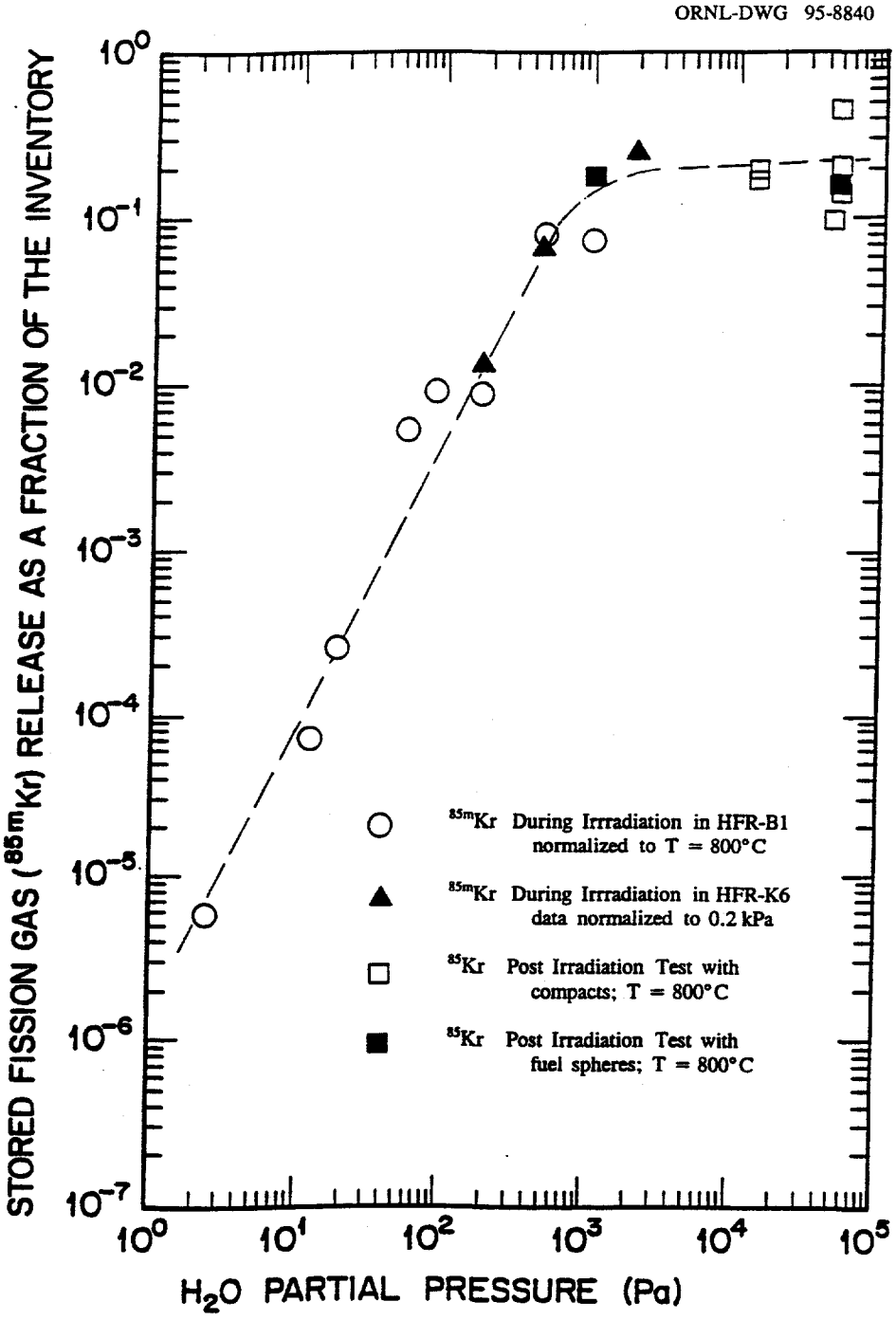

Fig. 6 The fractional transient release of fission gas as a function of the partial pressure of water vapor. Based on data from three independent experiments: HFR-B1 and HFR-K6 during irradiation and post irradiation testing using irradiated HFR-B1 compacts

observations. Firstly, the data from HFR-K6, which spans the range 0.2 to 2.4 kPa as shown in Fig. 6, agree with the data[4] below and also with the data[6,8,9,10] above 1 kPa. Secondly, the transition from a strong to a weak dependence of release on the partial pressure of water vapor has also been observed in experiments with samples containing UC_2.[11] The small value of α above 1 kPa may signal the onset of a transport-limiting mechanism. A further analysis indicates that α is temperature dependent. Note that α is temperature dependent below 1 kPa; above 1 kPa, there are data only at 800°C.

3.3 STAGE 2

3.3.1 During Irradiation and Post Irradiation

During stage 2, which begins after completion of the transient release under irradiation conditions, there is a constant, steady-state release of fission gas. This stage is characterized by the ratio $h_0 = (R/B)_{stage2}/(R/B)_{pre}$ where R/B is the steady-state, fractional fission gas release and the subscript pre refers to the period before water vapor addition, i.e., stage 0 of Fig. 1. In experiment HRB-17, water vapor pressures were held constant for periods of 3 to 11 d and resulted in a constant value of h_0 during these periods.

The ratio h_0 is independent of the partial pressure of water vapor over the range 0.02 to 0.2 kPa by direct measurement[1]; the ratio is also independent of isotopic variation. Based on the consistency of analytical results, a range extending to 2.0 kPa could reasonably be postulated. A qualitative theoretical argument has been presented[1] to account for this independence. The ratio apparently differs for the elements Kr and Xe to the same extent that the atomic volumes of these elements differ.[1]

In stage 2, interstitial fission gas atoms are released diffusively. The temperature dependence differs before and during water vapor addition. The activation energy is 65.8 kJ/mol before exposure of the fuel to water vapor[1] and is 23.6 kJ/mol under a constant partial pressure of water vapor during stage 2.[4] The latter activation energy accounts for the different values of h_0 measured at temperatures of 680 and 767°C in experiments HFR-K6 and HFR-B1, respectively. The mean value of h_0 in experiment HFR-K6 was 1.55. By using an activation energy of 23.6 kJ/mol and a temperature of 767°C, the predicted value of h_0 for experiment HRB-17 becomes 2.0 which is the value measured in experiment HRB-17 at 767°C. This consistency confirms the observation[1] that h_0 is independent of element, isotope, and the partial pressure of water vapor.

In the post irradiation tests, stage 2 has a profile complicated by peaks that occur only on repeated water vapor injections at specific partial pressures as further described in Section 3.2.2. The profiles generated on the first injection at a specific pressure in the cases of 14 and 45 kPa, show a steady state release declining in parallel with the background release based on the absence of water vapor. Consequently, the difference can be viewed as a constant relative release attributable to the effect of water vapor. In the case of the first injection at 50 kPa, a second peak appears to induce a steeper decline in the steady-state release than corresponds to the background release. This behavior remains to be elucidated.

3.4 STAGE 3

3.4.1 During Irradiation

During stage 3, which begins after the cessation of water vapor addition, the R/B declines; the decline is attributed to the sintering of the fuel aided by the neutron flux. The return of R/B to the pre-addition value implies return to a structure equivalent in release to the initial structure. The decline is characterized by a frequency factor, δ, which appears in the function $\exp[\delta(t - t_T)]$. Here t_T is the cessation time. The time at which the approach to the equivalent initial fuel structure is 95 % complete is given by the ratio $\sim 3/\delta$. The values of delta in experiments HFR-B1 and HFR-K6, both conducted in the high flux reactor (HFR) at Petten, The Netherlands, are the same (0.109/d). Consequently the fuel restructuring in both cases is 95 % complete after 27.5 d. The data of stage 3 and the fit to the data using the preceding value of δ are shown in Figs. 7a and 7b for experiments HFR-K6 and HFR-B1, respectively. At higher neutron fluxes, as in the high flux isotope reactor (HFIR) at ORNL, the value of δ is larger, being 0.425/d. The exact relation of δ and the neutron flux has yet to be determined.

3.4.2 Post Irradiation

During stage 3, which begins after the cessation of water vapor addition, the R/B declines as observed under irradiation conditions also. The characteristic times for decline, $3/\delta$, are in the range 10 to 49 h for the data of Fig. 4 as shown in Table 2. Times of this order are very small compared to the characteristic times under irradiation conditions. Compared to the

Table 2. Characteristic Times for Stage 3 under Postirradiation Conditions

P_{H2O}(kPa)	Δt_i(h)	Δt_c(h)
14	24	20
14	48	49
50	24	10
50	48	20
50	24	12
45	24	22

P_{H2O} = partial pressure of water vapor
Δt_i(h) = duration of water vapor injection
Δt_c(h) = characteristic time ($\sim 3/\delta$; see Section 3.4.1)

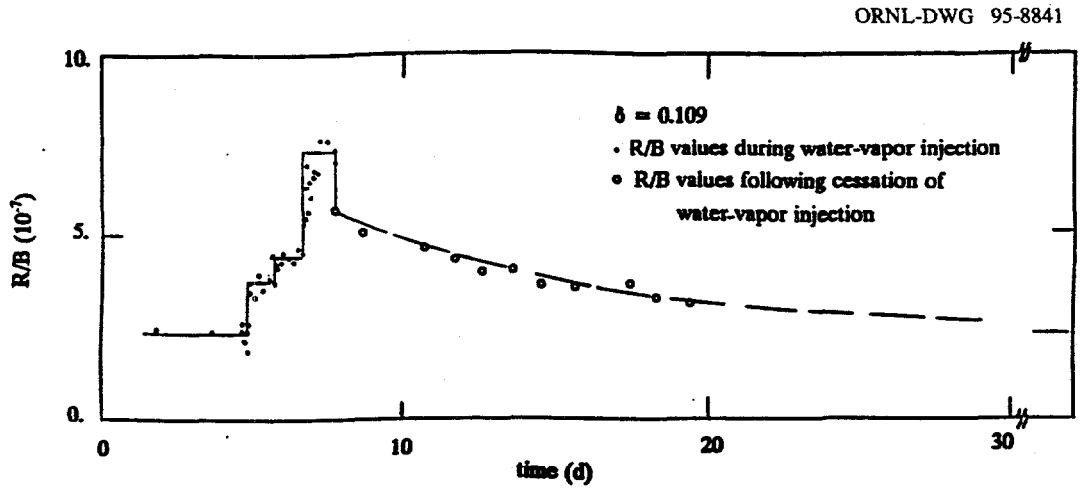

Fig. 7a The decline of R/B following the cessation of water vapor addition in experiment HFR-K6. Cycle 88.10, test 5 at 925°C. The relevant data are represented by circles and the curve is derived from the equation $(R/B)_{decline}/(R/B)_{pre} = 1 + 1.38\{\exp[\delta(t - t_T)]\}$ with $(R/B)_{pre} = 2.4E\text{-}7$, $\delta = 0.109/d$ and t in units of days (d)

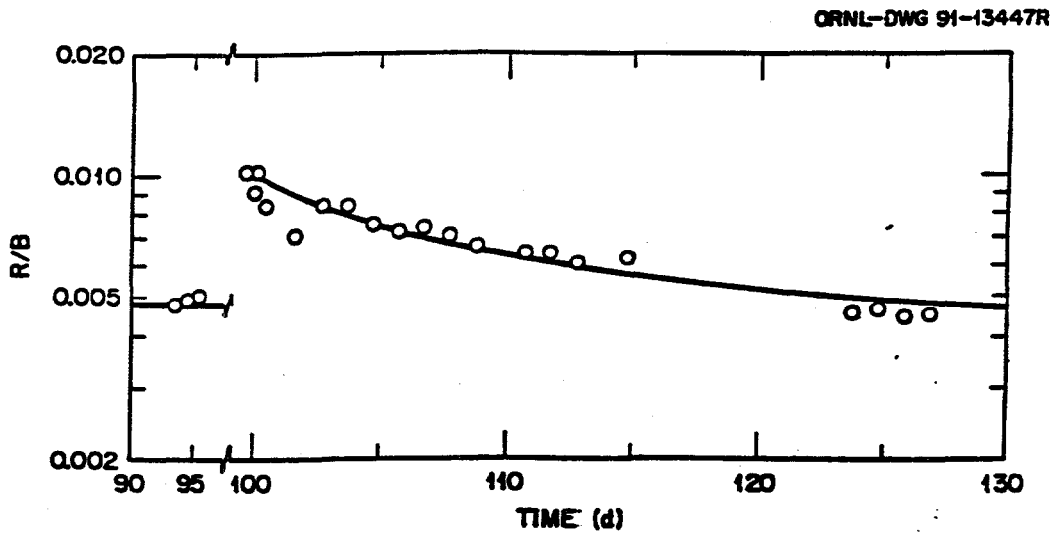

Fig. 7b The decline of R/B following the cessation of water vapor addition in experiment HFR-B1. Cycle 25 at 680°C. The data are represented by circles and the curve is derived from the equation $(R/B)_{decline}/(R/B)_{pre} = 1 + 1.3\{\exp[\delta(t - t_T)]\}$ with $(R/B)_{pre} = 4.6E\text{-}03$, $\delta = 0.109/d$ and t in units of days (d).

27.5 d characteristic time for the B1 and K6 irradiations in the HFR, the largest is only 7% as long. Further study of Fig. 4 reveals that (1) the higher the partial pressure of water vapor, the smaller the characteristic time for a given injection time and (2) the longer the water vapor injection, the larger the characteristic time at a given partial pressure.

That characteristic times are large under irradiation conditions and small under post irradiation conditions suggests that radiation damage (it's occurrence or absence) is the explanatory key. Deposition of large energies (> thermal energies) is postulated to create sites of high binding energy accessible to species derived from the injected water vapor and also to provide the energy for emission of these species from such sites. Cessation of the injection abolishes the reservoir of water vapor and initiates the outward migration of formerly bound species. These species are repeatedly bound at and emitted from sites of high energy in a balance that governs their migration rate. Higher neutron fluxes increase the rate of binding and emission and thus further promote the escape of the species from the fuel kernel. Removal of the species is associated with return to a fuel structure equivalent to that existing just prior to water vapor injection. Under post irradiation conditions, no additional energy is repeatedly deposited in the fuel. Thermal energies govern the emission at all times and from all accessible bonding sites. The residence times at the binding sites are apparently small and account for the rapid decline in R/B.

3.5 RESPONSE OF BARE KERNELS TO WATER VAPOR

Post irradiation experiments were also conducted with bare kernels removed from unbonded intact particles (see Table 1) and placed in graphite crucibles. These kernels were unconstrained in the presence of injected water vapor in contrast to the exposed kernels in the compacts and fuel spheres. In compacts, the exposed kernels were surrounded by pyrocarbon coating fragments and embedded in compact matrix material as shown ceramographically.[12] In fuel spheres, the exposed kernels, surrounded by failed coatings, were embedded in A3-3 matrix graphite. The bare kernels from the capsules responded extraordinarily strongly not only to concentration gradients of water derived species but also to temperature gradients induced during the temperature rise to 800°C at the beginning of the KORA experiments. In one of the two experiments with bare kernels from unbonded particles irradiated in HFR-B1, the temperature gradients induced an average fission gas release of 71% whereas in the other experiment, the concentration gradients induced an average transient release of 66%. These magnitudes imply randomness in the effect of the gradients or of structural changes induced in the process of removing the kernels from intact particles.

In the experiments with bare kernels from deconsolidated fuel spheres, there were also temperature- and concentration-gradient induced transient releases. The concentration gradients induced transient releases of 2.6% and 17% for the sets of 5 fuel kernels from fuel spheres AVR GLE-3 73/8 and 92/29, respectively. Thus for transient releases of 2.6, 17 and 66%, the corresponding burnups are 4.7, 9.2 and 19.6% FIMA. The transient releases are nearly proportional to the burnups.

Although the transient release from bare kernels is nearly proportional to the burnup, there is no significant dependence of the transient release on burnup for the constrained, exposed

kernels. Apparently the friability of the kernel increases with burnup and accounts for the increase in transient release from unconstrained bare kernels under the stress induced by concentration gradients. Note that the unconstrained bare kernels were exposed, for the same partial pressure of water vapor, to a much higher oxygen potential than were the constrained exposed kernels embedded in carbonaceous material.

4. SUMMARY

The effect of water vapor on the release of fission gas from fuel elements of high temperature, gas-cooled reactors has been investigated by the injection of water vapor into carbonaceous systems containing particles with exposed fuel kernels. During three irradiation experiments, HRB-17/18, HKF-K6 and HFR-B1, in which there were a known number of exposed kernels, water vapor was injected at partial pressures from 0.003 to 2.4 kPa. Post irradiation experiments were conducted in the KORA facility with compacts from HFR-B1, fuel spheres from irradiation in the AVR, and bare kernels from these configurations at pressures from 1 to 50 kPa.

During irradiation, the general sequential response of the embedded, exposed fuel kernels to the injection of water vapor consisted of three stages: (1) a rapid transient release of fission gas with a concomitant increase in the steady-state release, (2) a period of constant steady-state release, and, upon cessation of water vapor injection, (3) a decline in the release to prehydrolysis values.

During post irradiation testing, the general sequential response was similar to that observed during irradiation but with the superposition of a general decline in release (corresponding to the decline in the fission gas inventory). The decline in release after the cessation of water vapor injection occurred much more rapidly under post irradiation than under irradiation conditions.

The primary and secondary sources of released fission gas were identified as collectives (gas bubbles) and interstitial gas atoms through evaluation of the quantity λ^{-n}. Here λ is a decay constant and n a measure of the relative concentrations of the isotopes of a given element. In stages 0 (prehydrolysis) and 2, n was small as observed innumerable times for diffusive release. In stage 1 where the transient release dominated, the n values were large. Large n values are associated with gas bubbles as can be deduced by considering the net addition to and the decay of fission gas atoms within bubbles. In the post irradiation tests, such information could not be obtained as only one isotope, ^{85}Kr, was measurable.

The fractional transient release during irradiation was found to be the same for all isotopes of Kr and Xe (when ^{133}I was taken into account), to be dependent on a power of the water vapor pressure, the power being dependent on the temperature, and to have a large, associated activation energy (393 kJ/mol). Transient releases were observed under post irradiation conditions but the patterns were more complicated; these remain to be elucidated.

At 800°C, a comparison of the irradiation and post irradiation data for the transient release shows a dependence of the release on the partial pressure of water vapor to the 1.7 power

in the range 0.003 to 1 kPa and to the 0.07 power in the range 1 to 50 kPa. That the power values of the two groups differ for mechanistic reasons and not because of methodology or experimental conditions is supported by two observations. Firstly, the data from HFR-K6, which spans the range 0.2 to 2.4 kPa as shown in Fig. 6, agree with the data[4] below and also with the data[6,8,9,10] above 1 kPa. Secondly, the transition from a strong to a weak dependence of release on the partial pressure of water vapor has also been observed in experiments with samples containing UC_2.[11] The small value of the power above 1 kPa may signal the onset of a transport-limiting mechanism.

The steady state, fractional fission gas release in stage 2 is diffusive. The release can be characterized by the ratio, h_o, of the R/B during water vapor injection to that immediately preceding injection. This ratio, under irradiation conditions, is independent of the partial pressure of water vapor over the range 0.02 to 0.2 kPa and of isotopic variation. For the elements Kr and Xe, the ratio differs to the same extent as the atomic volumes of these elements differ. A qualitative theoretical argument has been presented to account for this independence. The ratio under post irradiation conditions has yet to be examined.

The temperature dependence of h_o differs before and during water vapor addition; the activation energy is 65.8 kJ/mol before and 23.6 kJ/mol during water vapor addition. By using these activation energies and the value of h_o at 680°C in experiment HFR-K6, the measured value of h_o at 767°C in experiment HFR-B1 is predicted.

During stage 3, which begins after the cessation of water vapor addition, the R/B declines. Under irradiation conditions, the characteristic time of the decline, τ_c, is inversely proportional to the neutron flux. Under post irradiation conditions, τ_c is much smaller than under irradiation conditions. Thermal energies govern the interaction of water derived species under post irradiation conditions whereas high energy depositions govern the interaction under irradiation conditions. The latter results in stronger binding and higher retentivity of the species than occurs in a thermal energy environment. Thus τ_c would be expected to be smaller in the thermal energy environment.

5. ACKNOWLEDGEMENTS

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APPENDIX A

THE DEPENDENCE OF FISSION GAS RELEASE ON THE VAPOR PRESSURE OF WATER AT 800°C

1. SOURCES AND DATA

The sources and data associated with the release of fission gas from collectives as a function of the partial pressure of water vapor are assembled and the data are normalized to a common temperature at which they may be compared. There are four sources:

S1. the release of ^{85m}Kr during irradiation of compacts in experiment HFR-B1 at a temperature of 767°C,

S2. the release of ^{85m}Kr during irradiation of fuel spheres in experiment HFR-K6 at a temperature of 680°C,

S3. the release of ^{85}Kr during post irradiation testing in KORA with HFR-B1 compacts at 800°C,

S4. the release of ^{85}Kr during post irradiation testing in KORA at 800°C with fuel spheres irradiated in the Arbeitsgemeinschaft Versuchs-Reaktor (AVR).

1.1 RELEASE OF ^{85M}Kr FROM COMPACTS DURING IRRADIATION IN EXPERIMENT HFR-B1

Data from the preliminary analysis[1] of experiment HFR-B1 are presented in Table 1. Shown are the quantities of fission gas released from collectives as a fraction of the inventory of ^{85m}Kr for given values of the partial pressure of water vapor and the temperature.

To normalize the data of Table 1 to a common temperature, T_o, the following relation[1] is used:

$$f(P,T_o) = f(P,T)g(P,T_0)/g(P,T) \quad (1)$$

where

$$g(P,T) = P^{-4.353 + 6503/T} \cdot \exp\{-4.7257(10^4/T)\} \quad (2)$$

and

$f(P,T_o)$ = fractional fission gas release at the common temperature,
$f(P,T)$ = measured fractional release at the experimental temperature,
T_o = the common temperature (1073 K) at which f data are compared,
P = water vapor pressure (Pa) in injection tests ($\equiv P_{H2O}$).

Table A1. HFR-B1 conditions and ^{85m}Kr release from compacts

Inj. No.[a]	Cycle	$P°_{H2O}$(Pa)[b]	P_{H2O}(Pa)[c]	T(°C)	10^4/T(K)	f(P,T)[d]
15a	89.06	1060	1050.0	820	9.149	7.6 E-2
14	89.04	550	510.7	866	8.780	1.1 E-1
13	89.02	250	184.2	915	8.418	2.9 E-2
12b	89.01	112	91.6	890	8.598	3.2 E-2
11	88.10	123	12.2	1040	7.616	61.4 E-2
5	88.01	90	56.5	925	8.347	4.1 E-2
3	87.09	45	2.8	1040	7.616	5.7 E-3
2	87.05	45	19.1	950	8.177	6.5 E-3

[a]Inj. No. = the sequential number of the water-vapor, injection test,
[b]$P°_{H2O}$ = the partial pressure of added water vapor,
[c]P_{H2O} = the calculated partial pressure of water vapor at the fuel compact surfaces,
[d]f(P,T) = the release of stored-fission gas as a fraction of the inventory at P_{H2O} and T. See Ref. 1.

Table A2. HFR-B1 conditions and ^{85m}Kr normalized release from compacts

Inj. No.	P_{H2O}(Pa)	T_o(K)	T(K)	f(P,T)	f(P,T_o)
15a	1050.5	1073	1093	7.60E-02	7.34E-02
14	510.7	1073	1139	1.10E-01	7.66E-02
13	184.2	1073	1188	2.90E-02	8.71E-03
12b	91.6	1073	1163	3.20E-02	8.81E-03
11	12.2	1073	1313	1.40E-02	7.13E-05
5	56.5	1073	1198	4.10E-02	5.31E-03
3	2.8	1073	1313	5.70E-03	5.69E-06
2	19.1	1073	1223	6.50E-03	2.63E-04

The f(P,T) data of Table 1, normalized to T = 800°C, are presented in Table 2. The data sought are given in the columns of Table 2 under the headings: P_{H2O}(Pa), T_o(K), and f(P,T_o).

Note that the function g(P,T), Eq. 2, cannot be used outside the ranges of P and T associated with the HFR-B1 experiment. A more detailed discussion of this issue is given in Appendix C of reference 1.

The least squares fit to the f(P,T_o) data of Table 2 as a function of P at T = 1073 K is given[1] by:

$$f(P,T) = 2.13E+13*P^{-4.353 + 6503/T} * e^{-4.7257E+4/T} \rightarrow 1.59E-6*P^{1.7076}. \quad (3)$$

1.2 RELEASE OF ^{85M}Kr FROM FUEL SPHERES DURING IRRADIATION IN EXPERIMENT HFR-K6

Data from the preliminary analysis (see Appendix B) of experiment HFR-K6[2,3] are presented in Table 3. Shown, are the quantities of fission gas released from collectives as a fraction, f(P,T_o), of the inventory of ^{85m}Kr for given values of the partial pressure of water vapor and a common temperature. The values of f(P,T_o) listed in Table 3 are the product {R_r*f(200 Pa, 1073 K)}:

Table A3. HFR-K6 conditions and ^{85m}Kr normalized release from fuel spheres

Inj. No.[(a)]	Cycle	T(K)[(b)]	P_{H2O}(Pa)[(c)]	R_r[(d)]	T_o(K)[(e)]	f(P,T_o)[(f)]
1	25	680	200	1.0	1073	1.35E-02
2	25	680	500	5.1	1073	6.89E-02
3	25	680	2000	16.8	1073	2.26E-01

[(a)]Inj. No. = the sequential number of the water-vapor, injection test,
[(b)]T(K) = the temperature of the experiment,
[(c)]P_{H2O}(Pa) = the partial pressure of water vapor in the experiment,
[(d)]R_r = the relative release derived by analysis (see Appendix B, page 36),
[(e)]T_o(K) = the common temperature (1073 K) at which f data are compared,
[(f)]f(P,T_o) = fractional fission gas release at the common temperature.

The data sought are given in the columns of the preceding table under the headings: P_{H2O}(Pa), T_o(K) and f(P,T_o)

1.3 RELEASE OF ^{85}Kr UNDER POST IRRADIATION CONDITIONS FROM COMPACTS IRRADIATED IN EXPERIMENT HFR-B1

Data[4,5] from the post irradiation heating of compacts 3.2.1and 3.2.2(irradiated in experiment HFR-B1) are presented in Table 4. The data in Table 4 are selectively taken from Table 19 of Ref. 4. Note here, that the writer, with a calculation procedure representing his understanding of the data, was able to calculate the results in Table 19 of Ref. 5 but not the results in Table 19 of Ref. 4. Thus there is a question about the values used in Table 4. This matter remains to be resolved.

Table A4. KORA conditions and ^{85}Kr release from irradiated compacts

Water Vapor				^{85}Kr release
Inj. No.[a]	t (h)[b]	P_{H2O}(kPa)[c]	T_o(K)[d]	$f(P,T_o)$[e]
1	24	1	1073	1.56E-02
2	24	1	1073	-1.03E-02
3	24	1	1073	-0.47E-02
4	24	14	1073	1.902E-01
5	48	14	1073	1.559E-01
6	24	50	1073	2.001E-01
7	48	50	1073	1.326E-01
8	23	50	1073	4.441E-01
9	24	45	1073	9.25E-02

[a]Inj. No. = the sequential number of the water-vapor, injection test,
[b]t = the time duration of the water vapor injection,
[c]P_{H2O} = the partial pressure of water vapor in the experiment,
[d]T_o = the common temperature (1073 K) at which f data are compared,
[e]$f(P,T_o)$ = fractional fission gas release at the common temperature.

The data sought are given in the columns of the preceding table under the headings: P_{H2O}(Pa), T_o(K) and $f(P,T_o)$

1.4 RELEASE OF ^{85}Kr UNDER POST IRRADIATION CONDITIONS FROM FUEL SPHERES IRRADIATED IN THE AVR

Data from the post irradiation heating of fuel spheres GLE-3, 89/30 and GLE-3, 92/7 are presented in Table 5. These data are taken from Ref. 5, Figs. 3 and 5, respectively. For the data from AVR GLE-3, 89/30, the assumption has been made[6,7] that three defective particles are releasing ^{85}Kr.

Table A5. KORA conditions and ^{85}Kr release from AVR fuel spheres

AVR Fuel Spheres	Water Vapor				^{85}Kr release
	Inj. No.[(a)]	Time (h)[(b)]	P_{H2O}(kPa)[(c)]	T_o(K)[(d)]	f(P,T_o)[(e)]
GLE-3, 89/30	1	10	1	1073	1.9E-01
GLE-3, 92/7	2	10	50	1073	1.6E-01

[(a)]Inj. No. = the sequential number of the water-vapor, injection test,
[(b)]t = the time duration of the water vapor injection,
[(c)]P_{H2O} = the partial pressure of water vapor in the experiment,
[(d)]T_o = the common temperature (1073 K) at which f data are compared,
[(e)]f(P,T_o) = fractional fission gas release at the common temperature.

2. SUMMARY OF FISSION GAS RELEASE DATA AS A FUNCTION OF THE PARTIAL PRESSURE OF WATER VAPOR AT 800°C

A summary of the data presented in Tables 1 through 5 is given in Table 6 on the following page. Note that the entries in column 6 and in rows 12, 13 and 14 were not further used. These values are at least a factor of 12 smaller than the average of all other data at partial pressures of water vapor in the range 1 to 50 kPa. In addition, two of these excluded values are negative and therefore have no physical significance.

Table A6. Summary of conditions and normalized krypton release

Source	Mode[a]	Isotope	T_0(°C)[b]	P(Pa)[c]	f(P,T_0)[d]	Ref.
S1	I	^{85m}Kr	800	1.05E+03	7.34E-02	1
	I	^{85m}Kr	800	5.11E+02	7.66E-02	1
	I	^{85m}Kr	800	1.84E+02	8.71E-03	1
	I	^{85m}Kr	800	9.16E+01	8.81E-03	1
	I	^{85m}Kr	800	1.22E+01	7.13E-05	1
	I	^{85m}Kr	800	5.65E+01	5.31E-03	1
	I	^{85m}Kr	800	2.8E+00	5.69E-06	1
	I	^{85m}Kr	800	1.91E+01	2.63E-04	1
S2	I	^{85m}Kr	800	2.00E+02	1.35E-02	2,3,4
	I	^{85m}Kr	800	5.00E+02	6.89E-02	2,3,4
	I	^{85m}Kr	800	2.00E+03	2.26E-01	2,3,4
S3	PI	^{85}Kr	800	1.00E+03	1.56E-02	5,6
	PI	^{85}Kr	800	1.00E+03	-1.03E-02	5,6
	PI	^{85}Kr	800	1.00E+03	-0.47E-02	5,6
	PI	^{85}Kr	800	1.40E+04	1.902E-01	5,6
	PI	^{85}Kr	800	1.40E+04	1.559E-01	5,6
	PI	^{85}Kr	800	5.00E+04	2.001E-01	5,6
	PI	^{85}Kr	800	5.00E+04	1.326E-01	5,6
	PI	^{85}Kr	800	5.00E+04	4.441E-01	5,6
	PI	^{85}Kr	800	4.50E+04	9.25E-02	5,6
S4	PI	^{85}Kr	800	1.00E+03	1.9E-01	5,7,8
	PI	^{85}Kr	800	5.00E+04	1.6E-01	5,7,8

[a] Mode = I under irradiation conditions: PI under post irradiation conditions
[b] T_0(°C) = the temperature at which the data have taken or to which they have been normalized,
[c] P(Pa) = the partial pressure of water vapor,
[d] f(P,T_0) = the release of fission gas stored in collectives as a fraction of the inventory.

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APPENDIX B

A COMPARISON OF THE EFFECT OF WATER VAPOR IN HFR-K6 WITH THAT IN HRB-17 AND HFR-B1

1. INTRODUCTION

In experiment HFR-K6, four fuel spheres were irradiated in three capsules in the Petten HFR reactor. There were two defective fuel particles within these fuel spheres. An opportunity was thus provided to observe the effect of water vapor on fission gas release by injection tests. The results of these tests have been analyzed in a preliminary fashion and the results compared with those for experiments HFR-B1 and HRB-17.

2. EXPERIMENT HRB-17

Prior experiments[1,2] involving water-vapor injections into a capsule containing fuel elements with coated fuel particles, some of which had exposed kernels, have provided a generic time-profile for fission gas release from kernels. The general sequential response of exposed fuel kernels to the addition of water vapor consists of three stages: (1) a rapid, transient release of fission gas with a concomitant increase in the steady state release, (2) a period of constant steady-state release, and, upon cessation of water vapor injection, (3) a decline in the release to prehydrolysis values except where configuration changes occur in the particles with exposed kernels. Two minor features in the generic profile are also included in the present analysis: (1) a two hour period for the release of fission gas from each UO_2[1] kernel during the rapid transient release of fission gas in stage 1,[2] and (2) a brief, but more rapid decrease in fission gas release at the beginning of stage 3 than later[1].

3. EXPERIMENT HFR-K6

3.1 TEMPERATURE TRANSIENT

During the irradiation of experiment HFR-K6 a planned, transient increase in temperature of 200°C was induced.[3] During this event, two peaks appeared in the effluent fission gas profile from capsule C. The companion capsules, A and B, yielded no such peaks and otherwise had fractional release values 1/3rd those of capsule C. The time profile of fission gas release during the period of increased temperature is shown in Fig. B1. The temperature was increased from ~1000°C to ~1200°C for a period of about 6 h beginning at 100 min. on the time scale used in Fig. B1. The two peaks and the increased steady-state release in capsule C were judged to reflect the presence of two defective, coated fuel particles[3], i.e., particles with kernels effectively exposed to the particle exteriors.

The profile for capsule C indicates both a transient and a steady state release of ^{88}Kr. To separate these contributions, the profile of capsule B was superimposed on that of capsule C in the time period between 300 and 450 min.. The result is shown in Fig. B2. The difference between these two profiles, as shown in Fig. B3 represents the transient releases

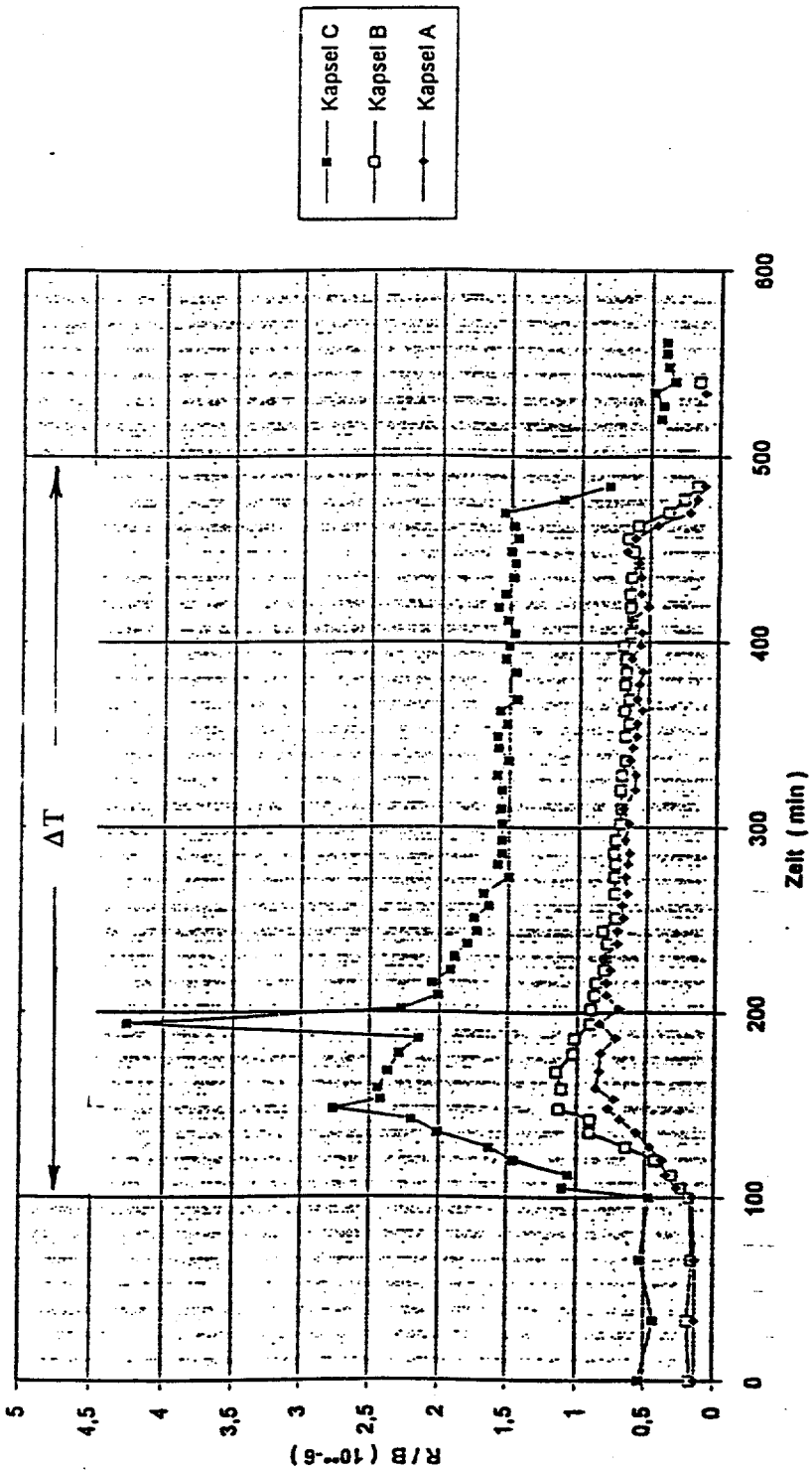

Fig. B1 Release of ^{88}Kr from Capsules A, B, and C in experiment HFR-K6. Cycle 19. The temperature was increased by 200°C to ≈1200°C beginning at about 100 min. Source: Forschungszentrum Jülich GmbH

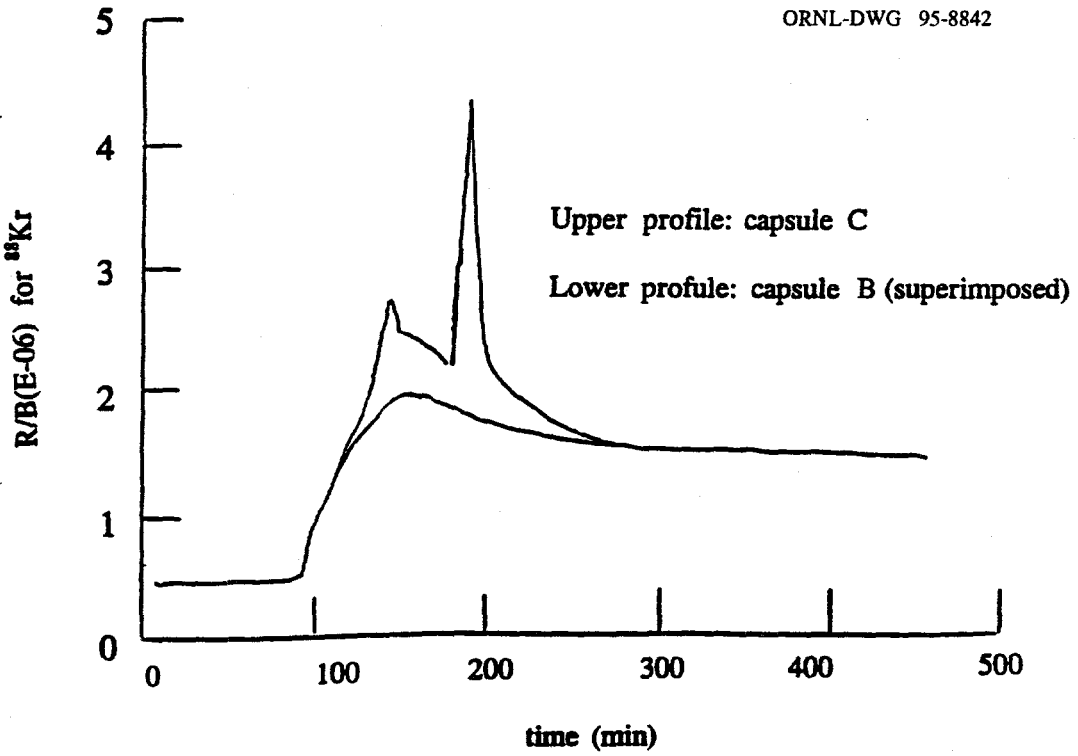

Fig. B2 Division of the ^{88}Kr profile into transient and steady state components.

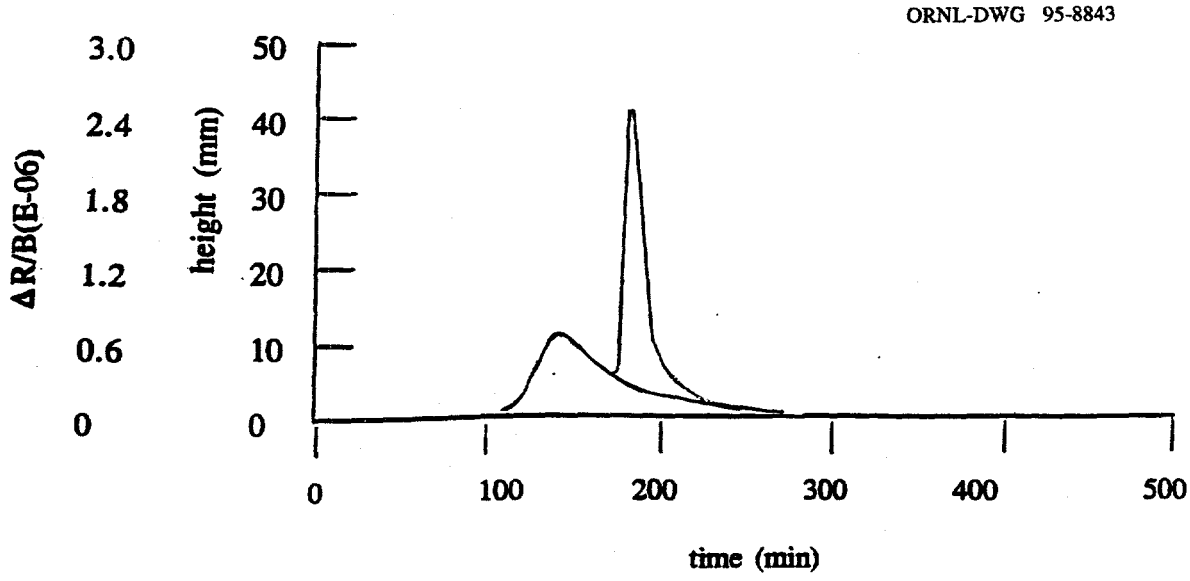

Fig. B3 The transient releases of ^{88}Kr from the two defective particles in experiment HFR-K6. Cycle 19.

in capsule C. From geometric considerations, assuming large scale homogeneity in the fuel sphere matrix material, the distribution of the transient release from a defective particle lying at the center of the fuel sphere should be symmetric and that for one lying near the surface of the fuel sphere should be asymmetric (assuming a continuum in the distribution asymmetry along any radius vector of the fuel sphere). This implies that the more strongly peaked distribution curve of Fig. B3 represents a defective particle more nearly centered in the fuel sphere than does the companion distribution curve.

The nature of the transient component of release following the increase of temperature can be assessed on the basis of the data shown in Fig. B4 and the relation:

$$R/B = g(I,F,T)/\lambda^n \qquad (1)$$

where

$g(I,F,T)$ = a function of inventory, (I), fission rate density, (F), and temperature, (T),
λ = isotope decay constant (1/s), and
n = a parameter

The result of applying Eq. 1, using the R/B values in Fig. B4 for the three isotopes ^{85m}Kr, ^{87}Kr, and ^{88}Kr, is the determination of the values of n at selected times before and during the increase in temperature and after the decrease in temperature. The n values as a function of the time (scale of Fig. B4) are as follows:

Time (min)	n(dimensionless)
50	0.16
148	0.50
193	0.70
350	0.16
472	0.14
565	0.17

The larger values of n occur only near the time of the peaks; otherwise, the n values are relatively small. The large values of n indicate the release of fission gas from collectives[1,2,4]; the relatively small values are consistent with diffusional release of single atoms. For further discussion see references 1 and 2.

The rapid rise in fission gas release in response to the temperature ramp portion at the beginning of the temperature transient, as shown in Fig. B1 for example, indicates rapid transport of fission gas from the fuel sphere to the gas sampling station. In contrast are the apparent "transit times" of the peak releases of fission gas from the defective particles. The times at which the peaks appear are postulated to depend, rather, on the temperature in the fuel kernel, the temperature gradient in the fuel kernel and the structure of the defective particles.

Consider two defective particles with gaps between two of the coatings (most likely the inner

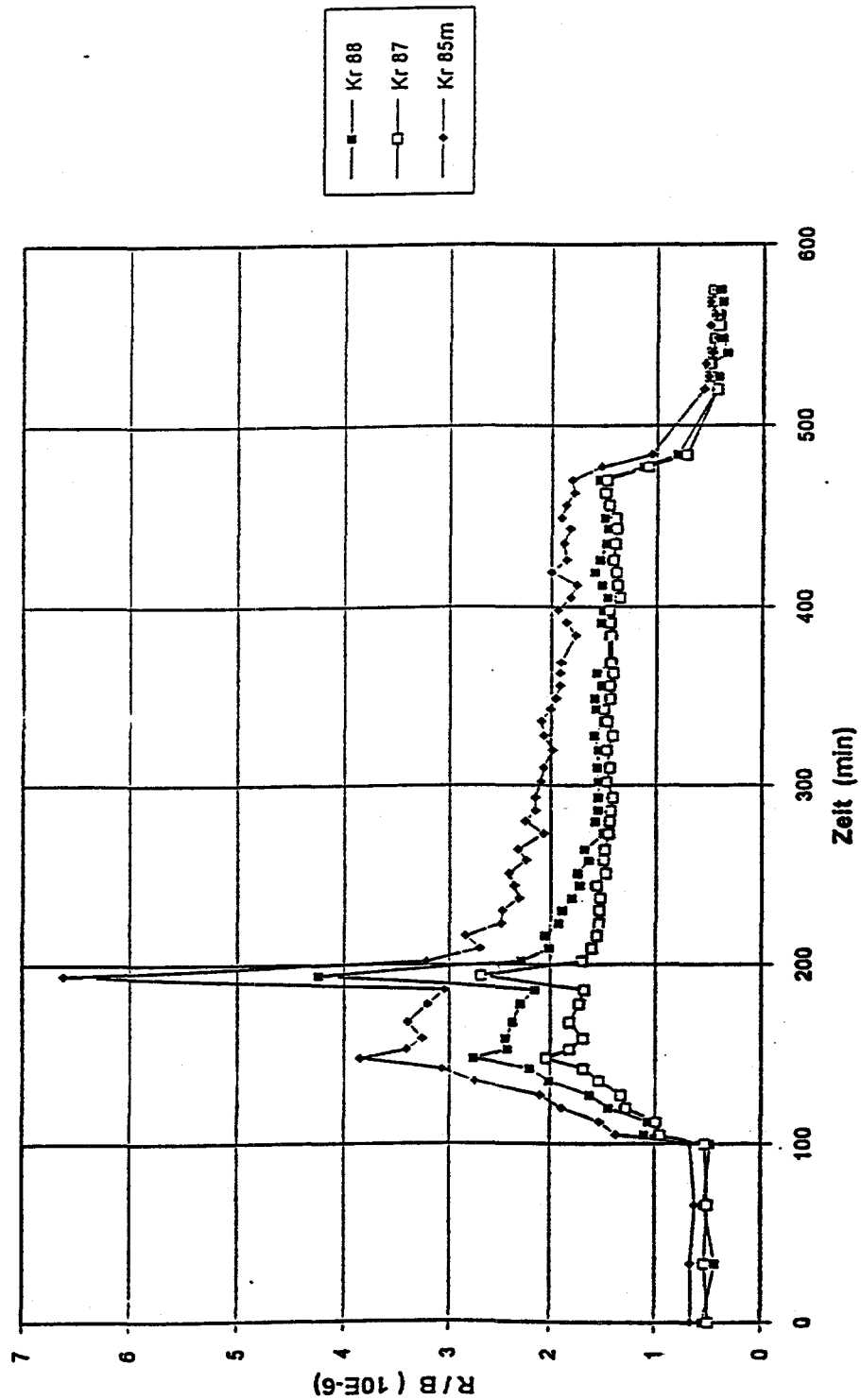

Fig. B4 Release of ^{85m}Kr, ^{87}Kr, and ^{88}Kr from Capsule C in experiment HFR-K6. Cycle 19. The temperature was increased by 200°C to 1200°C beginning at about 100 min. Source: Forschungszentrum Jülich GmbH

pyrocarbon and buffer coatings) or between the kernel and buffer coating. As the effective width of a gap increases, the kernel temperature increases. The effective width of a gap depends on the thermal conductivity of the gas mixture in the gap as well as the physical separation of the bounding materials. In experiment HFR-K6, the temperature ramp was developed by changing the composition of the gas mixture in the capsule. In particular, neon was added stepwise to helium (the carrier gas) to decrease the thermal conductivity and thereby to increase the temperature of material on the high temperature side of any gap. For the defective particles this resulted in an increase of the temperature of the kernel.

The time at which the peak release of fission gas from the defective particles occurs can now be described by applying the above postulate. Consider two defective particles with gaps of different physical widths but always containing gas mixtures having the same thermal conductivities. This implies that the kernel temperature is higher in the gap of the defective particle with the larger physical width. As the thermal conductivity in the gas mixture is decreased, the kernel temperatures rise and in the stepwise fashion of the neon addition. Consequently the kernel experiences a sequence of imposed temperature gradients. Above a temperature of the order of 1100°C, the imposition of a temperature gradient can apparently induce a momentary stress in the fuel which leads either to a movement of some of the fission gas collectives and the escape of the contained fission gases or to just the latter. As the temperature ramp continuous, the second defective particle with the smaller physical width eventually reaches the required temperature and in the presence of a temperature gradient releases fission gas as postulated. Thus the separation in time of the transient releases of fission gas depends on the difference of the physical widths of the gaps in the two defective particles. Note that the deduction from the asymmetry of the curves in Fig. B3, presented above, cannot be derived from the time separation of the peaks.

The behavior of the fuel in releasing fission gases under a stress induced by a temperature transient resembles, in regard to the release of fission gas contained in collectives, the behavior of fuel under a stress induced by a water-vapor transient.[1,2]

3.2 WATER-VAPOR INJECTIONS

Given the presence of two defective coated fuel particles in HFR-K6, the opportunity to monitor the response of the exposed fuel kernels to injected water vapor was taken.[3] The resulting R/B profile is shown in Fig. B5 In the following sections, the response of exposed fuel kernels in HFR-K6 to the responses in HRB-17 and HFR-B1 is compared, albeit crudely. In comparing the responses, knowledge of the sequence of events is necessary.

3.2.1 The Sequence of Events in HRB-17

In experiment HRB-17, water-vapor, at a fixed partial pressure, was added to a fuel element system containing exposed fuel kernels.[1] The pressure was maintained constant for periods ranging from 3 to 11 days; during these periods and beyond, the fission gas release was monitored. Following the cessation of water-vapor addition, the release declined to the preaddition value. The equality of the preaddition and terminal postaddition values of the fractional release implies a similar fuel structure, at least with regard to fission gas release. Thus, in subsequent water-vapor additions, interaction of water vapor at various partial

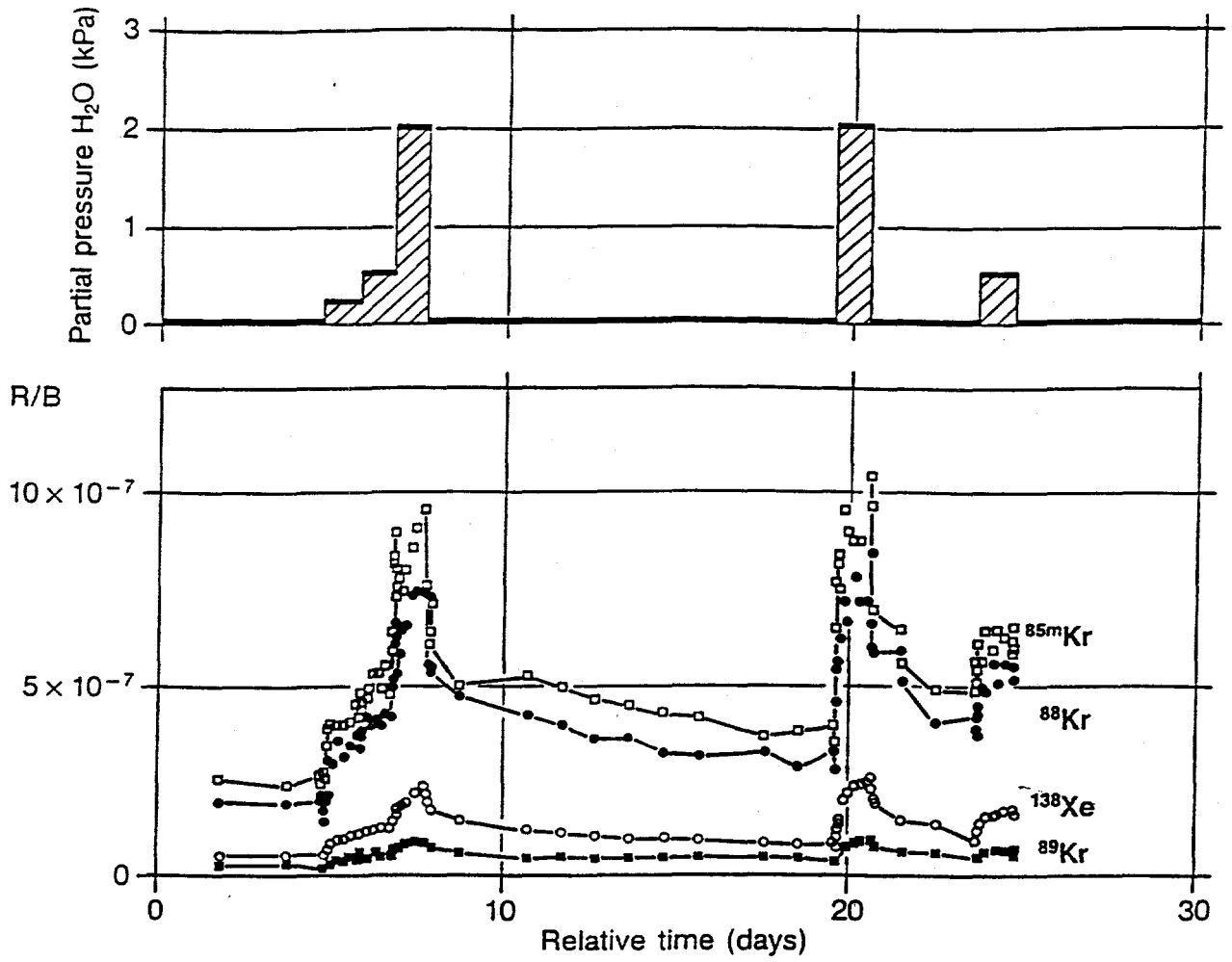

Fig. B5 Water-vapor injections and the related fission gas release during irradiation in experiment HFR-K6, irradiation. Cycle 25, fuel element HFR-K6/4. Source: Forschungszentrum Jülich GmbH

pressures always occurred with fuel kernels having release-equivalent structures. Each event, or as stated in section 2 above, each stage, was completed with regard to transient behavior of released fission gas before the next stage began or was induced to begin. The sequence was then repeated.

3.2.2 The Sequence of Events in HFR-K6

Two distinct sequences were employed in experiment HFR-K6.[3] In one, water-vapor was added in a step pattern, each successive step being a higher partial pressure of water-vapor. As there was no time allotted for fuel structure restoration between steps, each "water-vapor step" was imposed on a different fuel structure. Only at the end of the sequence with cessation of water-vapor addition was there a partial restoration of the release-equivalent fuel structure between the last step and the first step of the succeeding sequence. The second sequence consisted of two separated, water-vapor steps. See Fig. B5.

The water-vapor addition profiles, in the first sequence, consisted of three steps of heights 0.2, 0.5, and 2.0 kPa of water vapor and widths of ≈ 1 d over a period of ≈ 3 d and in the second sequence, of separated steps of 2.0 and 0.5 kPa, each for ≈ 1 d as shown in Fig. B5.

In these sequences, stage 2, the portion of the time profile during which the fractional release of fission gas is steady, was prevented from clearly developing either by incremental additions of water vapor or by cessation of water-vapor addition at fixed times. This is more fully described below.

3.2.3 Analysis of HFR-K6 Data

The analysis of HRB-17[1,2] is taken as a basis for the analysis of the reported data[3] from capsule C of experiment HFR-K6. The former analysis has led to the categorization of the fission gas release profile in terms of stages, in each of which the mechanisms governing the release are clearly enumerated. Furthermore, the analysis of HRB-17 has led to new quantitative relationships involving the response of the fuel to water vapor under HTGR conditions. In the design[3] and the initial analysis[3] of the water-vapor injections in HFR-K6, no recognition was given to the concomitant transient and steady release processes occurring in stage 1 of the generic release profile.[1] The consequence of this was an inaccurate analysis.

In addition to the sequences, there were differences of note between experiments HRB-17 and HFR-K6. Among these were the size and composition of the fuel element in which transport occurred and the number of particles with exposed kernels. In experiment HRB-17, the element was a cylindrical fuel compact with a central hole. In the fueled annulus, the radius vector had a length of 4.3 mm and there were 30 particles with exposed kernels (ek) distributed essentially homogeneously. Thus, the linear density was ≈ 7 ek/mm. In experiment HFR-K6, the element contained a fuel sphere of 25 mm radius. In the fuel sphere, there were 2 particles with exposed kernels. Thus the linear density was ≈ 0.08 ek/mm. The composition of the fuel compact in HRB-17 was a mixture of fuel particles, graphite shim (distorted spherical pieces of grade H-451 graphite) and fired carbonaceous material; in HFR-K6, the fuel particles were overcoated and were dispersed in grade A3 matrix graphite.

The analysis of HFR-K6 can be made only roughly. The sequences were restrictive (Sect. 3.2.2), the data are available at present only in graphical form (Fig. B5), and the frequency of measurement was low (0.4/h versus 2.3/h in HRB-17, stage 1).

3.2.3.1 Stage 1 Fission Gas Release

In stage 1 there is a rapid transient release of fission gas with a concomitant increase in the steady state release. Because of the low frequency of measurements in HFR-K6, an averaging method is used to establish the transient release in stage 1. Distinguishing stage 1 from stage 2 for the data shown in Fig. B5, is too imprecise. Rather, the transient release is calculated as the difference between average R/B data from Fig. B5, which represent the sum of stages 1 and 2, and the R/B for stage 2, determined independently.

Average values for R/B during periods of constant water-vapor pressure are shown in Fig. B6-A. The three long rectangles represent stages 1 and 2 in which both transient and steady state release occur. To account for the steady state contribution to the rectangular areas, the ratio $(R/B)_{post}/(R/B)_{pre}$, where pre and post refer to times before and after starting water-vapor addition, has been determined from independent data as described below in Section 3.2.3.2. The deduced value of the ratio is 1.56.

The rectangles of Fig. B6-B, as indicated by the lines at 3.25E-07 and 3.9E-07, incorporate the contributions of the steady state release in each "water-vapor step." The two different contributions of the steady state release to the first "water-vapor step" reflect the sequential contributions of one and then of two exposed kernels to the rectangular areas. Note that, R/B_{pre} represents the contributions of the two exposed kernels (plus a smaller contribution from the fuel sphere matrix "heavy metal" (U + Th + Pu) contamination) before water-vapor addition and R/B_{post} represents the steady state contribution during water-vapor addition. The sequential contributions of the exposed kernels to the measured release are examined in the second following paragraph. Also note that the assumption of constancy of the steady-state contributions in the latter half of the first and throughout the second and third "water-vapor steps" is based on measurements in experiment HRB-17.[1] In this experiment, the incremental increase in R/B via diffusive release from all exposed kernels was found to be independent of element, isotope and the partial pressure of water vapor in the range 0.02 to 0.2 kPa. For Fig. B6-B, the assumption is made that this constancy extends to 2.0 kPa. The adoption of this assumption leads to a consistency among data from several sources as described below and is thereby validated to that degree.

While the steady state release is independent of the partial pressure of water vapor, clearly the transient release as shown in Fig. B6-B is strongly dependent on the partial pressure. The areas marked t in Fig. B6-B are proportional to the partial pressure as will be shown. These areas, normalized to the area t of the 0.2 kPa water-vapor addition, become 1.0, 5.1, and 16.8 for the partial pressures of 0.2, 0.5, and 2.0 kPa, respectively. Using these relative areas and normalizing them with respect to independent experimental fractional release values at 0.2 kPa as shown in Fig. 6 (page 10), an agreement with other results from experiment HFR-B1 for both irradiation[5,6] and post irradiation[7] conditions is apparent. The three HFR-K6 data in the present analysis strengthen the conclusion of a significant change in the dependence of the release of fission gas from collectives on the partial pressure of water vapor above 1

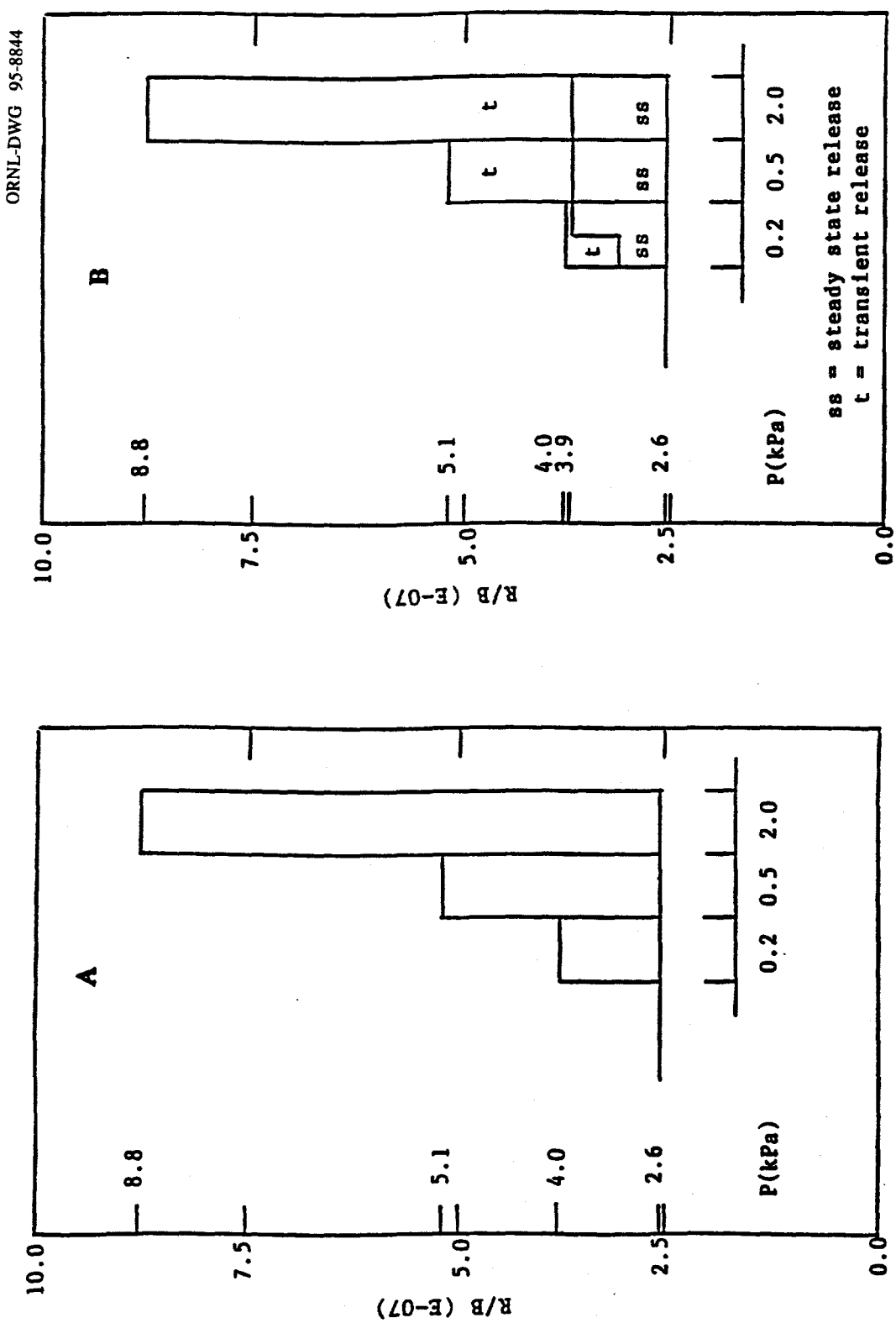

Fig. B6 Approximate analysis of the R/B of ^{85m}Kr as a function of the partial pressure of water vapor in experiment HFR-K6. Part A is the total response, part B shows contributions from steady state and transient release.

kPa. This value of a transition pressure could be dependent on the configuration and composition of the exposed kernels and the system in which they are embedded.

There is in Fig. B5, clear evidence for the sequential contribution of the exposed kernels to the measured release and their manifestation in the form of peaks during the two injection events at 2.0 kPa of water vapor. The peaks for each event are separated by about 20 h. This is considerably larger than observed (0.75 h) in the temperature transient event. However, in experiment HRB-17[1], the interaction of water vapor with the exposed kernels was observed to be sequential; the water vapor effectively moved as a front presumably being slowed and consumed by reaction with the carbonaceous material through which passage was necessary to reach each exposed kernel. In this case, the speed of movement was 0.6 mm/h. In HFR-K6, the speed is estimated to be $\leq$ 0.6 mm/h. This estimate involves the assumption that the defective particles which are within the fueled portion of the fuel sphere have a difference in radial location of $\leq$ 25 mm. These speeds are comparable and suggest that similar processes lead to the water-vapor-kernel encounter in both the HFR-K6 and HRB-17 experiments. In both cases, the materials reacting with the inward moving water vapor are the binder materials, possibly having different reactivities with water vapor.

3.2.3.2 Stage 2 Fission Gas Release

Stage 2 is a period of steady fractional release hereinafter referred to as the plateau period with steady fractional release $(R/B)_{plateau}$. For ^{85m}Kr and ^{88}Kr, the R/B profiles of Fig. B5 distinctly give the impression of a steady fractional release. For ^{89}Kr and ^{138}Xe the profiles have not reached the $(R/B)_{plateau}$ within the duration time ($\sim$ 1 d) of an injection at a constant partial pressure of water vapor. This may reflect structural changes in the fuel resulting in a relatively greater fission gas release for the short-lived isotopes. Presumably a longer injection time at a constant partial pressure of water vapor would have resulted in reaching $(R/B)_{plateau}$. However, for the present, only the profiles of the isotopes ^{85m}Kr and ^{88}Kr will be considered further.

In regard to stage 2, evaluating the consistency of fission gas behavior in experiments HRB-17, HFR-B1 and HFR-K6 is of interest. A convenient measure of this behavior is the ratio $(R/B)_{plateau}/(R/B)_{pre}$; the denominator is the R/B just prior to water vapor injection. The ratio $(R/B)_{plateau}/(R/B)_{pre}$ was determined[1] in experiment HRB-17 to be 2.0 at 767° C. Furthermore, this ratio was shown to be independent of element, isotope and the partial pressure of water vapor in the range 0.02 to 2.kPa. A theoretical argument has been presented[1,2] which gives a semi-quantitative understanding of these independencies. In addition, an activation energy of 23.6 kJ/mol applicable to stage 2, i.e., in the presence of water vapor, has also been determined[5] from experiment HFR-B1. By using the ratio value and the activation energy, the ratio $(R/B)_{plateau}/(R/B)_{pre}$ for experiment HFR-K6 at 680° C is predicted to be 1.56. From Fig. B5a, the upper limits to the ratio for HFR-K6 is seen to be 1.5 for ^{85m}Kr and 1.6 for ^{88}Kr. This indicates a high probability for consistency. Enhancing confidence in the consistency of the stage 2 results of experiments HRB-17, HFR-B1, and HFR-K6 is the application to stage 1 of the relative transient (t) release areas of Fig. B6-B as shown in Fig. 6 (page 10).

3.2.3.3 Stage 3 Fission Gas Release

The cessation of water-vapor injection is the beginning of stage 3. During stage 3, the R/B declines and approaches the prehydrolysis value of R/B provided no configuration changes have occurred in the relative locations of the kernel and coating layers. The decline in R/B is clearly evident in Fig. B5 following the termination of the first of the 2.0 kPa water-vapor injections. A quantitative description of the decline in the manner previously employed[1] is given, for stage 3, by the following equation:

$$R/B = \alpha + \beta \cdot \exp(-\delta[t - t_{03}]) \quad (2)$$

where R/B = steady-state fractional release
t = time (d),
t_{03} = time of the beginning of Stage 3
α = 2.4E-07,
β = 3.3E-07, and
δ = 0.109 (1/d)

Equation 2 and the parameters α, β, and δ provide a good fit to the data of stage 3 as shown in Fig. 7a (page 13). The governing parameter, δ, has the same value as used in the analysis of stage 3 in experiment HFR-B1[5]. Therefore, the curvature of the R/B profile in stage 3 and by implication, the processes occurring in stage 3 are the same in experiments HFR-K6 and HFR-B1. This similarity is expected to carry-over to experiment HRB-17 after further analysis.

3.2.4 Minor Features in Stages 1 and 3 Fission Gas Release

3.2.4.1 Stage 1

In stage 1 of experiment HRB-17, the transient release profile peaked at 2.0 ± 0.2 h for the isotopes ^{85m}Kr, ^{87}Kr, ^{88}Kr, ^{133}Xe, and ^{138}Xe. The sum of the contributions from individual exposed kernels was postulated to yield a peaked curve. The contributions occurred sequentially as demonstrated by the ionization gauge signals.[1] Each exposed kernel was assumed to release fission gas steadily over a period of two hours. This assumption yielded a smooth summation profile that matched the observed R/B profile.[1] For experiment HFR-K6, the transient profile is not smooth. The difference may be ascribed to the radial linear density of exposed kernels in HRB-17 and HFR-K6. The linear density of the former is 88 times larger than that of the latter (see Section 3.2.3). Thus for a given linear resolution, the transient release from individual particles with exposed kernels could be distinguishable in one case (HFR-K6) but not in the other (HRB-17).

3.2.4.2 Stage 3

In experiment HRB-17, immediately after the cessation of water-vapor injection, the decline in R/B was more rapid than at a later time.[1] For the isotopes ^{85m}Kr, ^{87}Kr, ^{88}Kr, and ^{138}Xe the slope of the initial decline was the same. For ^{133}Xe, and to a small extent for ^{135}Xe, the slope

was larger. The radioactive decay of ^{133}I accounted for the difference between the slope for ^{133}Xe and that common to ^{135}Xe and the krypton isotopes. Also in experiment HFR-K6, immediately after the cessation of water-vapor injection, the decline in R/B was more rapid than at a later time. The duration of the rapid decline was about 5 h in experiment HFR-K6 and about 15 h in experiment HRB-17.

4.0 SUMMARY

The comparison of experiments HRB-17, HFR-B1 and HFR-K6 has shown, to the extent possible with the available data, an identity in the major aspects of the behavior of fission gas release in the presence of water vapor from particles with exposed kernels in these three irradiation experiments. A more detailed analysis is planned.

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