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A REVIEW OF TRITIUM BEHAVIOR IN HTGR SYSTEMS

by
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ABSTRACT

This report reviews the available experimental evidence from laboratory and reactor studies pertaining to tritium production, capture, release, and transport within an HTGR leading to release to the environment. Possible mechanisms for release, capture, and transport are considered and a simple model was used to calculate the expected tritium release from HTGRs. Comparison with Federal regulations governing tritium release confirm that expected HTGR releases will be well within the allowable release limits. Releases from HTGRs are expected to be somewhat less than from LWRs based on the published LWR operating data. Areas of research deserving further study are defined but it is concluded that a tritium surveillance at Fort St. Vrain is the most immediate need.

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1. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

A review of available data pertaining to tritium transport in HTGRs has revealed that the mechanisms by which tritium is produced, transported, and released are reasonably well understood. Calculations with some of these data have shown that tritium releases should be well within the present Federal guidelines for nuclear plants. For example, the estimated maximum dose to an average adult for a typical 3000-MW(t) HTGR with a cooling tower is 0.38 milliRem/year, which is slightly more than one-tenth of the maximum allowed annual dose. For this reason, no further laboratory-scale work on tritium is required at this time. Fort St. Vrain H-3 levels should be monitored to verify that design predictions are conservative. If, in the future, Federal regulations pertaining to the release of radioactivity are tightened, then a better understanding of tritium migration will be required.

It is conceivable that in the future zero release plants may be mandatory, which will require a complete recycle of low-level tritiated water wastes and a much better understanding of tritium migration. Areas where more work would be beneficial are as follows:

1. A study of the tritium fission yield as a function of the energy spectrum of the neutron flux, the fuel type, and enrichment.
2. Better methods for detecting tritium-forming impurities in nuclear steam supply (NSS) construction materials.
3. Tritium release measurements from fuel particles as a function of burnup, temperature, nature of the kernel, and type of pyrolytic carbon coating.

4. A study of tritium chemisorption on graphite as a function of the partial pressure of tritium, temperature, irradiation field, and influence of other hydrogenous species (e.g., CH_4 , H_2).
5. The role of oxide films under realistic reactor conditions in reducing the tritium permeation of metals.
6. A thorough tritium study for the Fort St. Vrain HTGR.

To maintain perspective, the impact of projected tritium release on the environment is negligible. Worldwide tritium inventories in the atmosphere and surface waters reached a peak in the early 1960s as a result of weapons testing. They are not projected to reach this level again from all sources including the commercial nuclear reactor program even by the year 2000.

In view of these considerations, further laboratory studies on tritium are not justified at this time. Emphasis should be placed on obtaining data from operating reactors, in particular Fort St. Vrain.

2. INTRODUCTION

The purpose of this review was to examine all available data relevant to tritium production and migration in HTGRs in order to determine whether additional data should be obtained.

The complete experimental data can be used to set up a computer model describing tritium production, retention, and transport as a function of various operating parameters. This computer model could then be validated against results obtained from a tritium study of the Fort St. Vrain HTGR.

The transport of tritium from the reactor into the secondary coolant depends on five main processes:

1. Production of tritium in the reactor.
2. Release by diffusion of tritium into the primary coolant from reactor materials in which it is borne.
3. Retention of tritium on reactor core materials by recoil and chemisorption.
4. Removal of tritium by the reactor coolant purification and recovery system.
5. Tritium permeation through the steam generator tube materials.

Processes 1 through 4 determine the tritium concentration in the primary coolant, which in turn provides the driving force for tritium permeation of the steam generator tubes.

Tritium occurs in the earth's atmosphere as a result of nuclear reaction of cosmic radiations with nitrogen in the upper atmosphere. It is also formed during the explosion of thermonuclear weapons, and testing of these weapons has increased the tritium concentration in the earth's atmosphere.

Tritium is produced in all fission reactors via fission and from neutron activation of tritium-forming materials. It is also one of the candidate fuels for future fusion reactors and, in this application, the recovery and recycle of tritium from the main plasma fuel system and the removal and recovery of tritium from the blanket of fusion reactors could present a problem.

Discharge of tritium into the environment could pose a problem because it will accumulate over a relatively long period of time due to its long half-life of about 3.94×10^8 sec (12.5 yr). However, concern with tritium emissions arises only if it is ingested, because during decay tritium emits only a low-energy, low-penetrating-power beta particle.

No excessive unexpected tritium releases have been reported from nuclear plants. However, several accidents have occurred at processing plants which caused large quantities of tritium to be released. For example, 1.07×10^{16} dps (289,000 Ci) of tritium were released from Livermore Radiation Laboratory in Livermore, California on August 6, 1970 (Ref. 1), and 1.77×10^{16} dps (479,000 Ci) of tritium were released from the Savannah River Plant due to a process valve failure on May 5, 1974 (Refs. 1, 2). Release of such quantities from HTGRs is not possible since such releases exceed the total expected tritium production. However, as with all other radionuclides, measures are taken to ensure that radioactivity is confined within the reactor building, and releases to the environment are controlled to small fractions of the total produced.

In nuclear reactors, tritium is capable of diffusing through metals at high temperatures such that it enters the secondary coolant via transport

through the steam generator tubes. Any spillage of water from the secondary coolant (e.g., from sample lines or boiler feedpumps) will expose workers to low-level contamination, and discharge of these wastes from the plant may become a problem because the legal restrictions on tritium discharge may be exceeded. The current method of disposing of tritiated wastes is to inject them into the cooling-water exit line. However, with a virtually closed cooling-water system (such as when using a cooling tower), there is very little water exiting from the plant with which to dilute the tritiated water wastes. With once-through cooling, tritium discharge will not be a problem because of the high dilution available.

An understanding of tritium transport in HTGRs is important not only to prevent violations with respect to plant discharges but also to evaluate the behavior of tritium during reprocessing.

In the future, HTGRs might be used for process heat applications. In this case, tritium can permeate into the process heat loop and contaminate the product. Since steam reforming is a prime process heat application where the gaseous products will be used as a domestic energy source, the tritium contamination of the process gases and the possible ensuing dose rates to the general public must be accurately determined.

3. TRITIUM PRODUCTION

3.1. GENERAL

The primary tritium production mechanism is ternary fission due to thermal neutrons. A fission yield of tritium from U-235 has been measured (Refs. 3-12) with a value between 0.8×10^{-4} and 1.3×10^{-4} tritium atoms per fission (i.e., 1.25×10^4 to 1.0×10^4 fissions per tritium atom) (Table 1). Additional information on the fission yield of tritium under nuclear reactor conditions is required since the yield will depend upon: (1) the energy spectrum of the neutron flux, (2) the enrichment of the fuel, and (3) the type of fuel used. In particular, the fast fission tritium yields of U-235, U-238, Th-232, and of U-233 (of importance later in the reactor life) are unknown.* In principle, fast fission yields should be higher than for thermal neutrons.

Tritium is also generated in an HTGR by neutron capture reactions. The principal sources are:

1. $\text{He-3}(n,p)\text{H-3}$ $\sigma(2200 \text{ m/s}) = 5.4 \times 10^{-25} \text{ m}^2$ (5400 barns)
2. $\text{Li-6}(n,\alpha)\text{H-3}$ $\sigma(2200 \text{ m/s}) = 9.53 \times 10^{-26} \text{ m}^2$ (953 barns)
3. $\text{B-10}(n,\alpha)\text{Li-7}$ $\sigma(2200 \text{ m/s}) = 4.01 \times 10^{-25} \text{ m}^2$ (4010 barns)
4. $\text{Li-7}(n,n\alpha)\text{H-3}$ $\sigma(E > 0.18 \text{ MeV}) = 1.53 \times 10^{-29} \text{ m}^2$ (153 mbarns)
5. $\text{B-10}(n,2\alpha)\text{H-3}$ $\sigma(E > 0.18 \text{ MeV}) = 5.0 \times 10^{-30} \text{ m}^2$ (50 mbarns)

* Measurements are in progress at General Atomic on fast fission yields of tritium from samples irradiated in the blanket region of the EBR-II reactor.

TABLE 1
TRITIUM FISSION YIELD

Source	Tritium Atoms/Fission ($\times 10^{-4}$)				
	U-233	U-235	Pu-239	Pu-241	Cf-252
Thermal Neutrons					
Ref. 3	1.1	0.85 ± 0.09			
Ref. 4	0.88 ± 0.07	0.75 ± 0.08	1.51 ± 0.10		2.22 ± 0.07
Ref. 5		0.95 ± 0.08			
Ref. 6		0.8 ± 0.01			
Ref. 7		0.87			
Ref. 8			2.3	0.26	
Ref. 9		0.5 - 1.0			
Ref. 10		1.26			
Ref. 11		1.24			
Fast Neutrons					
Refs. 3, 12		2.0 - 2.2			

Other possible reaction schemes are:

1. $\text{H-1}(n,\gamma)\text{H-3}$
2. $\text{B-11}(n,T)\text{Be-9}(n,\alpha)\text{Li-6}(n,\alpha)\text{H-3}$
3. $\text{C-12}(n,\alpha)\text{Be-9}(n,\alpha)\text{Li-6}(n,\alpha)\text{H-3}$
4. $\text{O-16}(n,N-15)\text{H-2} (n,\gamma)\text{H-3}$
5. $\text{N-14}(n,C-12)\text{H-3}$

These latter reactions are of negligible importance compared to the first five reactions listed as principal sources due to small concentrations of the reactive material, a low reaction cross section, and/or a high reaction threshold energy.

A possible major source of tritium from fast neutrons is expected to be from the reaction:

$$\text{B-10}(n,2\alpha)\text{H-3} \quad \sigma(E > 0.18 \text{ MeV}) = 5.0 \times 10^{-30} \text{ m}^2 (50 \text{ mbarns})$$

The fast neutron flux in HTGRs is significant, but its contribution to tritium production is unknown. For example, in Fort St. Vrain the fast neutron flux (average) is calculated to be $3.6 \times 10^{13} \text{ n/cm}^2\text{-sec}$ ($E > 0.18 \text{ MeV}$) compared to the calculated thermal flux (average) which is $6.0 \times 10^{13} \text{ n/cm}^2\text{-sec}$ ($E < 0.18 \text{ MeV}$).

Even if the current tritium calculation procedures are considered sufficiently accurate, an exact knowledge of the tritium-forming impurities present in the reactor is still required. Of most importance is the Li-6 content of core materials, including fuel element graphite, fuel and fuel matrix, reflector graphite, control materials, and core insulation. The total lithium content of these materials is extremely low, bordering on the

experimental accuracy of most analytical methods of Li measurement, and Li-6 is obtained from its natural abundance in lithium.* Also of importance is the He-3 content of helium, which is also extremely low (atom ratio He-3/He-4 of about 2×10^{-7} for He obtained from gas wells) and can be expected to vary depending on the source of supply.

Current impurity levels of tritium-forming materials expected to be present in HTGRs are given in Table 2.

3.2. TRITIUM FROM TERNARY FISSION

Tritium yields for the thermal neutron fission of U-235 have been reported between 0.8×10^{-4} and 1.3×10^{-4} atoms of tritium per fission (Refs. 3-12); values for U-233 are stated to be similar (Table 1). Fast neutron fission yields for U-235 of about 2.2×10^{-4} have been reported (Refs. 3, 12, 13).

The rate of production of tritium by fission can be calculated from the relation:

$$\frac{d(N_T)}{dt} = KWY_t - \lambda(N_T) \quad , \quad (3-1)$$

where N_T = number of tritium atoms produced at time t

K = fission rate at unit power = 3.121×10^{16} fissions/sec-MW

W = reactor power, MW

t = time period, sec

Y_t = number of tritium atoms produced per fission

λ = tritium decay constant = 1.793×10^{-9} /sec

* A new method of detecting very small Li concentrations (isotope dilution/emission mass spectrometry) has recently become available which should improve our knowledge of Li impurities in HTGR materials.

TABLE 2
TRITIUM-FORMING IMPURITY LEVELS IN REACTOR COMPONENTS

	Expected Level
Lithium	
Core graphite	0.05 ppm ^(a)
Core matrix	0.50 ppm
Reflector (temporary)	0.05 ppm
Reflector (permanent)	0.05 ppm
Boron	
Control rod	~30% B
Burnable poison	~1% B
Reflector	10.3% B
Helium-3	
Coolant	0.1 - 0.2 ppm ^(b)

(a) ppm by weight.

(b) ppm by volume.

Equation 3-1 can be integrated to give:

$$\begin{aligned} A_t &= \text{activity of tritium after time } t(\text{dps}) \\ &= KWY_t (1 - e^{-\lambda t}) \end{aligned} \quad (3-2)$$

It is also possible to make allowance for the fact that the availability of the reactor during operation is not 100% but, for example, only 80%.

Equation 3-2 would then be

$$\begin{aligned} A_t &= \text{activity of tritium after time } t(\text{dps}) \\ &= KWY_t (1 - e^{-\lambda t f}) \end{aligned} \quad (3-3)$$

where f is the plant availability factor.

3.3. TRITIUM FROM Li-6

The rate of production of tritium from the neutron irradiation of Li-6 is determined by solution of the differential equations

$$\frac{dN_1}{dt} = -\phi_1 \sigma_1 N_1 \quad (3-4)$$

and

$$\frac{dN_2}{dt} = \phi_1 \sigma_1 N_1 - \lambda_2 N_2 \quad (3-5)$$

where N_1 is Li-6 and N_2 is H-3 and

$$N_1 = N_o e^{-\phi_1 \sigma_1 t} \quad (3-6)$$

and

$$N_2 = \frac{\phi_1 \sigma_1 N_o}{\lambda_2 - \phi_1 \sigma_1} \left(e^{-\phi_1 \sigma_1 t} - e^{-\lambda_2 t} \right) , \quad (3-7)$$

or converting to activity and including an availability factor f,

$$\begin{aligned} A_t &= \text{activity of tritium after time } t(\text{dps}) \\ &= -\frac{\phi_1 \sigma_1 N_o}{\phi \sigma_1} \left(e^{-\phi_1 \sigma_1 t f} - e^{-\lambda_2 t f} \right) \cdot \\ &\quad 1 - \frac{\lambda_1}{\lambda_2} \end{aligned} \quad (3-8)$$

3.4. TRITIUM FROM He-3

The gross generation rate of tritium from He-3 is given by

$$\frac{dN_3}{dt} = \sigma_1 \phi_1 N_4 , \quad (3-9)$$

where N_3 is the tritium formed due to He-3 irradiation and N_4 is the He-3 concentration in the primary coolant. The rate of change of He-3 content of the primary circuit coolant will be:

$$\frac{dN_4}{dt} = F_H N_4^o - F_H N_4 - \sigma_1 \phi_3 N_4 , \quad (3-10)$$

where N_4^o = concentration of He-3 in the makeup helium

F_H = fractional makeup rate for helium coolant

ϕ_3 = average neutron flux experienced by the total helium inventory

or,

$$\frac{dN_4}{dt} = F_H N_4^0 - (F_H + \sigma_1 \phi_3) N_4 \quad (3-11)$$

Integration of Eq. 3-11 gives the concentration of He-3 and hence the tritium generation rate:

$$N_4 = \frac{\sigma_1 \phi_3 N_4^0 \exp[-(F_H + \sigma_1 \phi_3)t] + F_H N_4^0}{F_H + \sigma_1 \phi_3} \quad (3-12)$$

Substituting for N_4 in Eq. 3-9, gives the tritium generation rate as:

$$\frac{dN_3}{dt} = \sigma_1 \phi_1 \left\{ \frac{\sigma_1 \phi_3 N_4^0 \exp[-(F_H + \sigma_1 \phi_3)t] + F_H N_4^0}{(F_H + \sigma_1 \phi_3)} \right\} \quad (3-13)$$

Use of this relation has shown (Ref. 14) that the tritium generation rate will fall to an equilibrium value in about 40 days as long as the helium leak rate is less than 0.2% of the circulating coolant per day.

3.5. TRITIUM FROM B-10

Tritium production from B-10 is calculated from solution of the differential rate equations (Ref. 15):

$$\frac{dN_5}{dt} = -\phi \bar{\sigma}_{BL} N_5 \quad (3-14)$$

$$\frac{dN_6}{dt} = \phi \bar{\sigma}_{BL} N_5 - \hat{\phi} \sigma_{LH} N_6 \quad (3-15)$$

$$\frac{dN_7}{dt} = \hat{\phi} \bar{\sigma}_{LH} N_6 - \hat{\phi} \sigma_{BH} N_5 - \lambda N_7 \quad , \quad (3-16)$$

where ϕ = total flux

$\hat{\phi}$ = flux above 3.3 MeV

$\bar{\sigma}_{BL}$ = average self-shielded cross section in going from B-10 to Li-7

$\bar{\sigma}_{LH}$ = average cross section in going from Li-7 to H-3

$\bar{\sigma}_{BH}$ = average cross section from B-10 to H-3

N_5 , N_6 , and N_7 are the number of atoms present of B-10, Li-7, and H-3, respectively. The solution to this equation was reported by Haire (Ref. 15) to be:

$$\begin{aligned} \frac{N_7(t)}{N_5^0} = & \frac{\hat{\phi}\bar{\sigma}_{LH}\bar{\phi}\bar{\sigma}_{BL}}{\hat{\phi}\bar{\sigma}_{LH} - \bar{\phi}\bar{\sigma}_{BL}} \left(\frac{\exp(-\bar{\phi}\bar{\sigma}_{BL}t)}{\lambda - \bar{\phi}\bar{\sigma}_{BL}} - \frac{\exp(-\hat{\phi}\bar{\sigma}_{LH}t)}{\lambda - \hat{\phi}\bar{\sigma}_{LH}} \right) + \frac{\hat{\phi}\bar{\sigma}_{BH} \exp(-\bar{\phi}\bar{\sigma}_{BL}t)}{\lambda - \bar{\phi}\bar{\sigma}_{BL}} \\ & - \left[\frac{\hat{\phi}\bar{\sigma}_{LH}\bar{\phi}\bar{\sigma}_{BL}}{\hat{\phi}\bar{\sigma}_{LH} - \bar{\phi}\bar{\sigma}_{BL}} \left(\frac{1}{\lambda - \bar{\phi}\bar{\sigma}_{BL}} - \frac{1}{\lambda - \hat{\phi}\bar{\sigma}_{LH}} \right) + \frac{\hat{\phi}\bar{\sigma}_{BH}}{\lambda - \bar{\phi}\bar{\sigma}_{BL}} \right] \exp(-\lambda t) \quad (3-17) \end{aligned}$$

Table 3 compares calculated tritium production from various sources after 1 yr of operation as reported by three different workers (Refs. 14-16). The results are normalized to a thermal power output of 3000 MW(t). The values differ due to the assumptions made, the impurity levels chosen, and the mode of calculation used. For example, in calculating tritium production from ternary fission, Forsyth (Ref. 14) ignored tritium decay and used a fission yield of 1.3×10^{-4} . On the other hand, Compere et al. (Ref. 16) and Haire (Ref. 15) used a fission yield of 1.0×10^{-4} . Forsyth and Compere et al. assumed a 100% availability, whereas Haire used 80%.

The tritium-forming impurity levels assumed were similar. Forsyth used the room temperature neutron cross sections for Li and He rather than those at reactor temperatures. Forsyth assumed that the He was irradiated 20% of the time; Haire assumed only 6%. Forsyth and Haire assumed only a thermal flux, whereas Compere et al. considered the influence of both by thermal and fast flux. Forsyth ignored the tritium production from B-10.

TABLE 3
COMPARISON OF CALCULATED TRITIUM PRODUCTION RATES
FOR A 3000-MW(t) HTGR
(Curies/yr) (a)

Case (b)	Ternary Fission	Li-6	B-10		He-3	Total
			Fast	Slow		
1	9,213	3843	410	376	1771	15,614
2	11,000	2813	919		3680	18,412
3	19,866	2376	(Ignored)		6716	28,958

(a) 1 Curie = 3.7×10^{10} dps.

(b) Basic data

Case 1. Fission yield = 1×10^{-4}
(Compere, Li = 0.05 ppm
Ref. 16) He-3 = 0.2 ppm
4 to 6% He in core
Neutron flux = 6×10^{13} n/cm²-sec (slow)
 = 3.6×10^{13} n/cm²-sec (fast)
 $\sigma_{\text{He-3}} = 2280$ barns; $\sigma_{\text{Li-6}} = 408$ barns; $\sigma_{\text{B-10}} = 1630$ barns

Case 2. Fission yield = 1×10^{-4}
(Haire, Li (design) = 0.05 ppm
Ref. 15) (expected) = 0.01 ppm
He-3 = 0.2 ppm
6% He in core
Neutron flux = 1×10^{14} n/cm²-sec
 $\sigma_{\text{He-3}} = 2800$ barns; $\sigma_{\text{Li-6}} = 463$ barns

Case 3. Fission yield = 1.3×10^{-4}
(Forsyth, Pu-239 fission yield = 2.3×10^{-4}
Ref. 14) Pu-241 fission yield = 2.6×10^{-5}
Low enriched fuel (7%)
Li-6 = 0.06 ppm
He-3 = 0.2 ppm
20% He in core
Neutron flux = 2.8×10^{13} n/cm²-sec
 $\sigma_{\text{Li-6}} = 930$ barns; $\sigma_{\text{He-3}} = 5400$ barns

Overall, the values given by Haire (Case 2 in Table 3) are preferred, but the uncertainties in fission yield, Li-6, and He-3 concentrations must be recognized. Table 4 shows the expected tritium production figures for the 2000-, 3000-, and 4000-MW(t) HTGRS as calculated by Haire (Ref. 15).

3.6. SUMMARY

The mechanisms by which tritium is produced in the HTGR are well established, namely ternary fission and neutron activation of He-3, Li-6, and B-10. Uncertainties in the tritium production rate in the HTGR are associated with an imprecise knowledge of fission yield, and with accurately assessing tritium-forming impurity levels. More work in these areas would be beneficial.

TABLE 4
SUMMARY OF TRITIUM CALCULATIONS^(a)

	2000-MW(t) HTGR		3000-MW(t) HTGR		4000-MW(t) HTGR	
Source	Annual Production Rate (Ci/yr) (b)	Release to Coolant (Ci/yr)	Annual Production Rate (Ci/yr)	Release to Coolant (Ci/yr)	Annual Production Rate (Ci/yr)	Release to Coolant (Ci/yr)
Ternary fission	7.42×10^3	3.71×10^1	1.0×10^4	55	1.44×10^4	81
He-3 activation	2190	2190	3.29×10^3	3290	5100	5,100
Li-6 activation						
Core graphite	216 ^(c)	216	310 ^(c)	310	1800 (0.1 ppm)	1,800
Core matrix	1159	1159	1809	1809	2527 (1.0 ppm)	2,527
Reflector (temporary)	41 ^(c)	41	62 ^(c)	62	450 (0.1 ppm)	450
Reflector (permanent)	18	18	40	40	350 (0.1 ppm)	350
B-10 activation						
Control rod	825	825	1100	1100	1054	1,054
Burnable poison	139	139	208	208	278	278
Reflector	2	2	3	3	5	5
Total		<u>4627</u>		<u>6877</u>		<u>11,645</u>

(a) From Ref. 15.

(b) 1 Curie = 3.7×10^{10} dps.

(c) 0.01 ppm Li assumed.

4. TRITIUM RELEASE FROM REACTOR COMPONENTS INTO THE PRIMARY COOLANT

4.1. RELEASE FROM FUEL PARTICLES

Before tritium formed via ternary fission in the fuel particles can escape into the helium coolant, it must permeate several barriers. It must diffuse:

1. Out of the fuel kernel.
2. Through the low-density carbon buffer layer.
3. Through the inner high-density pyrocarbon layer.
4. Through the SiC layer (TRISO particles only).
5. Through the outer high-density pyrocarbon layer.

In this way, tritium can escape from a fuel particle. Before it reaches the coolant stream, the tritium must also diffuse through the matrix material to the nearest helium gap between the fuel rod and the moderator. Elleman (Refs. 17, 18) has found that tritium was not significantly retained in matrix material at 1273°K. Therefore, it would appear that the main barriers to tritium release are within the fuel particle.

The diffusion of tritium from low burnup oxide fuel kernels appears to be high according to measurements made by Elleman. While he was unable to quantitatively measure the diffusion coefficient for tritium in 10:1 ThO₂:UO₂ kernels, his results suggested that the value was similar to that

previously reported by Wheeler (Ref. 19) for tritium diffusion in UO_2 :

$$D = 0.037 \exp(-7200 \pm 450/T^\circ\text{K}) \text{ cm}^2/\text{sec} \quad . \quad (4-1)$$

Elleman also measured the tritium diffusion through pyrolytic carbon coatings deposited on lithium aluminate kernels. In the temperature range 1073° to 1473°K the coated LiAlO_2 kernels were found to quickly release tritium.

The transport through pyrolytic carbon was studied by recoil injection and by coating transport techniques. It was found that most of the tritium produced had recoiled into the particle buffer zone (about 92%) with the remainder retained in the core. Typical release curves showed a sudden breakthrough after a period of annealing. Elleman used this 'breakthrough' time to calculate the coating diffusion coefficient. In addition, the steady-state flux of tritium atoms established after breakthrough was used to determine the kernel diffusion coefficient. Both methods gave diffusion coefficients that were in broad agreement. The diffusion coefficient for tritium transport in pyrolytic carbon can be represented by:

$$D(\text{cm}^2/\text{sec}) = (700 \pm 580) \exp(-38,000/T) \quad . \quad (4-2)$$

In some experiments where total release was expected, about $23 \pm 4\%$ of the tritium was found to be retained. This could be tritium that had recoiled into the pyrolytic carbon crystallites such that it was permanently held. It is not known whether the tritium permanently held depends upon the tritium concentration present.

The release of tritium from fuel particles and compacts has been studied by Graber and Jones (Ref. 20) at different temperatures between 1125° and 1848°K and burnup levels up to 75% FIMA with both BISO and TRISO coated particles containing UC_2 , UO_2 , and $(\text{Th},\text{U})\text{C}_2$ kernels. The results are given in Tables 5 and 6 and Figs. 1 and 2.

TABLE 5
RETENTION OF TRITIUM IN BISO FUEL PARTICLES

Sample No.	Average Fuel Temp (°K)	Days Capsule at Power	Type	Capsule No.	Fuel Kernel	FIMA Burnup (%)	No. of Fuel Part. Per Run	Batch No.	Experimental Values			
									% Retained Based on		Average Percent Retained Based on	
									Ru-106	Total Zr	Ru-106	Total Zr
37	1023	26	HTI	P14	(Th,U)C ₂	5.7	3	3222-77E	75	82	73	49
38							3		69	23		
60							6		77	41		
61							6		72	48		
58	1198	192	HTI	P19	(Th,U)C ₂	23	3	4000-695E	79	--	71	--
59							3		63	--		
56	1223	26	HTI	P14	(Th,U)C ₂	5.7	3	3222-77E	92	37	95	97
57							3		97	157		
42	1248	192	LTI	P19	(Th,U)C ₂	13	3	4000-660E	90	86	88	71
43							3		85	55		
32	1438	192	HTI	P19	(Th,U)C ₂	21	3	4000-695E	25	26	26	37
31							3		27	48		
81	1123	253	LTI	P13L	UC ₂	60	3	4403-113E	75	--	74	--
82							3		74	--		
68	1548	253	LTI	P13L	UC ₂	75	6	4403-113E	22	--	23	--
69							6		27	--		
70							2		21	--		
66	1748	253	HTI	P13L	UC ₂	75	5	3516-47E	22(a)	--	20	--
67							4		19(a)	--		
73	1123	253	LTI	P13L	UO ₂	60	6	4413-35E	71	--	69	--
74							6		67	--		
71	1548	253	LTI	P13L	UO ₂	75	6	4413-35E	43	--	41	--
72							6		38	--		

(a) Coating integrity not of good quality as shown by microradiographs (see Fig. 4.1c).

TABLE 6
RETENTION OF TRITIUM IN TRISO FUEL PARTICLES

Sample No.	Average Fuel Temp (°K)	Days Capsule at Power	Capsule No.	Fuel Kernel	FIMA Burnup (%)	No. of Fuel Part. Per Run	Batch No.	Experimental Values			
								% Retained Based on		Average Percent Retained Based on	
								Cs-137	Total Zr	Cs-137	Total Zr
40	1223	281	P22	(Th,U)C ₂	19	3	4155-151E	96	95	94	103
41						3		91	111		
47	1513	127	P21	(Th,U)C ₂	12	3	3923-113E	86	96	84	85
48						3		85	92		
49						3		74	69		
50						3		81	81		
50A						1		94	--		
64	1848	253	P13L	(Th,U)C ₂	26	7	4263-75E	30	--	29	--
65						6		28	--		
44	1148	253	P13L	UO ₂	60	3	4413-67E	100	97	98	117
45						3		92	138		
46A						1		101	--		
79	1548	253	P13L	UO ₂	75	3	4413-67E	75	--	72	--
80						3		68	--		
76	1723	253	P13L	UO ₂	75	5	4413-67E	53	--	50	--
77						5		46	--		
53	1123	253	P13L	UC ₂	60	3	4413-5E	73	--	74	74
54						3		75	--		
27						3		--	74		
62	1523	253	P13L	UC ₂	75	6	4413-5E	32	23	34	24
63						5		35	24

Fig. 1. Release of tritium during anneal of TRISO coated UO_2 particles (from Ref. 20)

Fig. 2. Release of tritium during anneal of TRISO coated UC_2 particles (from Ref. 20)

Studies on the TRISO coated particles showed the following trends:

1. Tritium release from different kernel types followed the trend $UO_2 > UC_2 > (Th,U)C_2$.
2. The degree of tritium release depended on burnup and temperature.
3. TRISO coatings were more effective in retaining tritium than BISO. A limitation on the study was that the $(Th,U)C_2$ particles were only investigated at low burnup (<25% FIMA), whereas UC_2 and UO_2 particles were tested only at high burnup (>60% FIMA).

Studies on the BISO coated particles showed that:

1. Tritium retention was $UO_2 > UC_2 > (Th,U)C_2$.
2. At low burnup (<25% FIMA), the tritium retention characteristics of $(Th,U)C_2$ particles were very temperature dependent (i.e., 70% retained below 1248°K but only 15% at 1438°K).
3. Although the coating was known to be broken on one of the UC_2 particles at 75% FIMA burnup, the tritium retention was equal to that of a particle having an intact coating. Again, a limitation of the study was that UO_2 and UC_2 particles were only investigated at burnups above 60% FIMA, while $(U,Th)C_2$ particles all had a burnup <25% FIMA.
4. Tritium retention depended upon temperature and burnup.
5. At 1023°K and 60% burnup, UO_2 and UC_2 retained >70% of the tritium; at 1548°K and 75% burnup the UO_2 particles retained 41% tritium but the UC_2 particles only retained 23%.

The experimental error on these measurements was about $\pm 10\%$. In order to calculate the total amount of tritium formed, a value for the tritium

fission yield must be used which is uncertain by about $\pm 15\%$. Therefore, the absolute values reported here are fairly inaccurate. However, comparison between the various results shows likely deviations in performance within the experimental accuracy of the measurements.

As part of the same study, measurements were also made on compacts irradiated in fuel element D13-05 in the Peach Bottom HTGR core. The results presented in Table 7 show that although the pyrolytic-carbon coated $(\text{Th,U})\text{C}_2$ particles were 80 to 100% failed, only 20 to 30% of the tritium produced in the fuel was released from the compacts.

Studies in Germany have shown that tritium does not escape from the AVR type of fuel particles^{*} at average temperatures and burnup. Further independent studies have shown that the pyrocarbon layers are extremely effective in trapping tritium, presumably by means of a chemisorption mechanism.

At HRB in Germany, Lange and Walter (Ref. 21) have studied the retentive ability of pyrocarbon coated spherical particles of $(\text{U,Th})\text{O}_2$ or $(\text{U,Th})\text{C}_2$ having various irradiation histories at irradiation temperatures between 873° and 1523°K and burnups between 7 and 17% FIMA. The particles were irradiated partly loose and partly embedded in the graphite matrix of a fuel element. Tritium originally present in the fuel particles was determined from Cs-137 activity, fission yield, and the half-life, assuming Cs-137 to be quantitatively retained in the fuel particle. The particles were $(\text{U,Th})\text{O}_2$ (U:Th = 1:5) with an outer pyrolytic carbon coating 90 μm thick. The particles were irradiated 94 days at 1323°K to 7% burnup. For four of the five experiments, the tritium retention was greater than that calculated. It could be that some Cs-137 had migrated from the particle, which is known to occur at elevated temperatures. The results are shown in Table 8. It was concluded by Lange and Walter that at a burnup of 17% FIMA and temperatures of up to 1523°K , at least 90% of the tritium produced is

^{*} Particles used in the AVR pebble bed reactor are not exactly the same as either BISO or TRISO particles used in the HTGR but are similar to BISO particles.

TABLE 7
RETENTION OF TRITIUM IN PEACH BOTTOM COMPACT 18 IRRADIATED IN
FUEL ELEMENT D13-05(a)

Location	Ru-106 Found (g)	Tritium Found (dpm)	Tritium Calculated (dpm)	Tritium Retained (%)
Top	1.5×10^{-7}	1.2×10^7	1.7×10^7	71
Upper middle	1.8×10^{-7}	1.4×10^7	2.0×10^7	70
Lower middle	2.4×10^{-7}	2.0×10^7	2.7×10^7	74
Bottom	1.3×10^{-7}	1.2×10^7	1.5×10^7	80
Average				74 ± 7

(a) Particle coatings were known to be $\geq 80\%$ failed.

TABLE 8
TRITIUM RETENTION IN IRRADIATED PyC COATED (U,Th)O₂ PARTICLES
(HRB STUDIES) (a)

Particle	H-3 (Measured) (nCi)	H-3 (Computed) (nCi)
1	241	222
2	270	297
3	112	109
4	118	117
5	253	222

(a) Particle data
 Type: WO 468
 Kernel: (U,Th)O₂, U:Th = 1.5
 Outer coating: PyC, diameter = 90 μm, ρ = 1.92
 Irradiation data
 Time = 94 days
 Temperature = 1323°K
 Burnup = 7% FIMA

retained. This conclusion broadly agrees with the TRISO coated particle work performed at GA.

Walter et al. (Ref. 22) have recently published new results on the release of tritium from coated fuel particles. The burnup was 7% FIMA and the irradiation temperature was 1473°K. Measurements between annealing temperatures of 1673° and 2173°K showed that tritium release increased with temperature and time. The tritium release was described by the relation:

$$T_1 = T_0 (1 - e^{-Et}) \quad , \quad (4-3)$$

where T_1 = tritium released

T_0 = tritium originally present

E = release factor, which is a function of temperature, sec^{-1}

t = time at temperature, sec

The values for the release factor E at different temperatures between 1673° and 2173°K are given in Table 9; Fig. 3 shows the release as a function of temperature.

Release studies were also reported by Walter et al. (Ref. 22) for other fuel particles irradiated to different burnup values and having slightly different pyrocarbon coatings. The results are given in Table 10. For five of the six fuel particle types, the measured tritium activity exceeded that calculated.

Walter et al. also measured the distribution of tritium in a fuel particle at different irradiation temperatures between 1323° and 1743°K (Table 11). Most of the tritium (>95%) was found in the pyrocarbon coatings. About 20% was found in the outer layer and the rest in the two inner layers. The calculated and the measured tritium content agreed within experimental error ($\pm 10\%$).

TABLE 9
TRITIUM RELEASE FROM COATED FUEL PARTICLES IN THE TEMPERATURE
RANGE 1673° to 2173°K(a)

Annealing Temp (°K)	Release Factor E ^(b) (h ⁻¹)
1673	$(1 \pm 0.3) \times 10^{-4}$
1773	$(3.7 \pm 0.3) \times 10^{-4}$
1873	$(2.1 \pm 0.2) \times 10^{-3}$
1973	$(8.5 \pm 0.8) \times 10^{-3}$
2023	$(2.2 \pm 0.2) \times 10^{-2}$
2073	$(4.1 \pm 0.5) \times 10^{-2}$
2173	$(9.6 \pm 0.9) \times 10^{-2}$

(a) Particle data

Kernel: (U,Th)O₂, U:Th = 1:5

Inner buffer layer: diameter = 64 μm, porous

Middle PyC layer: diameter = 32 μm, ρ = 1.6

Outer PyC layer: diameter = 90 μm, ρ = 1.92

Irradiation data

Temperature = 1473°K

Burnoff = 7% FIMA

(b) Average of many individual measurements.

Fig. 3. Tritium release from coated fuel particles - temperature dependence of release factor, E (from Ref. 22)

TABLE 10
AMOUNT OF TRITIUM IN IRRADIATED COATED FUEL PARTICLES

	WM 517	WO 521	WO 468	WO 468	Particles from AVR	
Kernels U:Th = 1:5	(U,Th)C ₂	(U,Th)O ₂	(U,Th)O ₂	(U,Th)O ₂	(U,Th)C ₂	(U,Th)C ₂
Inner buffer layer						
Diameter, μm	53	70	64	64	30	53
Density	Porous	Porous	Porous	Porous	Porous	Porous
Middle PyC layer						
Diameter, μm	91	32	32	32	~ 70	123
Density, g/cm^3	1.94	1.6	1.6	1.6	~ 2	~ 2
Outer PyC layer						
Diameter, μm		95	90	90		
Density, g/cm^3		1.94	1.92	1.92		
Irradiation temp, $^{\circ}\text{K}$	873-1173	873-1273	1323	1523		
Irradiation time, days	264	264	94	102		
Burnoff, % FIMA	16.7	16.8	7	12	11	9.6
Measured tritium in one particle, ^(a) nCi	336	483	199	558	52	359
Calculated tritium in one particle from Cs-137, nCi	343	446	193	512	48	334

(a) Average of at least five single measurements.

TABLE 11
TRITIUM DISTRIBUTION IN COATED FUEL PARTICLES^(a)

Irradiation Temp (°K)	Tritium Distribution in Particles (%)			Total Quantity of Tritium	
	Outer PyC Coating	Buffer + Inner PyC Coating	Kernel	Measured (nCi)	Calculated (nCi)
1323 ^(b)	15	79	6	300	248
1523 ^(b)	16	83	1	525	490
1523 ^(b)	17	82.6	0.4	539	556
1743 ^(b)	27	71.6	1.4	277	266
1743 ^(b)	19	79.6	1.4	253	212
1323 ^(c)	98.8		1.2	188	200
1743 ^(c)	97.8		2.2	87	98

(a) Particle data

Kernel: (U,Th)O₂, U:Th = 1:5

Buffer coating: diameter = 64 μm, porous

Inner PyC coating: diameter = 32 μm, ρ = 1.6 g/cm³

Outer PyC coating: diameter = 90 μm, ρ = 1.92 g/cm³

Irradiation data

Burnup = 12% FIMA

(b) PyC coating chemically destroyed.

(c) Particles mechanically broken.

In contrast to these measurements, a more recent study (Ref. 23) at KFA (Jülich) Institute for Reactor Development has shown that fuel particles (type WO 468 f) during a 18,000-sec (5-hr) annealing time at 1173°K released between 10 to 15% of the tritium calculated to be present from the fission yield.

The radial distribution of tritium in coated fuel particles has been investigated by Rohrig (Ref. 24). The method used was to gradually etch the coatings to give solutions containing tritium and other fission products. The solutions were neutralized and distilled and the tritiated water obtained was measured using liquid scintillation counting. Figure 4 shows two profiles from high-temperature isotropic (HTI) PyC coated BISO particles as-irradiated and after a postirradiation anneal. After annealing, the tritium distribution was unaltered. The maximum tritium concentration in the outer zone is not yet understood.

Release measurements with both coated particles and graphite agree well with the earlier reported results from Walter *et al.* (Ref. 22) and suggest that diffusion is a long-term rate-controlling mechanism. The results for AS2-500 graphite are shown in Fig. 5.

Arrhenius plots of calculated reduced diffusion coefficients for matrix and graphite are plotted in Fig. 6. The coarse-grain graphites yield the lower curve, while the upper line is given by the fine-grain matrix. For both types of graphite, the apparent activation energy is about 2.5×10^5 J/mol (60 kcal/mol). The two curves can be superimposed simply by considering the ratio of the squares of grain sizes, which strongly implies that grain radius determines the real diffusion length.

Elleman (Refs. 25, 26) compared the results of his study with the experiments of Graber and Jones (Ref. 20) on irradiated BISO and TRISO coated particles. The results are given in Tables 12 and 13. The upper and lower limits for the calculated percentages reflect the uncertainties in the diffusion coefficient values. The results shown in Tables 12 and 13

Fig. 4. Tritium concentration profile in coated particles (from Ref. 24)

Fig. 5. Tritium release curves for AS2-500 graphite samples (from Ref. 22)

Fig. 6. Arrhenius plot of reduced diffusion coefficients as a function of temperature (from Ref. 24)

TABLE 12
COMPARISON BETWEEN OBSERVED AND CALCULATED TRITIUM RETENTION IN IRRADIATED
BISO COATED PARTICLES

Kernel	Batch No.	Average Fuel Temp (°K)	Days at Power	Capsule No.	Observed Tritium Retained ^(a) (%)	Calculated Tritium Retained (%)
(Th,U)C ₂	3222-77E	1023	26	P-14	61	100
(Th,U)C ₂	4000-695E	1198	192	P-19	71	12-100
(Th,U)C ₂	3222-77E	1223	26	P-14	96	100
(Th,U)C ₂	4000-660E	1248	192	P-19	79	12-100
(Th,U)C ₂	4000-695E	1438	192	P-19	32	0-13
UC ₂	4403-113E	1123	253	P13L	74	100
UC ₂	4403-113E	1548	253	P13L	23	0
UC ₂	3516-47E	1748	253	P13L	20	0
UO ₂	4413-35E	1123	253	P13L	69	100
UO ₂	4413-35E	1548	253	P13L	41	0

(a) Numbers reported are the averages of multiple measurements presented by Graber and Jones (Table 4.2 of Ref. 20).

TABLE 13
COMPARISON BETWEEN OBSERVED AND CALCULATED TRITIUM RELEASE FROM
IRRADIATED TRISO COATED PARTICLES

Kernel	Temperature (°K)	Heating Time (hr)	Tritium Release (%)	
			Observed ^(a)	Calculated
UO ₂	1173	13	11	0.002 - 0.02
UO ₂	1273	14	1	1 - 10
UO ₂	1373	12	2	2 - 25
UO ₂	1473	12	1	4 - 40
UO ₂	1573	12	5	50 - 100
UO ₂	1673	10	9	100
UC ₂	1173	6	0.6	0.002 - 0.02
UC ₂	1273	12	6.9	1 - 10
UC ₂	1373	12	3.3	2 - 25
UC ₂	1473	14	5.2	4 - 40
UC ₂	1573	13	20	50 - 100
UC ₂	1673	12	8.1	100

^(a) Graber and Jones (Ref. 20).

are similar except above 1473°K where 20 to 40% retention is observed whereas calculations predict total release.

The tritium diffusion coefficient in pyrolytic carbon displays an unusually high temperature dependence, which explains why tritium is retained almost completely at 973° to 1073°K but is quickly released in postirradiation annealing between 1373° and 1573°K.

While all the evidence is not unanimous, it appears that tritium is not released from intact fuel particles at low burnups (<7%) and temperatures (<1000°K). The results of the Peach Bottom samples (Table 7) show that substantial tritium retention can occur even in failed particles. It is possible that the nature of the fuel kernel and the type of pyrolytic carbon coating and matrix material can influence tritium release.

While insufficient data exist to quantify the effects, the currently available data suggest that tritium release from fuel particles depends upon burnup, temperature, the nature of the kernel, and the type of pyrolytic coating. Long-term tests have not been made. It is conceivable that the pyrolytic coatings become increasingly permeable to tritium due either to strain or creep and also fission product attack on the ceramic coating. Aside from the Peach Bottom data (Table 7), it appears that very little tritium remains in the kernel. Most tritium is held in the pyrolytic carbon layers, either trapped by recoil or chemisorption or due to the formation of fission product hydrides.

4.2. RELEASE FROM GRAPHITIC REACTOR COMPONENTS

Tritium is produced within the graphite moderator, reflector blocks, and the matrix material from Li-6 and B-10 impurities. A small quantity is also obtained from the reaction sequence

It is possible that some tritium produced in this way is retained in its place of birth (i.e., by recoil) and some would be capable of migrating out into the helium coolant. Elleman's results (Refs. 25, 26) indicate that about 20% of the tritium produced could be permanently held in the graphite structure.

Figure 7 shows the results of studies (Ref. 22) of tritium release at different temperatures from graphite containing 0.1 ppm Li irradiated at 8×10^{13} n/cm²-sec. The results imply that tritium release from graphite is a diffusion-limited process since the release is proportional to the square root of time.

Figure 8 shows some results on the influence of annealing temperature on tritium release conducted at KFA (Ref. 23) and HRB (Ref. 27). The HRB results are preliminary data. KFA explained their results by assuming that a combined diffusion/desorption mechanism was responsible for the release. They considered chemisorption and molecule dissociation at the graphite surface and absorption and diffusion into the graphite bulk.

Some data (Refs. 28, 29) are also available for hydrogen desorption from:

1. Nuclear graphite (type TSP) between 1300° and 1650°K.
2. Spectroscopic graphite (AGKSP) at 1200°K.
3. Hydrogen-treated graphite (TSP) at 1358°K.

Some of these results are shown in Fig. 9 (Refs. 30-32). As a first approximation it can be assumed that the desorption of hydrogen and tritium are similar. Hydrogen (and therefore perhaps tritium also) is known to react with graphite above 633°K, which could provide an additional retention mechanism (Ref. 33). Methane is the principal product. The rate constant for methane production was found to vary from 2.0×10^{-16} (633°K) to 3.3×10^{-12} mol/g-sec (1073°K).

Fig. 7. Tritium release isotherms from annealed/irradiated graphite probes (from Ref. 22)

Fig. 8. Influence of annealing temperature on tritium release from graphite (from Refs. 21 and 23)

Fig. 9. Hydrogen desorption from nuclear graphite (TSP) at different temperatures (Elovich plot) (from Refs. 30, 31, 32)

Very little information is available on the influence of a high neutron flux field on the behavior of tritium in graphite; however, experience with the operating gas-cooled reactors indicates that considerable quantities of tritium are retained by graphite. For example, a recent analysis (Ref. 22) of some "pebble bed" fuel graphite from the AVR reactor showed a uniform tritium concentration of 5×10^6 dps/g graphite (135 μ Ci/g graphite) throughout the 6-cm-diameter graphite "pebble."

Table 14 gives the results of recent analyses (Ref. 34) of graphite from Peach Bottom fuel element E0601, which show much lower loadings of tritium.

4.3. RELEASE FROM CONTROL ROD MATERIALS

Tritium is generated by the $B-10(n,2\alpha)H-3$ reaction from B_4C contained in the control materials. These are control rods and reflector blocks containing B_4C encapsulated in vented metal canisters and uncanned burnable poison rods. It is important to know the fraction of this tritium which is released to the coolant and to understand the chemisorption characteristics of control materials for sorbing tritium from the coolant gas.

Some measurements (Ref. 35) have been made on the amount of tritium retained within B_4C pellets. The results (Figs. 10 and 11) show between 20 and 80% of the tritium produced by the $B-10(n,2\alpha)H-3$ reaction is retained, the amount being dependent upon a complex function of irradiation temperature but not the burnup level. This retention effect was thought to be due to the way in which tritium combined chemically with the B_4C . Annealing at temperatures well above the irradiation temperature was necessary to release tritium from the B_4C pellets.

4.4. SUMMARY

In summary, data on the rate of release of tritium from core materials are quite sparse. The data indicate, however, that release from failed particle kernel materials is rapid. Failed pyrolytic carbon coatings also

TABLE 14
TRITIUM DISTRIBUTION IN PEACH BOTTOM FUEL ELEMENT E0601^(a)

Sleeve - radial distribution in cut specimens

At compact 7

Axial position	1	2	3	4	5	6	7	8	9	10	Total
H-3, $\mu\text{Ci/g}$	10.8	8.3	6.4	6.7	6.8	6.7	5.0	10.5	28.7	45.6	135.5

At compact 16

Axial position	1	2	3	4	5	6	7	8	9	10	Total
H-3, $\mu\text{Ci/g}$	28.5	25.0	19.5	17.2	15.5	16.9	15.7	10.3	11.3	--	159.9

At compact 26

Axial position	1	2	3	4	5	6					Total
H-3, $\mu\text{Ci/g}$	1.4	1.0	0.7	0.6	0.5	0.4					4.7

Spine - axial distribution in cut specimens

Wt, g	3.75	2.95	4.32	4.30	4.16	3.26	2.66	5.7			30.57
H-3, $\mu\text{Ci/g}$	0.5	0.6	1.5	1.7	1.8	1.6	1.1	1.1			9.9

^(a) Irradiated 384 effective full power days.

Fig. 10. Tritium retained in boron carbide (from Ref. 35)

Fig. 11. Temperature dependence of tritium retention on B_4C pellets (from Ref. 35)

do not significantly retain tritium, although there appears to be a permanent retention of about 20% of the tritium inventory. Release from graphite and control materials is poorly understood, but both B_4C and graphite appear to be extremely retentive toward tritium under reactor operating conditions. Intact fuel particles are virtually completely retentive at temperatures below $\sim 1073^\circ K$, above which increasing portions of tritium would be expected to be released.

5. TRITIUM REMOVAL

5.1. REMOVAL BY CHEMISORPTION ON GRAPHITE

It is known that both tritium and hydrogen can be chemisorbed onto graphite at high temperatures. However, only one set of measurements has been made in the temperature range of interest for HTGR operation. No information is available on the influence of neutron flux and irradiation upon the sorption properties of tritium on graphite. Since chemisorption is a chemical reaction between molecules and certain energetic sites on the surface of a solid, it might be expected that a radiation field would create more active sites in the graphite and/or activate the gas molecules by ionization or dissociation and so increase the amount of chemisorption.

Out-of-pile measurements made on A-3 graphite at HRB showed that tritium chemisorption increases with temperature and time. Further, the BET surface of the graphite also gradually increased (Table 15). The temperature dependency of tritium chemisorption is shown in Fig. 12. In another test, a 6-cm graphite "pebble" was equilibrated at 873°K for 100 hr with helium containing 570 dps/cm³ (STP) helium [1.54×10^{-2} μ Ci tritium/cm³ (STP) helium]. The tritium concentration profile through the graphite sphere is shown in Fig. 13. A comparison of these results with the tritium concentration observed in graphite balls from the AVR indicates that a much larger chemisorption of tritium occurs at reactor operating conditions.

In addition, several workers have measured the chemisorption of hydrogen on graphite; however, the measurements were made at lower temperatures than those to which HTGR graphite is exposed. Equilibrium was apparently reached within a few hours.

TABLE 15
TRITIUM SORPTION ON A-3 GRAPHITE AT 873° AND 1073°K

Exposure Time (hr)	Temp (°K)	Adsorbed Amount ($\mu\text{Ci/g}$)	BET After Loading (m^2/g)
0	873	0.47	0.85
4		0.63 0.87	
12.5	973	1.25 1.41	
24	873	1.44 1.55	
47	873	1.76 2.67	
96.5	873	2.57 2.93	
168	873	4.12	1.1-1.5
190	873	5.2 6.42	2.1
333	873	10.0 20.6 23.3 24.3	6-8
10	1073	1.7 1.8	
24	1073	2.2 2.2	1.8
49.5	1073	3.6 4.4	1.8
120	1073	5.1 5.2	1.7
300	1073	11.5	2.4

Fig. 12. Temperature dependence of tritium sorption on A-3 graphite (from Ref. 27)

Fig. 13. Tritium concentration profile through an AVR graphite sphere (from Ref. 27)

Measurements made on Graphon, a graphitized carbon black, and on nuclear-grade graphite type TSP are given in Figs. 14 and 15. The results are limited to below 873°K and a pressure of 67 Pa (6.7×10^{-4} atm). It is important to notice that tritium and hydrogen chemisorption both increase with temperature.

The kinetics of chemisorption of hydrogen on carbon and graphites is complex. Barrer and Rideal (Ref. 30) established that at about 873°K the rate of chemisorption of hydrogen on carbon changed from an exponential dependence upon temperature to a square root temperature dependence. This indicates that the diffusion of hydrogen to inner graphite surfaces is slower than the rate of chemisorption and therefore is rate limiting in this temperature region.

In summary, the mechanisms by which tritium is held in graphite are poorly understood. Unfortunately, because so little information is available, it is not possible to incorporate tritium retention by graphite (or control materials) into model calculations. However, graphite could prove to be a very significant sink for tritium under reactor operating conditions. By neglecting this phenomenon, calculations of tritium release to the primary coolant would be conservatively high.

5.2. REMOVAL BY RECOIL

Tritium is generated in nuclear reactors as a triton, which is the tritium nucleus without an orbiting electron (i.e., a positively charged tritium ion) and is highly reactive. Upon production the triton could energetically recoil into the graphite surface where it could displace hydrogen in a C-H bond or carbon in a C-C bond. This recoil action might produce additional active sites upon which further chemisorption could occur. It is not known what fraction of tritium trapped by recoil is held irreversibly. The results of Elleman (Refs. 25, 26) suggest that about 20% might be permanently held.

Fig. 14. Sorption of hydrogen on Graphon (from Ref. 30)

Fig. 15. Sorption of hydrogen on TSP nuclear graphite between 1100° and 1770°K (from Ref. 30)

5.3. REMOVAL BY THE PURIFICATION SYSTEM

In order to avoid deleterious effects, undesirable impurities that enter the primary coolant either by desorption from the core at startup or during operation must be removed. Principally these impurities are:

1. H_2O , N_2 , and O_2 from graphite outgassing.
2. H_2O , CO , CH_4 , CO_2 , and H_2 from steam in-leakage and subsequent reaction with graphite.
3. H_2 and CH_4 from reaction of oil contaminants with graphite.
4. N_2 and O_2 from air ingress during maintenance and venting operations.

These impurities are removed by the purification system, which also removes tritium. The Fort St. Vrain HTGR helium purification system consists of:

1. High-temperature (605°K) bed of activated carbon spiked with potassium for iodine removal.
2. Sintered metal filter unit for dust removal.
3. Chiller (322°K) for removing high water concentrations.
4. Molecular sieve bed for removing water and carbon dioxide.
5. Liquid-nitrogen-cooled charcoal bed for removing N_2 , CH_4 , CO , and fission gases (Kr and Xe).
6. Titanium sponge bed (573° to 673°K) for hydrogen and tritium removal.

An alternative purification system considered for future HTGR design uses a CuO bed for H₂ and CO oxidation and subsequent removal.

It is important to ascertain the extent of retention of tritium in the various units of the purification train. However, no measurements have been made of the removal of tritium from the primary coolant by the purification system. It is currently assumed that tritium will behave as hydrogen. Thus, the species HT would be removed by the titanium sponge bed, and the species HTO would be removed by the drier beds. However, it seems likely that the point in the purification system where tritium is removed will be dependent on the water level in the helium because this will determine the fraction of tritium in the form of HTO.

If relatively high water concentrations occur in the helium coolant (i.e., during steam leakage into the reactor), the chiller will trap some of the tritium as HTO, as well as an additional amount due to the exchange reaction:

which has a favorable equilibrium constant. Equilibrium constants for the reaction are given in Table 16. These values are described by the relation:

$$\log K_1 = 0.292 \log T + (3365/T) - 1.055 \quad . \quad (5-2)$$

A further possibility is that tritium may concentrate on the molecular sieve drying bed as HTO due to an exchange reaction between HT in the coolant and H₂O sorbed on the bed (in accordance with Eq. 5-1). The degree of exchange that occurs might depend upon the water loading on the molecular sieve.

The isotopic exchange between tritium and water vapor in an inert atmosphere has been studied by Yang and Gevantman (Ref. 36). The reaction

TABLE 16
EQUILIBRIUM CONSTANTS FOR THE REACTION $\text{HT} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{HTO}$

Temp (°K)	Experimental Equilibrium Constant	Theoretical Equilibrium Constant
289.0	7.75 ± 0.04	6.47
293.2	6.47 ± 0.02	6.24
298.0	6.25 ± 0.05	6.01
329.3	5.05 ± 0.05	4.84
352.6	4.37 ± 0.05	4.23
384.2	3.76 ± 0.04	3.64
431.4	3.10 ± 0.06	3.03
480.1	2.64 ± 0.04	2.54
575.9	2.17 ± 0.02	2.08

had a second order rate constant of $1.13 \times 10^{-14} \text{ cm}^3/\text{dps-sec}$ ($1.5 \times 10^{-3} \text{ cm}^3/\mu\text{Ci-hr}$). At an initial concentration of $3.7 \times 10^4 \text{ dps/cm}^3$ ($1 \mu\text{Ci/cm}^3$), the half-time of the oxidation reaction was $5.9 \times 10^9 \text{ sec}$ ($6.6 \times 10^4 \text{ days}$) and that of the exchange reaction was $2.42 \times 10^9 \text{ sec}$ ($2.8 \times 10^4 \text{ days}$). Hence, the conversion of elemental tritium to tritiated water vapor in air is a very slow process. However, catalytic reactions on metal surfaces are known to increase the conversion rate [c.f. the rate constants found by Eakins and Hutchinson (Ref. 37) in the presence of certain catalysts]. Unless the molecular sieve is an active catalyst, the rate of conversion of elemental tritium to tritiated water should be extremely slow under normal conditions at these concentrations.

Experience with the CO_2 -cooled reactors in both England and Italy (Ref. 38) has shown that significant quantities of tritium are present in the water obtained after regeneration of the alumina driers. The tritium activity found was about $3.7 \times 10^6 \text{ dps/cm}^3 \text{ H}_2\text{O}$ ($100 \mu\text{Ci/cm}^3 \text{ H}_2\text{O}$).

Experiments are needed to ascertain the rate and degree of exchange of HT with water sorbed on molecular sieves. Finally, tritium will be absorbed by the titanium sponge bed along with hydrogen. Whereas no sorption data for tritium on titanium sponge are available, there are several predictable differences in the behavior of tritium compared to hydrogen. The dissociation pressure of titanium tritide is higher than that of titanium hydride, which means that the tritide is less stable so that breakthrough of tritium could occur before hydrogen at the same concentration level. This is further substantiated by the fact that tritium has only one-third the solubility of that of hydrogen in alpha-palladium (Ref. 39).

While it is clear that tritium will be totally removed from the purification stream, it is by no means clear how tritium will be distributed among the various purification traps.

5.4. PERMEATION OF THE STEAM GENERATOR TUBES

The main problem posed by tritium in HTGRs is caused by the fact that it can permeate through certain metals at high temperature, such as through the steam generator tubes. Therefore, in order to assess the magnitude of any tritium discharge problem, the factors that affect tritium permeation through metals must be identified and well understood.

5.4.1. Hydrogen Permeability Studies

While the permeation of hydrogen through metals has been extensively studied, there is relatively little information available on the temperature and pressure region of interest for HTGRs.

Values of permeability coefficients for hydrogen permeation of various metals and alloys are shown in Table 17. Figure 16 shows the temperature dependence of K for several metals and alloys (Ref. 41).

5.4.1.1. Hydrogen Permeation of Ferritic Steels. Yang (Refs. 42-45) has measured the permeation of hydrogen through carbon steel and T-22 (2-1/4 Cr 1 Mo). The results are shown in Fig. 17. Rohrig et al. (Refs. 46, 47) have measured the permeability of hydrogen through 13 Cr 44 Mo ferritic steel at 773°K and different pressures. The results are depicted in Fig. 18. A comparison of the results shows that increasing the chromium content of the alloy decreases the hydrogen permeability of the metal. The use of high chromium alloys for the steam generator tubes would reduce the tritium permeation problem.

5.4.1.2. Hydrogen Permeation of Incoloy 800. The permeation of hydrogen through Incoloy 800 has been measured by Yang et al. (Refs. 42-45) over a temperature range of 700° to 1000°K and hydrogen pressures between 47 to 1×10^5 Pa (0.35 to 760 torr). The results are shown in Fig. 19.

TABLE 17
ACTIVATION ENERGIES FOR DIFFUSION AND PERMEATION CONSTANTS FOR
HYDROGEN PERMEATION OF METALS(a,b)

Metal	Q (cal/mol)	K_o $\left(\frac{\text{cm}^3 \text{ (STP) mm}}{\text{sec-cm}^2\text{-torr}^{1/2}} \right)$
Hastelloy N	13,800	1.9×10^{-3}
Hastelloy B	16,675	1.82×10^{-2}
Nickel	13,400	1.00×10^{-2}
Iron	9,100	1.45×10^{-3}
304 SS	16,100	8.56×10^{-3}
316 SS	16,075	1.54×10^{-2}
321 SS	16,075	1.54×10^{-2}
430 SS	11,200	3.62×10^{-3}
PH15-7Mo SS	20,000	7.86×10^{-2}
Haynes 25	15,100	3.29×10^{-3}
Molybdenum	20,100	9.57×10^{-3}
Tungsten	29,340	1.85×10^{-2}
Niobium	3,430	1.05×10^{-2}
Platinum	18,600	1.85×10^{-2}
Palladium	4,500	6.15×10^{-2}
Vanadium	14,200	5.4
Copper	18,560	1.11×10^{-2}

(a) From Ref. 41.

(b) $J = K_p / x \sqrt{p}$

$K_p = K_o \exp(-Q/RT).$

Fig. 16. Temperature dependence of the permeability constant for hydrogen in several metals and alloys (from Ref. 41)

Fig. 17. Hydrogen permeability through T-22 and low carbon steel at various temperatures (from Refs. 42-45)

Fig. 18. H₂ permeation through a ferritic steel at low pressures (from Refs. 46 and 47)

Fig. 19. Permeation of hydrogen through Incoloy 800 (from Refs. 42-45)

As part of the German program on process heat applications of very high temperature gas-cooled nuclear reactors (VHTGR), Rohrig et al. (Refs. 46, 47) measured hydrogen permeation of Incoloy 800 over the temperature range 873° to 1223°K and between hydrogen partial pressures of 50 and 5×10^4 Pa (0.5 to 500 mbar). These results are given in Fig. 20. Where a comparison of these results is possible (873° and 973°K), good agreement is observed at hydrogen pressures below 133 Pa (1 torr). Above this pressure, the Germans report higher permeation rates.

5.4.1.3. Deuterium Permeation of Metals and Alloys. In permeation studies completed at ORNL (Ref. 41) deuterium was chosen as the permeating gas in order to avoid problems associated with the ORNL mass spectrometer measuring system. The objectives of this study were threefold:

1. To study the chemical stability of the oxide.
2. To investigate the pressure dependence of hydrogen permeation through an oxide-metal composite.
3. To study the pressure dependence of permeation, especially with regard to the integrity of the oxide film.

Permeation rate data for deuterium permeation through unoxidized and oxidized metal and alloy specimens at 1.3 Pa (0.01 torr) are given in Table 18. Compositions of the materials used are given in Table 19.

5.4.2. Tritium Permeation Studies

5.4.2.1. Tritium Permeation of T-22 Metal. Yang et al. (Refs. 42-45) measured the permeation of tritium through T-22 at different temperatures and partial pressures at a fixed tritium/hydrogen ratio. Equations describing tritium permeation through T-22 as a function of temperature are given in Table 20. Some of the results at a low hydrogen level are shown in Table 21. The results are recorded in the sequence in which they were measured. The scatter in the data could be due to the condition of the

Fig. 20. H_2 permeation versus temperature and pressure (from Refs. 46, 47)

TABLE 18
DEUTERIUM PERMEATION THROUGH UNOXIDIZED AND OXIDIZED METALS AND ALLOYS

Material	Temp (°K)	Permeation Rate ^(a) at 1 Torr, Metal Thickness = 1 mm [cm ³ (STP)/hr-cm ²]	Pressure Range (torr)
Ni	896	$(1.6 \pm 0.2) \times 10^{-2}$	9×10^{-4} to 750
Hastelloy N	878	$(2.7 \pm 0.2) \times 10^{-3}$	4×10^{-3} to 31.4
304L stainless steel (initial)	970	$(2.3 \times 10^{-3})^{(b)}$	31.4
304L stainless steel (after 18 hr)	970	$(2.6 \pm 0.5) \times 10^{-4}$	3×10^{-2} to 31.4
304L stainless steel	1058	$(4.5 \pm 0.4) \times 10^{-4}$	5×10^{-2} to 31.4
406 stainless steel (oxidized with D ₂ -2.6% D ₂ O, 72 hr)	915	$(1.6 \pm 0.3) \times 10^{-5}$	1 to 750
Incoloy 800	922	$(1.6 \pm 0.2) \times 10^{-3}$	1 to 750
Incoloy 800 (after oxidation with D ₂ -2.6% D ₂ O at 1017°K)	922	$(4.7 \pm 0.4) \times 10^{-6}$	10 to 750
Incoloy 800 (exposed to H ₂ O at 811°K, 233 bars, 10 ³ hr before testing)	804	$(6.3 \pm 0.4) \times 10^{-4}$	1.3 to 750
Croloy T9 ^(c) (oxidized with D ₂ -2.6% D ₂ O, 72 hr)	846	$(6.6 \pm 0.5) \times 10^{-5}$	7 to 750
Croloy T9 (same specimen as above after 932°K oxidation)	843	$(5.7 \pm 0.4) \times 10^{-6}$	10 to 750
Croloy T22 ^(d)	558	$(1.8 \pm 0.1) \times 10^{-4}$	1 to 750
Croloy T22	853	$(8.0 \pm 0.1) \times 10^{-3}$	1 to 750
Croloy T22 (oxidized with D ₂ -2.6% D ₂ O at 853°K)	853	$(6.0 \pm 0.2) \times 10^{-3}$	3 to 750

(a) 95% confidence level from a least-squares fit.

(b) Extrapolated to 1 torr assuming half-power pressure dependence.

(c) ASTM-A-213-T9.

(d) ASTM-A-213-T22.

TABLE 19
MATERIALS USED IN PERMEATION STUDIES

Material	Nominal Composition ^(a) (%)
Nickel, ASTM B-161, Grade A	Ni; 0.25 max. Cu; 0.40 max. Fe; 0.35 max. Mn; 0.35 max. Si; 0.15 max. C; 0.01 max. S
304L stainless steel	Fe; 18 to 20 Cr; 8 to 12 Ni; 2.00 max. Mn; 1.00 max. Si; 0.045 max. P; 0.030 max. S; 0.03 max. C
406 stainless steel	Fe; 14 Cr; 3.9 Al; 0.4 Ni; 0.4 Mn; 0.4 Si; 0.3 Ti; 0.08 C
Incoloy 800	Fe; 32.0 Ni; 20.5 Cr; 0.35 Si; 0.75 Mn; 0.30 Cu; 0.04 C
Hastelloy N	Ni; 15 to 18 Mo; 6 to 8 Cr; 4 Fe; 0.04 to 0.08 C; 0.5 Al; 0.01 B
T9, ASTM A-213-T9	Fe; 8 to 10 Cr; 0.9 to 1.1 Mo; 0.30 to 0.60 Mn; 0.25 to 1.00 Si; 0.15 max. C; 0.03 max. P; 0.03 max. S
T-22, ASTM A-213-T22	Fe; 1.9 to 2.6 Cr; 0.87 to 1.3 Mo; 0.30 to 0.60 Mn; 0.5 max. Si; 0.15 max. C; 0.03 max. P; 0.03 max. S

(a) Composition given is that supplied by the manufacturer or obtained from the handbooks.

TABLE 20
TRITIUM PERMEATION RATE THROUGH T-22

Tritium-Helium Mixture	Specific Activity ($\mu\text{Ci}/\text{standard cm}^3$)	$P_{\text{total}} = 1 \text{ bar}$ Partial Pressure of Gaseous Impurities (ppm)					Temp Range ($^{\circ}\text{K}$)	Number of Data Points	Least-Square Relationship Between Permeation Rate P ($\mu\text{Ci}/\text{cm}^2\text{-hr/mm}$) and Temperature ($^{\circ}\text{K}$)
		H_2	O_2	H_2O	CH_4	CO			
1	3.62×10^{-5}	50	4.9	4.0	<1	<1	565-778	24	$P = 1.05 \exp(-7690/T)$
2	2.10×10^{-4}	230	6.0	4.0	<1	<1	610-778	15	$P = 2.04 \exp(-7450/T)$
3	8.45×10^{-4}	610	28	4.6	<1	<1	577-781	20	$P = 6.09 \exp(-7380/T)$
4	6.14×10^{-3}	6500	2.7	4.0	<1	<1	573-767	17	$P = 3.41 \exp(-5070/T)$

TABLE 21
TRITIUM PERMEATION RATE THROUGH T-22 AT LOW H₂ LEVEL^(a)

Run No. (b)	Temp (°K)	Permeation Rate (μCi/cm ² -hr/mm)
1	573	1.49 x 10 ⁻⁶
2	573	1.39 x 10 ⁻⁶
3	573	1.25 x 10 ⁻⁶
4	623	5.17 x 10 ⁻⁶
5	623	6.04 x 10 ⁻⁶
6	623	8.21 x 10 ⁻⁶
7	672	1.77 x 10 ⁻⁵
8	672	1.87 x 10 ⁻⁵
9	672	1.74 x 10 ⁻⁵
10	719	2.68 x 10 ⁻⁵
11	719	2.81 x 10 ⁻⁵
12	719	3.00 x 10 ⁻⁵
13	777	5.22 x 10 ⁻⁵
14	777	5.39 x 10 ⁻⁵
15	777	5.56 x 10 ⁻⁵
16	565	9.43 x 10 ⁻⁷
17	565	9.15 x 10 ⁻⁷
18	673	7.78 x 10 ⁻⁶
19	673	8.37 x 10 ⁻⁶
20	673	7.97 x 10 ⁻⁶
21	778	3.60 x 10 ⁻⁵
22	778	3.70 x 10 ⁻⁵
23	610	4.74 x 10 ⁻⁶
24	610	5.21 x 10 ⁻⁶

(a) Source specific activity = 3.62 x 10⁻⁵ μCi/cm³, equivalent to p_{HT} = 2.14 x 10⁻⁸ torr. Impurity contents: H₂ = 50 ppm, O₂ = 4.9 ppm, CO < 1 ppm, CH₄ < 1 ppm, H₂O = 4.0 ppm.

(b) Run number represents sequence of experiments.

material influencing tritium permeation. Measurements with differing tritium/hydrogen ratios are in progress.

5.4.2.2. Tritium Permeation of Incoloy 800. Workers at ORNL (Ref. 48) have used a mixed isotope technique to measure the permeability of tritium through Incoloy 800 with a controlled steam atmosphere on the inside of the tube. Hence, the influence of surface oxidation on tritium permeation was determined. A long-term experiment (>2000 hr) was conducted on Incoloy 800 at 930°K with the inside of the tube continuously purged with a sweep gas of Ar/H₂O with a H₂O partial pressure of 0.3×10^5 Pa (0.3 bar). The total pressure of the sweep gas was 0.9×10^5 Pa (0.9 bar). The tritium permeability of the metal dropped continuously with time (a factor of 160 in 7.26×10^6 sec (84 days), which was attributed to the oxidation of the metal to form a protective oxide coating. The results are shown in Fig. 21. The permeability rapidly decreased for 1.29×10^5 sec (36 hr), and then linearly decreased at a much slower rate as a function of the square root of time. This indicated that the surface of the Incoloy 800 sample was completely covered with an oxide layer after 1.29×10^5 sec (36 hr). Before steam was added, the measured permeability coefficient was 2.67×10^6 cm³ (STP)-mm/cm²-sec-torr^{1/2} and after 4.0×10^6 sec (1936 hr), it was 1.67×10^8 cm³ (STP)-mm/cm²-sec-torr^{1/2}.

Measurements were also made on the tritium permeation through nickel between 636° and 910°K. The relation found was:

$$\log_e P_T = -0.906 \frac{-636 \times 10^3}{T} ,$$

or

$$P_T = 6.65 \times 10^{-3} \exp(-6360/t) ,$$

where P_T is in cm³ (STP)-mm/cm²-sec-torr^{1/2}.

Fig. 21. Permeability of tritium through Incoloy 800 at 930°K exposed to steam at 0.32×10^5 Pa on the downstream side (from Ref. 48)

5.4.3. Influence of Oxide Coatings

Some data for oxidized specimens are given in Table 18 and Fig. 21. Most studies on tritium diffusion have concentrated on diffusion through water reactor fuel claddings; it was shown in these studies that surface oxide films can lower the permeation rate. The effect on Zircoloy-2 is very striking; a surface layer reduced the tritium diffusion coefficient by eight orders of magnitude below bulk diffusion coefficients at typical clad temperatures (Ref. 18).

Tritium permeation through steam generator materials might be reduced either by natural oxide films or by the addition of deposited surface films. Elleman (Ref. 18) has made a preliminary study of deposited Cr and Zr films. The following samples were investigated:

1. As-received Incoloy 800.
2. Electropolished Incoloy 800.
3. Electropolished, air oxidized Incoloy 800 (1073°K for 4.32×10^4 sec (12 hr)).
4. Electropolished Incoloy 800 with evaporated Zr layer (0.1 to $1 \mu\text{m}$).
5. Same as (4) plus air oxidized (1073°K for 4.32×10^4 sec (12 hr)).
6. Electropolished Incoloy 800 with evaporated Cr layer (0.1 to $3 \mu\text{m}$).
7. Same as (6) plus air oxidized (1073°K for 4.32×10^4 sec (12 hr)).

Tritium release rates from electropolished Incoloy 800 were consistent with the classical diffusion solutions where the release fraction (F_R) with time is given by:

$$F_R = 4/R_t \sqrt{\frac{Dh}{\pi}} \quad 0 \leq f \leq 0.3 \quad , \quad (5-3)$$

where R_t = tritium recoil range, cm
 D = diffusion coefficient, cm^2/sec
 h = heating time, sec

At 773°K the diffusion coefficient for tritium in Incoloy 800 was found to be $5 \pm 4 \times 10^{-10} \text{ cm}^2/\text{sec}$. This is several orders of magnitude lower than results on austenitic steels reported by other workers under comparable conditions. It is possible that the Incoloy 800 specimens used possessed a very thin oxide film which reduced the permeation rate of tritium.

Experiments with oxidized specimens showed a rapid buildup of tritium at the alloy-coating interface, followed by diffusion of tritium through the coating. Elleman suggests that the observed transport through the coating is controlled by entry of tritium atoms into the coating at the interface rather than by diffusion control through the coating. This is consistent with the possibility that diffusion through oxides is molecular via defects, whereas through the metal it occurs interstitially as atoms. In other words, the formation of molecular tritium and entry into the oxide film via defects (rather than actual transport in the film) is the rate-limiting step.

The observed influence of oxidation and coating thickness effects are shown in Fig. 22. It was observed that coating breakthrough times could not be simply related to coating thickness, which also implies that transport through the coating is not the rate-limiting step.

While chromium oxide film reduced the tritium permeation rate by a factor of ten, in general the Zr surface barrier film did not prove too

Fig. 22. Effects of oxidation and coating thickness on the release of tritium from Incoloy 800 (from Ref. 18)

successful. Furthermore, in those experiments oxidation of Incoloy 800 did not produce the expected reduction in tritium migration. This is contrary to the data previously given in Fig. 21.

Workers at ORNL and KFA (Germany) have also investigated the influence of oxide films. The ORNL results (Refs. 41, 48) were included in Table 18 and Fig. 21. Hydrogen permeation studies on oxidized and unoxidized specimens of Incoloy 800 studied at KFA are shown in Figs. 20 and 23. In accordance with their model, oxide layers on either side of the steam generator tubes should inhibit permeation of hydrogen and tritium. Figures 23 and 24 (Ref. 47) show the impeding effect of oxide films on Incoloy 800 at different pressures (constant T) and at different temperatures (constant P). The authors state that the upper curve in Fig. 24 could only be obtained by a long-duration annealing treatment of the specimen in pure hydrogen. The lower curves in Fig. 24 were obtained with a moisture content controlled atmosphere. The authors explain that the different curves were obtained for a test series in which the temperature was increased or decreased (as due to an accidental power failure to the furnace), which caused cracking of the protective oxide layer such that permeation increased.

Recent work at ORNL (Ref. 48) on the influence of oxide films on the steam side of the generator tubes has shown that a dramatic reduction in tritium permeation of Incoloy 800 at 830°K can be obtained. The results are shown in Fig. 21. Whether such a dramatic effect is also possible with low Cr alloys such as T-22 is not yet known.

Very recently, Yang et al. (Refs. 42-45) have investigated the influence of hydrogen, either in the helium coolant or on the downstream side of the T-22 sample tube, on the tritium permeation rate. The important conclusion reached from this work was that the presence of hydrogen (equivalent to 200 ppm at reactor pressure) hardly influences the tritium permeation rate. This was found to be true irrespective of whether or not the hydrogen flux was in the same direction as the tritium flux.

Fig. 23. Influence of oxide film on H_2 permeation (from Refs. 46, 47)

Fig. 24. H_2 permeation versus $1/T$ for a clean oxide surface (from Refs. 46, 47)

This is important in process heat applications. The results showed that the rate of hydrogen or tritium permeation depends upon:

1. Whether the helium coolant is reducing or oxidizing (i.e., the impurity levels of CO, CO₂, O₂, H₂O, and H₂).
2. Nature of operating conditions (i.e., cooling of the sample tubes caused cracking of the protective oxide layer).
3. Surface condition of the steam generator tubes.

In summary, it appears that oxide films are capable of reducing hydrogen permeation by several orders of magnitude. Defects in the protective layer will reduce this barrier effect. The effectiveness of oxide films in restricting permeation might well depend upon their structure, chemical composition, and stability, which may be determined by operational conditions.

5.4.4. Pressure Dependence of Tritium and Hydrogen Permeation Rates

Several investigators have observed that the pressure dependence of the permeation rate of hydrogen appears to show some peculiarities at low pressures. At high pressures the permeability of hydrogen followed a $P_{H_2}^{1/2}$ relation, which infers that the hydrogen permeates as the atomic form. At low pressures, however, a linear dependence on pressure was observed, while at even lower pressures the $P_{H_2}^{1/2}$ relation was again followed. No reasonable explanation of these observations had been made until recently when Strehlow and Savage (Ref. 42) suggested that very thin oxide coatings on the metal surfaces might be responsible. They pointed out that a slight nonintentional surface oxidation was difficult to avoid on most metals (Ni and Ni-based alloys, which have a very low affinity for oxygen, being a possible exception). They concluded that these thin oxide films were only of importance when the hydrogen driving pressures were very low. Hydrogen

is known to permeate through oxides as molecular hydrogen, and the permeation is directly proportional to pressure. At very low pressures, the only permeability was via defects in the oxide coating.

The system "metal + oxide coating" can be considered to consist of a linear and a nonlinear resistance connected in series. Defects or holes in the oxide coating which allow direct access of hydrogen to the bare metal can be thought of as a parallel resistance. Using an analogy with Kirchoff's laws for electric current, the permeation flow (the whole current in electrical terms) is the sum of the permeation flows (the partial currents in electrical terms). Thus,

$$J = J_1 + J_2 \quad . \quad (5-4)$$

The current through the oxide is:

$$J_1 = L_{ox} (P_{H_2} - P_M) \quad , \quad (5-5)$$

where L_{ox} is the permeation conductivity of the oxide layer and P_M is the effective hydrogen pressure at the metal/oxide interface.

On the other hand (assuming Fick's and Sievert's laws hold for both layers),

$$J_1 = L_{M1} P_M^{1/2} \quad (5-6)$$

and

$$J_2 = L_{M2} P_{H_2}^{1/2} \quad , \quad (5-7)$$

where L_{M1} = conductivity of that portion of the metal which is oxide coated

L_{M2} = conductivity of that portion of the metal which is directly accessible to hydrogen

It can be shown that the permeation rate is given by the relation

$$J = L_{M1} \left[\sqrt{\left(\frac{L_{M1}}{2L_{ox}}\right)^2 + P_{H_2}} + \frac{L_{M2}}{L_{M1}} \sqrt{P_{H_2}} - \frac{L_{M1}}{2L_{ox}} \right] \quad (5-8)$$

When $L_{M2} \ll L_{M1}$,

$$J = L_{M1} \left[\sqrt{\left(\frac{L_{M1}}{2L_{ox}}\right)^2 + P_{H_2}} - \frac{L_{M1}}{2L_{ox}} \right] \quad (5-9)$$

At high pressures,

$$J \approx L_{M1} \sqrt{P_{H_2}} = \frac{K}{x} \sqrt{P_{H_2}} \quad (5-10)$$

At low pressures,

$$J \approx L_{ox} \cdot P_{H_2} \quad (5-11)$$

Equation 5-8 gives the pressure dependence of the permeation flux for the case of a defect-free oxide film. This relation agrees well with results obtained by Rohrig et al. (Refs. 47, 48) for hydrogen permeation through a ferritic steel at low pressures (Fig. 18).

5.5. SORPTION ON METAL SURFACES

Tests in Sweden (Ref. 49) have shown that tritium will sorb upon metal oxide films that are in contact with tritiated water. Stainless steel and carbon steel discs that had oxide films on their surfaces contained between 3.7×10^4 to 7.4×10^4 dps/g oxide (100 to 200 μ Ci/g oxide). With correct water treatment of the secondary coolant, oxide films should be relatively thin. Therefore, this mechanism of tritium retention may not be significant.

5.6. DIFFUSION THROUGH THE STAINLESS STEEL LINER AND THE PCRV CONCRETE

Some tritium diffusion can be expected through the stainless steel containment liner into the liner cooling water system and through the concrete of the PCRV. However, the amount that will diffuse via this path is small compared to that which diffuses through the steam generator tubes.

5.7. SUMMARY

While there are some data on H_2 permeation, there is only a little information available on tritium permeation rates through HTGR steam generator materials (i.e., T-22 and Incoloy 800). Areas where further work is desirable on HTGR steam generator materials are:

1. Permeation at high temperatures.
2. Influence of alloying metals.
3. Permeation rates at very low tritium pressures.
4. Influence of natural barriers (e.g., oxide films) that may form under reactor operating conditions.

However, current work in progress at ORNL and at KFA (Germany) should considerably improve the data base. It remains to be seen whether oxide films can dramatically reduce tritium transport through operating HTGR steam generators as is observed to occur in laboratory tests.

6. TRITIUM CONCENTRATION LEVELS IN OPERATING HTGRs

Currently operating experience with HTGRs is limited to three fairly small prototype reactors. Nonetheless, a study of the conditions existing in these reactors may indicate the tritium concentration levels to be expected in future LHTGRs. The reactors are:

1. 20-MW(t) Dragon reactor in England, an experimental reactor which was operated by the UKAEA as part of the OECD High-Temperature Reactor Project.
2. 40-MW(e) Peach Bottom 1 reactor in Pennsylvania, U.S., which was designed and built by General Atomic with support from ERDA and the High-Temperature Reactor Development Associates, Inc., and is owned and was operated by the Philadelphia Electric Company.
3. 15-MW(e) prototype pebble bed reactor (AVR) in Jülich, Germany.

In addition, two demonstration reactors, the Fort St. Vrain 330-MW(e) reactor (USA) and the 300-MW(e) pebble bed reactor at Schnehausen (Germany), will begin power operation in the near future.

6.1. DRAGON REACTOR

Some typical results (Refs. 50, 51) for the tritium concentration in the primary coolant are given in Table 22. Studies have been made of the influence of reactor impurities by use of controlled impurity injections

TABLE 22
TRITIUM MEASUREMENTS AT DRAGON (ENGLAND) (a)

Date	Primary Coolant Tritium ($\mu\text{Ci}/\text{cm}^3(\text{STP})$ He	Primary Coolant Hydrogen (vpm)
July 1, 1971	4.5×10^{-6}	4
July 14, 1971	1.6×10^{-4}	25
August 3, 1971	1.2×10^{-4}	25
August 6, 1971	4.5×10^{-4}	100
August 12, 1971	3.9×10^{-4}	35
August 18, 1971	6.8×10^{-4}	130

(a) Reactor operating conditions
 Power = 20 MW(t)
 Primary coolant pressure = 19.25 bars
 Core inlet temperature = 658°K
 Core outlet temperature = 1073°K
 Purification system flow = 222 m³ (STP)/hr

under steady-state reactor conditions. These tests are briefly summarized as follows:

1. Water injection: CH_4 , CO_2 , CO , and H_2 concentrations all increased. Termination of the injection caused all the concentrations, including tritium, to slowly decrease back to their original level.
2. Hydrogen injection: Both the methane and the tritium concentrations increased, whereas the water, CO , and CO_2 concentrations were not significantly affected.
3. Methane injection: The hydrogen and the water concentrations increased; after termination of the injection the levels slowly decreased. The CO_2 and CO levels gradually increased for about 2 days. The tritium at first remained steady but then decreased in harmony with the hydrogen concentration.

The highest tritium levels were associated with the highest hydrogen concentrations (about 100 ppm) produced during the hydrogen injection experiments.

6.2. PEACH BOTTOM HTGR

Several tritium surveys have been made at Peach Bottom (Ref. 52), all of them since the installation of the second fuel charge. The last tritium survey was performed during an experiment in which H_2 was injected into the primary circuit. The results, summarized in Table 23, show that the tritium concentration in both the primary and the secondary coolant increased gradually between August 1970 and August 1974, the period during which the surveys were taken. This gradual increase may be due to combinations of the following factors which occurred during operation of core 2:

1. Steady increase in the number of failed fuel particles.
2. Release related to burnup.

TABLE 23
TRITIUM MEASUREMENTS AT PEACH BOTTOM 1 (a,b)

Date	Primary Coolant [$\mu\text{Ci}/\text{cm}^3$ (STP) He]	Secondary Coolant ($\mu\text{Ci}/\text{cm}^3$ H ₂ O)
August 1970	--	6.8×10^{-5}
Sept-Oct. 1971	1.5×10^{-5}	1×10^{-4}
Feb. 1973	4×10^{-5}	1.5×10^{-4}
June 1973	9×10^{-5}	2.2×10^{-4}
Sept. 1973	1.5×10^{-5}	2.5×10^{-4}
March-April 1973	4×10^{-5}	2.8×10^{-4}
Aug. 1974	1×10^{-5} to 2×10^{-4}	1.5 to 3.2×10^{-4}

Influence of H₂ Concentration

H ₂ in Primary Coolant (vpm)		
4	1×10^{-5}	1.5×10^{-4}
20	4×10^{-5}	1.9×10^{-4}
40	4.5×10^{-5}	1.91×10^{-4}
60	5.0×10^{-5}	1.92×10^{-4}
80	6.0×10^{-5}	1.93×10^{-4}
100	7.5×10^{-5}	1.94×10^{-4}
120	8.0×10^{-5}	1.95×10^{-4}
140	15.0×10^{-5}	2.0×10^{-4}
160	20.0×10^{-5}	2.25×10^{-4}

(a) From Ref. 53.

(b) Operating conditions

Power = 115.5 MW(t)

Primary coolant pressure = 23.6 bars

Core inlet temperature = 617°K

Core outlet temperature = 1000°K

Purification system flow = 508.7 m³ (STP)/hr

Steam temperature = 811°K

3. Fuel temperature increase.
4. Steady increase in hydrogenous impurity content (causing a desorption of tritium from the graphite core due to competitive chemisorption).

6.3. AVR (GERMANY)

Various test programs have been completed (Ref. 53) in order to better understand the importance of tritium. These tests include a startup test where the secondary coolant was replaced, an injection of tritium into the primary coolant, and altering the steam temperature. The following observations were made:

1. After startup of the reactor, the secondary coolant was replaced with a new water charge; a synonymous and spontaneous increase in the tritium concentration (after 1 hr) was measured in both the primary and the secondary coolant (i.e., unretarded diffusion).
2. Injecting tritium into the primary circuit for several days did not influence the secondary coolant tritium concentration.
3. Decreasing the steam temperature from 778° to 723°K, which lowers the steam generator wall temperature, did not affect the secondary coolant tritium concentration over the test period of several weeks.

In addition, methane and hydrogen injection experiments were performed as described below.

6.3.1. Methane Injection

Injection of methane over a period of 4.32×10^5 sec (5 days) increased the primary coolant tritium concentration by a factor of 20 to

100. After a delay time of about 2.52×10^4 sec (7 hr), the tritium concentration in the secondary coolant doubled. When the methane feeding was stopped, its concentration in the coolant dropped rapidly due to thermal decomposition and sorption. The hydrogen and tritium concentrations also decreased. Most of the hydrogen supposedly produced from methane was also thought to be sorbed. Restarting the methane injection caused a marked increase in the tritium concentration in both the primary and secondary circuits. It was suggested that a Fe_3O_4 layer on the steam side of the steam generator acts as a diffusion barrier and that tritium enrichment can occur in the Fe_3O_4 layers. It was concluded that methane dissociates faster than hydrogen so that if the methane impurity level is high, more atomic tritium is produced at the steam generator surface (i.e., from CH_3T rather than HT).

6.3.2. Hydrogen Injection

A hydrogen injection test of 2.42×10^6 sec (4 weeks) duration showed that while both the tritium and the hydrogen concentration levels increased fourfold to fivefold, the secondary coolant tritium concentration increased by a factor of 1.2 to 1.5 with a time delay of about 2.52×10^4 sec (7 hr). These results are shown in Table 24. This inhibition of tritium migration is explained as being due to a retardation of the dissociation of HT because of the excess of hydrogen present in the coolant that is also dissociating.

In this test a 2.52×10^4 sec (7 hr) delay was observed before the tritium concentration in the secondary coolant increased after hydrogen injection, but only a 3.6×10^3 sec (1 hr) delay occurred after startup with fresh secondary coolant. This was attributed to cracks or fissures in the protective oxide layers on steam generator tubes which are resealed during plant operation.

In terms of the role of hydrogen and the relative tritium concentrations in the primary and secondary coolants, agreement with Peach Bottom

TABLE 24
TRITIUM MEASUREMENTS AT AVR (GERMANY) ^(a)

Date	Primary Coolant [$\mu\text{Ci}/\text{cm}^3$ (STP) He]	Secondary Coolant ($\mu\text{Ci}/\text{cm}^3$ H ₂ O)
May 31, 1973	1.5×10^{-3}	5.7×10^{-3}
July 5, 1973	$0.8 \text{ to } 7.4 \times 10^{-3}$	$3.3 \text{ to } 9.0 \times 10^{-3}$
Aug. 23, 1973	$0.3 \text{ to } 0.5 \times 10^{-3}$	3.0×10^{-3}
Jan. 24, 1974	0.6×10^{-3}	4.6×10^{-3}
June 4, 1974	0.9×10^{-3}	6.0×10^{-3}

Influence of H₂ Concentration

Hydrogen in primary coolant (vpm)		
12	0.9×10^{-3}	6×10^{-3}
70	5.0×10^{-3}	8×10^{-3}
75	6.5×10^{-3}	9.5×10^{-3}
70	7.5×10^{-3}	10.0×10^{-3}

(a) Reactor operating conditions

Power = 45 MW(t)

Primary coolant pressure =

Core inlet temperature = 547°K

Core outlet temperature = 1073°K

Purification system flow = 65 m³ (STP)/hr

Steam temperature = 778°K

results is quite good. A sixfold hydrogen increase gave a sevenfold tritium increase in the primary coolant, which caused a 1.6-fold tritium increase in the secondary coolant. At Peach Bottom a fivefold rise in H_2 gave a fourfold rise in tritium in the primary coolant, which caused a 1.3-fold increase in tritium concentration in the secondary coolant.

Comparing the results for the three reactors (Tables 22 through 24) shows that tritium levels in the primary coolant at AVR, Dragon, and Peach Bottom are in the ratio 100:10:1. Reactor conditions were similar and it is not known why such differences should occur. The impurity levels of components that produce tritium (He-3, Li-6, and B-10) could be different. For example, in the AVR an impure form of graphite (carbon stone) was used as permanent reflector material. This material might have had a high Li content. Furthermore, the lower values at Peach Bottom and Dragon could be due to the action of the fuel element purge/fission product trapping system that was installed in these reactors.

An extrapolation of Peach Bottom tritium data to predict the situation in LHTGRs could be misleading because the purge system might have kept the primary coolant tritium level very low. Such might not be the case in LHTGRs, which have no purge system.

6.4. SUMMARY

The available tritium data from the three prototype HTGRs have demonstrated extremely small tritium releases to the environment. Such releases easily comply with the latest U.S. Federal guidelines. However, there are large differences in the tritium concentrations reported for these three reactors which can, in part, be traced to differences in system design, operating conditions, and materials of construction.

7. PREDICTED TRITIUM LEVELS IN FUTURE HTGRs

Several attempts have been made to predict the migration of tritium through the various pathways possible in an HTGR system (Fig. 25). It has been the objective of several workers to develop a model which accurately predicts the fate of tritium during the lifetime of a typical HTGR. These models are described in the following sections.

7.1. WORK AT ORNL

A computer code has been recently developed by workers at ORNL (Ref. 16) for prediction of the distribution and release of tritium in HTGRs as a function of design, operational, and material parameters. The code is demonstrated by a prediction of expected tritium levels in the Fort St. Vrain reactor. Briefly, the computer model works by dividing the reactor into source regions, such as the core or the control rods, and assigning an average slow and fast full-power neutron flux to each region. Calculations are then made region by region or chain by chain, where a chain is the particular nuclear sequence from which tritium is generated (e.g., He-3, Li-6, etc.) Source and sink compartments are, respectively, where the tritium is born and where it migrates via different regions. A coupled set of linear first-order differential equations is developed for each region or chain which describes the transfer from any source to any sink compartment. The following assumptions are made:

1. Total release of H-3 from cracked particles, but total retention by intact particles. One percent of the particles is assumed to be broken.

Fig. 25. Tritium pathways in an HTGR

2. Of the tritium produced in graphite and control rods, 99% is assumed to be retained and not released. The remaining 1% is assumed to be instantaneously released.
3. Some of the H-3 that is formed from He-3 is held by recoil in graphite or control rods. Arbitrary rules are used to determine the quantity retained, which is dependent upon the region. Between 50 and 70% is assumed to be retained.
4. The chemisorption behavior of T_2 or HT is assumed identical to H_2 and to depend directly upon the H_2 concentration in the primary coolant.
5. The permeation of the steam generator tubes is considered to obey both Sievert's and Fick's laws (i.e., H_2 dissolves in metal proportional to the P_{H_2} , and permeability depends also on $P_{H_2}^{1/2}$). An empirical correction to the rate is made to allow for tritium permeation being slower than H_2 permeation (60% taken).

Conclusions from the study are that:

1. The H-3 concentration in both the primary and the secondary coolants at FSV are predicted to be lower than that observed at Peach Bottom, although the latter was known to contain 10 to 20% failed fuel particles.
2. An increase in the primary coolant hydrogen concentration decreases the H-3 permeability, which is contrary to the available experimental evidence.
3. The assumptions made concerning the release from fuel (zero from intact particles) and the permanent retention of tritium by solids (recoil) control the magnitude of the tritium concentrations observed. These assumptions do not appear to be justified if the available experimental evidence given earlier is reviewed.

4. Tritium levels decrease after 1 yr of operation, which is due solely to He-3 burnout and the imposed assumptions that restrict release from fuel and graphite.

In conclusion, while the concept of the computer code is correct, the gross assumptions made appear to prevent the model from giving a reasonable guide to the behavior of tritium in HTGRs. Although a computer code to study tritium release is very desirable, it is clear that this model is not satisfactory and should be improved by incorporation of the available experimental evidence and updated when more information becomes available.

7.2. PREVIOUS WORK AT GA

Previous calculations of tritium migration performed at GA have been extrapolated from the conditions observed in the Peach Bottom reactor. It was assumed that the parameters controlling tritium diffusion at Peach Bottom and in LHTGRs are similar:

1. Helium-side and water-side steam generator tube surface chemistry.
2. Primary coolant composition.
3. Steam generator alloy materials.
4. Steam generator tube temperature profiles.
5. Hydrogen partial pressure in primary coolant.

Tritium diffusion rates were compared by applying these factors to the observed Peach Bottom yearly diffusion rate of 3.7×10^{10} dps/yr (1.0 Ci/yr), i.e.,

$$D_{\text{LHTGR}} = \frac{A_1 \cdot PT_1 \cdot \text{DIFF}_1 \cdot D \cdot \text{Temp}_1 \cdot (P_{\text{H}_2})_2 \cdot (D)_2}{A_2 \cdot PT_2 \cdot \text{DIFF}_2 \cdot D \cdot \text{Temp}_2 \cdot (P_{\text{H}_2})_1},$$

where

- 1 = LHTGR data
- 2 = Peach Bottom data
- D = yearly tritium diffusion rate for the respective plant,
dps/yr (Ci/yr)
- A = diffusion surface area
- PT = tritium partial pressure
- DIFF = diffusivity of steam generator tubing material
- D•Temp = relative diffusivity at temperatures in the respective
plant
- P_{H_2} = partial pressure of hydrogen in the primary coolant
helium

However, it is debatable whether an extrapolation of Peach Bottom data to LHTGR conditions is the most appropriate way of estimating tritium levels in LHTGRs. This is because the installed fuel element purge system at Peach Bottom (not a design feature of LHTGRs) may have been responsible for the very low tritium activity levels observed in the primary coolant.

An alternative approach is given in Appendix C and these equations are used in the following section to calculate the expected tritium release from LHTGRs.

7.3. SAMPLE CALCULATION OF TRITIUM RELEASES FROM LHTGRs

The model described in Appendix C has been used to calculate expected tritium releases from HTGRs. The data base used for these calculations is given in Appendix D. The limitations of this model should be recognized. The relations are derived from mass balance considerations at steady state. Hydrogen permeability studies have been used to calculate the expected tritium permeabilities because sufficient tritium permeability data are not yet available. Credit is not taken for the effect of oxide films in retarding tritium permeability because the required data are also lacking. Sorption of tritium on graphite has not been considered because quantitative relations between P_{HT} and tritium sorbed are unavailable. The role of a radiation field in tritium sorption on graphite is also unknown.

It has been assumed that tritium is totally released from graphite and control rods, whereas only 5% escapes from intact fuel but 100% is released from failed fuel particles. Releases from the fuel may be somewhat higher, but there should be a fairly effective retention of tritium by graphite and control rods. Therefore, it can be safely assumed that this model will calculate maximum values for tritium release. The maximum annual total body dose to any individual from all liquid effluent pathways is 3 mRem (see Appendix A) which, as can be seen from Table 25, is much greater than the calculated exposure of the maximum individual adult for all the HTGR types considered. Hence, tritium release from LHTGRs, predicted with conservative assumptions, is well below Federal guide lines. Therefore, further laboratory studies to better understand tritium migration should be assigned relatively low priority at the present time.

TABLE 25
ESTIMATED TRITIUM RELEASES FROM HTGRs

	1000 MW(t)	2000 MW(t)	3000 MW(t)	4000 MW(t)
Release to primary coolant, Ci/yr	2963	6064	9027	12,374
Steady-state tritium level in the primary coolant				
Partial pressure (as HT), N/M ²	5.16×10^{-4}	4.9×10^{-4}	6.9×10^{-4}	7.4×10^{-4}
Specific activity, $\mu\text{Ci}/\text{cm}^3$ He at 50 atm	6.56×10^{-3}	6.08×10^{-3}	8.75×10^{-3}	9.38×10^{-3}
Total activity, Ci	3.5	6.1	12.3	16.8
Permeation through steam generator tubes, molecules T ₂ /hr	2.44×10^{17}	6.28×10^{17}	1.34×10^{18}	1.92×10^{18}
Steady-state tritium concentration in the secondary coolant, $\mu\text{Ci}/\text{cm}^3$ H ₂ O	8.6×10^{-3}	4.9×10^{-3}	6.5×10^{-3}	6.8×10^{-3}
Tritium removed by purification system, Ci/yr	2759	5538	7904	10,761
Concentration of tritium in discharges from the plant, $\mu\text{Ci}/\text{cm}^3$ H ₂ O	1.9×10^{-5}	2×10^{-5}	3.2×10^{-5}	3.1×10^{-5}
Annual tritium discharge from the plant, Ci	204	526	1123	1613
Estimated dose from tritium in river at blowdown outfall, mRem/yr ^(a)				
Maximum individual adult	0.15	0.20	0.64	1.07
Average adult	0.09	0.12	0.38	0.64

(a) Factor of 35 assumed for river dilution.

8. LIST OF SYMBOLS

A	Surface area of steam generator, m^2
A_t	Activity of tritium after time t, dps
B	Flow rate of helium through purification system, moles/sec
C	Conversion factor: g tritium to dps/g tritium
CF_t	Reconcentration factor for tritium
Ch	Tritium chemisorbed on graphite, dps/g graphite
D	Tritium diffusion coefficient, cm^2/sec
D_g	Gaseous diffusion coefficient, cm^2/sec
D_R	Amount of tritium removed, dps/sec
D_{LHTGR}	Calculated tritium diffusion rate for the LHTGR, dps/yr
DIFF	Diffusivity of steam generator tubing for tritium
DTEMP	Relative diffusivity at temperatures in the respective nuclear plant
D_{ipr}	Dose factor for species i through pathway p to organ r
$\frac{D(N_i)}{dt}$	Rate of production by fission of species i, atoms/sec
dps	Disintegrations/sec (3.7×10^{10} dps $\equiv$ 1 Ci)
E	Temperature-dependent release factor for tritium from coated fuel particles, sec^{-1}
F	Flow rate of liquid effluent from nuclear plant, m^3/sec
F_R	Tritium release fraction from electropolished Incoloy 800
F_H	Fractional makeup rate for helium coolant
f	Plant availability factor
G	Tritium removed in the purification system, moles/sec

H	Helium inventory in the primary loop, g
h	Heating time, sec
J_i	Permeation rate of species i
K	Fission rate at unit power, fissions/sec-MW
K_i	Equilibrium constant for reaction i
K_o	Preexponential factor in the Arrhenius relation for gas permeability of metals
K_p	Permeability coefficient, cm^3 (STP) mm/cm ² -sec-torr ^{1/2}
L	Conversion factor for moles tritium to disintegrations per second (dps)
L_{ox}	Permeation conductivity of oxide layer
L_{M1}	Permeation conductivity of oxide coated metal
L_{M2}	Permeation conductivity of metal
M	Molecular weight of tritium
M_p	Mixing ratio of reactor liquid effluent and river at the point of exposure or withdrawal of drinking water
N_i	Number of atoms of species i
N_4^o	Concentration of He-3 in makeup helium
P_H	Hydrogen permeation rate, cm^3 (STP) mm/sec-cm ² -torr ^{1/2}
P_T	Tritium permeation rate, cm^3 (STP) mm/sec-cm ² -torr ^{1/2}
P_t	Tritium permeation through steam generator tubes, moles/sec
P_{H_2}	Hydrogen partial pressure in helium coolant, N/m ²
P_{HT}	Partial pressure of HT, N/m ²
P_{T_2}	Tritium partial pressure, N/m ²
P_M	Effective hydrogen partial pressure at the metal/oxide interface, N/m ²
Q	Activation energy for gas permeation, Kjoules/mole

Q_2	Release rate of tritium, dps/yr or Ci/yr
R	Net tritium release from reactor components, dps/yr or Ci/yr
R_t	Tritium recoil range, cm
R_{ipr}	Dose rate from nuclide i to organ r via pathway p , mRem/yr
T	Absolute temperature, °K
T_1	Tritium released from coated fuel particles
T_o	Tritium originally present in coated fuel particles
TA	Tritium activity in primary coolant, dps
TR	Total tritium release, dps/yr or Ci/yr
t	Time, sec
t_p	Transit time for tritium to reach point of exposure, sec
U	Amount of tritium leaving the plant in the cooling tower blowdown stream, moles T_2 /sec
U_p	Body intake rate of the contaminated water
V	Amount of tritium leaving plant via the air ejector, moles T_2 /sec
W	Reactor power, MW(t)
X	Amount of tritium leaving plant via the steam deaerator, moles T_2 /sec
Y	Total volume of effluent leaving the nuclear plant, $\text{cm}^3 \text{H}_2\text{O}/\text{sec}$
Y_t	Number of tritium atoms produced per fission (fission yield), atoms/fission
Z	Concentration of tritium in the blowdown effluent, $\text{dps}/\text{cm}^2 \text{H}_2\text{O}$ or $\text{Ci}/\text{cm}^3 \text{H}_2\text{O}$
λ	Tritium decay constant, sec^{-1}
σ_i	Neutron cross section of species i , m^2
ϕ_i	Average neutron flux experienced by species i , $\text{n}/\text{cm}^2\text{-sec}$

APPENDIX A
LEGAL REQUIREMENTS PERTAINING TO TRITIUM DISCHARGE
FROM NUCLEAR PLANTS

A.1. INTRODUCTION

At the present time there is no legal limit restricting the release of tritium from HTGRs. In the United States the regulations regarding discharge of radionuclides from nuclear plants are specified in 10CFR50, Appendix I. The finalized version of this appendix was recently published in the Federal Register by the Nuclear Regulatory Commission (NRC) (Ref. 54). This document provides guidelines for design objectives and limiting conditions for operation to meet the "as low as practicable" (ALAP) criterion for radioactive effluent discharges from LWRs. It attempts to quantitatively define the requirements for effluent release to unrestricted areas from LWRs to ensure that they are kept "as low as practicable." It does not stipulate radiation protection standards; these are given in 10CFR20.

The finalized Appendix I of 10CFR50 is less stringent than an earlier version. While Appendix I applies only to LWRs, it has been applied to Fort St. Vrain, and it can be expected that similar regulations will eventually be applied generally to HTGRs.

With respect to regulations enforced outside the United States, most countries follow the recommendations of the International Committee on Radiation Protection (ICRP), which has proposed the maximum permissible concentrations of tritium oxide in air and water given in Table A-1. Using the ICRP regulations, Forsyth (Ref. 14) has shown that airborne release of all tritium produced in an HTGR would not violate the limit set for the tolerable burden of tritium oxide in body tissue. Further, he showed that

TABLE A-1
ICRP REGULATIONS ON THE
MAXIMUM PERMISSIBLE CONCENTRATIONS (MPC)
OF TRITIUM OXIDE IN AIR AND WATER

MPC of Tritium Oxide for Plant Personnel for 40-hr Week ($\mu\text{Ci}/\text{cm}^3$)		MPC of Tritium Oxide for 168-hr-Week Exposure ($\mu\text{Ci}/\text{cm}^3$)		MPC of Tritium Oxide for General Public ($\mu\text{Ci}/\text{cm}^3$)	
In Air	In Water	In Air	In Water	In Air	In Water
8×10^{-6}	0.1	2×10^{-6}	0.03	2×10^{-8}	3×10^{-4}

neither tritium oxide nor tritium will present a breathing hazard to HTGR operating personnel.

A.2. FINALIZED VERSION OF 10CFR50, APPENDIX I (Ref. 54)

A.2.1. Regulations Concerning Liquid Discharges

The new version of 10CFR50, Appendix I, does not have a concentration limit on tritium discharges or a maximum total activity that can be discharged.* Instead, the maximum annual total body dose to any individual from all liquid effluent pathways is 3 mRem, while the maximum allowable dose to any organ is 10 mRem.** The estimation of this exposure must be made with those potential land and water use and food pathways that could actually exist at the reactor location under consideration (i.e., the hypothetical cow at the site boundary has been eliminated).

A.2.2. Regulations Concerning Gaseous Discharges

The calculated annual dose rates from airborne activity at any location near ground level occupied by the public must not exceed 10 mrad for gamma radiation and 20 mrad for beta radiation.

A.2.3. Radioiodine and Particulate Matter Discharge

The amount of radioactive iodine and radioactive material that may be released is restricted by a maximum annual body dose, or a dose to any organ of any individual, from all possible pathways of exposure to 15 mRem/hr/light water reactor. The food pathways used in these calculations must actually exist at the location under consideration.

*Formerly, the maximum tritium concentration in liquor that could be discharged to a natural body of water was $0.21 \text{ dps/cm}^3 \text{ H}_2\text{O}$ ($5 \times 10^{-6} \text{ } \mu\text{Ci/cm}^3 \text{ H}_2\text{O}$). The total annual maximum activity release (excluding tritium) was $1.85 \times 10^{11} \text{ dps}$ (5 Ci).

**To illustrate how stringent these dose levels actually are, a dose of 1 mRem/hr is received from a high altitude jet flight and the average American receives 75 mRem/yr from x-ray examination.

A.2.4. Cost/Benefit Ratio

The new regulations stipulate that gas/water radioactive waste systems of reasonably demonstrated technology must be installed at the reactor site in order to protect the public (defined as those people living within a 50-mile radius) from radiation exposure.

In order to assess the "as-low-as-practicable" condition in terms of a cost/benefit ratio, the committee has selected, as an interim measure, the following cost penalties to utilities that violate the conditions of 10CFR50:

1. \$1,000 per total body-man-Rem.
2. \$1,000 per thyroid-man-Rem.

These values are conservative and are only meant to be guidelines. Lower values will be accepted if the utility can demonstrate that lower values should be used in a particular case.

A.2.5. Per Reactor Versus Per Site Basis

Contrary to the proposed 10CFR50, the design objectives are expressed on a per light-water-cooled nuclear power reactor basis rather than on a per site basis.

No site limits are stipulated, but doses from multireactor sites are expected to be lower than the sum of the doses from the individual reactor sites.

A.2.6. Licensee and Commission Guidelines

The new regulations give some guidelines as to the corrective action that must be taken by the licensee if it appears that radioactive release

rates will exceed the design objectives. The regulations state that if release rates in any 3-month period indicate that annual releases will exceed twice the annual design levels, then corrective action must be taken. Thus, corrective action would be required if the offsite dose rate during any 3-month period exceeded any of the following:

1. Liquid effluents

Whole body	6 mRem/yr
Skin or any organ	20 mRem/yr

2. Gaseous effluents

Whole body	10 mRem/yr
Skin or any organ	30 mRem/yr

In addition, the commission staff is advised to take corrective action if annual rates, based on a 3-month surveillance, are likely to exceed 4 to 8 times the design objectives.

A.2.7. Implementation of Guidelines

The regulations stipulate how the commission staff is to implement the 10CFR50, Appendix I, regulations.

A.3. DOSE RATE ESTIMATION IN LIQUID DISCHARGES

The new regulations do not define a maximum tritium concentration in water discharges from the reactor site as did the proposed version. Instead, tritium discharges in liquid effluents are regulated by the total body or organ dose rate. The total body or organ dose depends upon the release of all radionuclides. The most important tritium pathways are drinking water and eating fish.^{*} Eating tritium-contaminated fish will

^{*} Air submersion, shoreline activities (e.g., sunbathing, fishing), and swimming contribute a negligible amount to the dose rate from tritium (soft beta radiation) and so are not considered.

give a dose rate of about 1/40 of that for drinking water under similar conditions for exposure of the maximum individual adult.

The accepted model for calculating environmental radiation doses is one recently proposed by Soldat et al. (Ref. 55). The dose rate from ingestion of water^{*} is calculated from the relation:

$$R_{ipr} = 3.17 \times 10^{-11} \sum \frac{Q_i CF_t}{F} M_p U_p D_{ipr} e^{-\lambda_i t_p}, \quad (A-1)$$

where

R_{ipr} = dose rate from nuclide i to organ r via pathway p, mRem/yr)

CF_t = reconcentration factor

Q_i = release rate of tritium, dps/yr

F = flow rate of the liquid effluent, m³/sec

M_p = mixing ratio at the point of exposure or withdrawal of drinking water

t_p = transit time required for tritium to reach the point of exposure, sec

λ_i = radiological decay constant of tritium, sec⁻¹

3.17×10^{-11} = a constant which converts (dps/yr)/m³/sec) to dps/liter

U_p = intake rate of the contaminated water

D_{ipr} = dose factor (which depends upon the penetrating power of the emitted radiation) for species i through pathway p to organ r

* The dose rate from ingestion of organisms (e.g., fish) is simply obtained by adding a biological accumulation factor inside the summation term.

APPENDIX B

RELATIONS THAT GOVERN PERMEATION OF GASES THROUGH METALS

Permeation of gases through metals is usually discussed in terms of Fick's first law of diffusion in one dimension:

$$J = -D_g \frac{dC}{dx} \quad , \quad (B-1)$$

where J is the permeability, D_g is the gaseous diffusion coefficient (cm^2/sec), and dC/dx is the concentration gradient of the gas through the metal thickness x .

Sievert's law (Ref. 56) states that the equilibrium concentration of a diatomic gas dissolved in a metal is given by:

$$C = K_s p^{1/2} \quad , \quad (B-2)$$

where K_s is the Sievert's law constant in $\text{cm}^3(\text{STP})\text{-mm}/\text{cm}^2\text{-torr}^{1/2}$ and p is the pressure (torr).

Combining Fick's law with Sievert's law (for small tube wall thickness) gives

$$J = \frac{K_p}{x} (p_1^{1/2} - p_2^{1/2}) \quad , \quad (B-3)$$

where K_p includes both the diffusion coefficient and Sievert's law constant and is called a permeability coefficient [$\text{cm}^3(\text{STP})\text{-mm}/\text{cm}^2\text{-sec-torr}^{1/2}$]. The subscript 1 refers to upstream pressure while 2 refers to downstream pressure. When the downstream pressure is low,

$$J = \frac{K_p}{x} p_1^{1/2} \quad . \quad (B-4)$$

The $\sqrt{p}$ dependence of J assumes that the diatomic gas permeates through the metal lattice in the atomic state.

K_p may be written in the form of the Arrhenius relation:

$$K_p = K_0 \exp(-Q/RT) \quad , \quad (B-5)$$

where Q is the activation energy for gas permeation, R is the gas constant, and T is the absolute temperature. By specifying the pre-exponential factor K_0 and Q , the permeation behavior of the metal can be established.

APPENDIX C
A SIMPLE APPROACH TO TRITIUM MIGRATION

Considerable research (e.g., Ref. 57) has been conducted on the passage of hydrogen through metals, whereas little information is available on tritium transport. Studies indicate that the tritium permeation rate is $1/\sqrt{3}$ times that of the corresponding hydrogen rate, and this value is used as our basic assumption. If one considers gas transport through metals, the following processes may be relevant in determining the permeation rate:

1. At the metal surface
 - a. Chemisorption of the gas molecules on the surface.
 - b. Dissociation of gas molecules into atoms.
 - c. Passage of adsorbed atoms from the surface to the metal interior with the possibility of forming a hydride phase.
2. In the metal interior
 - a. Diffusion of atoms through the metal phase via defects, vacancies, or grain boundaries.
3. At the outgoing surface
 - a. Desorption of gas atoms from the surface.
 - b. Recombination of desorbed gas atoms into molecules.

It is known that these processes are not identical for hydrogen and tritium. Lacking specific information it is assumed that the two gases behave identically, apart from the factor $1/\sqrt{3}$ which is due to the mass differences of the hydrogen and tritium atoms.

C.1. RELATION BETWEEN TRITIUM AND HYDROGEN PERMEABILITY

All models of tritium permeation consider an equilibrium at the metal surface where chemisorption and gas dissociation take place. Classical thermodynamic arguments are used to obtain a relation between the possible reactions involving hydrogen and tritium in the primary coolant (ignoring the possible exchange of tritium with H_2O and CH_4). These reactions are:

The equilibrium constants for these reactions are related by the relationship:

$$\frac{K_2}{K_4} = \frac{K_3^2}{K_1} \quad (C-5)$$

Relations C-1 through C-5 can be used to determine the tritium atom concentration. For example, using Eqs. C-1 and C-3 and solving for $[H]$ gives

$$[H] = \sqrt{K_1 H_2} = \frac{K_3 [HT]}{[T]} \quad , \quad (C-6)$$

and from Eq. C-5,

$$[T] = \frac{K_3 [HT]}{\sqrt{K_1 [H_2]}} = \frac{\sqrt{K_2}}{K_4} \frac{[HT]}{\sqrt{[H_2]}} \quad . \quad (C-7)$$

If

$$P_T = \frac{P_H [T]}{\sqrt{3} [H]} \quad , \quad (C-8)$$

where P_T = permeability of tritium through the metal

P_H = permeability of hydrogen through the metal

$[T]$ = tritium atom concentration in the metal at the surface

$[H]$ = hydrogen atom concentration in the metal at the surface

then,

$$P_T = \frac{P_H K_3 [HT]}{\sqrt{3} \sqrt{K_1 [H_2]} \sqrt{K_1 [H_2]}}$$

$$= \frac{K_3}{K_1} \frac{P_H}{\sqrt{3}} \frac{[HT]}{[H_2]} \quad . \quad (C-9)$$

Replacing concentrations by partial pressures gives

$$P_T = \frac{K_3}{K_1} \frac{P_H}{\sqrt{3}} \frac{P_{HT}}{P_{H_2}} \quad , \quad (C-10)$$

where P_H = hydrogen permeation through the steam generator tubes, moles/
unit time

p_{HT} = partial pressure of tritium (as HT) in the helium coolant,
 N/m^2

p_{H_2} = partial pressure of hydrogen (as H_2) in the helium coolant,
 N/m^2

Hence, tritium permeation should be inversely proportional to hydrogen pressure; however, this was not observed by Yang et al. (Ref. 45) in their studies. Inspection of Eq. C-10 shows that tritium permeation depends directly on the permeation rate for hydrogen and is inversely proportional to hydrogen partial pressure. At the very low pressures involved in this work, and observed by others (Ref. 41), the hydrogen permeation rate is a linear function of hydrogen pressure, i.e.,

$$P_H = (\text{constant}) p_{H_2} \quad . \quad (C-11)$$

Substituting for P_H in Eq. C-10 gives*

$$P_T = \frac{(\text{constant})}{2\sqrt{3}} p_{HT} \quad . \quad (C-12)$$

This shows that the tritium permeation rate should be independent of hydrogen pressure provided the hydrogen permeation rate is a linear function of hydrogen pressure.

C.2. AMOUNT OF TRITIUM REMOVED BY THE HELIUM PURIFICATION SYSTEM

The titanium sponge bed in the purification system is assumed to quantitatively remove the tritium (as HT). All tritium is assumed to be

* K_4 varies between 3.45 at 600°K to 3.81 at 1000°K (Ref. 58).

K_1 varies between 2×10^{-33} at 600°K to 5×10^{-18} at 1000°K (Ref. 59).

It may be assumed that $K_1 \approx K_2$, so that $K_1 \approx 2K_3$.

present as HT, which is valid as long as the H_2O and CH_4 concentration levels in the helium are negligibly small (i.e., no CH_3T or HTO formation).

Hence,

$$D_R = \frac{P_{HT}}{P_{He}} BL \quad , \quad (C-13)$$

where P_{HT} = partial pressure of HT, N/m^2

P_{He} = pressure of helium, N/m^2

B = flow rate of helium through the purification system,
moles/sec

D_R = amount of tritium removed, dps/sec

L = conversion factor for moles of tritium to dps

C.3. NET TRITIUM RELEASE FROM REACTOR COMPONENTS (GRAPHITE, BORON RODS, AND FUEL)

At steady state, the release of tritium from reactor components into the helium coolant equals that lost from the coolant via leakage, decay, removal in the purification system, or diffusion through the steam generator tubes. Ignoring leakage and decay,

$$R = G + P_t \quad , \quad (C-14)$$

where R = net tritium release from reactor components

G = tritium removed in the purification system, moles/sec

P_t = tritium permeation through the steam generator tubes,
moles/sec

Using relations C-12 and C-13 in C-14 gives

$$R = P_{HT} \left[L \frac{B}{P_{He}} + \frac{(\text{constant})}{2\sqrt{3}} \right] \quad . \quad (C-15)$$

C.4. TOTAL TRITIUM RELEASE FROM REACTOR COMPONENTS

For transients,

$$TR = R + Ch \quad , \quad (C-16)$$

where TR = total release, dps/yr

Ch = amount of tritium chemisorbed on the graphite, which
depends upon temperature and P_{HT} , dps/g graphite

The total release TR is obtained by a consideration of possible time-dependent releases from fuel, graphite, boron control rods, reflector graphite, and boronated graphite. Tritium production from uranium or thorium contamination, broken fuel particles, and from He-3 should also be considered under steady-state conditions, $TR = R$.

C.5. TRITIUM ACTIVITY IN THE PRIMARY COOLANT

Tritium activity (TA) in the primary coolant is:

$$TA = \frac{P_{HT}}{P_{He}} WC \quad , \quad (C-17)$$

where TA = steady-state tritium activity in the primary coolant, dps or Ci

W = helium inventory in the primary loop, g

C = conversion factor = 3.56×10^{14} dps/g H-3 (9670 Ci/g H-3)

C.6. TRITIUM CONCENTRATION IN LIQUID DISCHARGES LEAVING THE PLANT

Under steady-state conditions, the amount of tritium entering the secondary coolant via permeation of the steam generator tubes equals that leaving the secondary coolant. Exit pathways for tritium from the secondary coolant are:

1. Sampling lines, leakage, and blowdown. These sources are collectively discharged from the plant via dilution with the cooling tower blowdown water.
2. Losses to the atmosphere due to the venting action of the deaerator and the air ejector systems.

Thus,

$$P_t = U + V + X \quad , \quad (C-18)$$

where U = amount of tritium leaving the plant in the cooling tower blowdown stream, moles T_2 /sec

V = amount of tritium leaving via the air ejector, moles T_2 /sec

X = amount of tritium leaving via the steam deaerator, moles T_2 /sec

If losses via the deaerator and the air ejector are ignored, the concentration of tritium in the blowdown effluent (Z) is given by:

$$Z = \frac{P_t MC}{Y \times 10^{-6}} \quad , \quad (C-19)$$

where P_t = tritium permeability, moles T_2 /sec

Y = total volume of water leaving the plant (blowdown, evaporation, and drift), $\text{cm}^3 \text{H}_2\text{O}/\text{sec}$

M = molecular weight of tritium (as T_2)

C = conversion factor, Curies of tritium per gram = 3.56×10^{14} dps/g (9670 Ci/g)

These relationships can be used to determine the likely distribution of tritium in HTGRs and the expected tritium discharge levels to the environment. These relations were used to calculate the expected tritium activity releases from LHTGRs.

APPENDIX D

DATA BASE AND SPECIMEN CALCULATION OF TRITIUM RELEASE FROM HTGRs

D.1. DATA BASE

See Tables D-1 through D-7.

D.2. CALCULATIONS

D.2.1. Average Tritium Permeation Through Steam Generator Tubes

Using Eqs. C-11, C-12, and C-15,

$$\begin{aligned}
 P_T &= \frac{R}{\left(1 + \frac{\sqrt{3} P_{He} P_{H_2}}{P_H P_{He}}\right)} \\
 &= \frac{\left(\frac{2963 \times 6.023 \times 10^{23}}{9600 \times 6 \times 365 \times 24}\right)}{\left(1 + \frac{1.732 \times 6.4515 \times 10^{28} \times 22.414 \times 10^3}{8118 \times 3.8 \times 10^4 \times 6.023 \times 10^{23}}\right)} \\
 &= 2.44 \times 10^{17} \text{ molecules } T_2/\text{hr}
 \end{aligned}$$

D.2.2. Steady-State Tritium Level

$$\begin{aligned}
 P_{HT} &= \frac{2R}{\left(\frac{P_{He}}{\sqrt{3} P_{H_2} + P_{He}}\right)} = \frac{\left(\frac{2 \times 2963 \times 6.023 \times 10^{23}}{9600 \times 6 \times 365 \times 24}\right)}{\left(\frac{8118 \times 6.023 \times 10^{23}}{1.732 \times 22.414 \times 10^3} + \frac{6.4515 \times 10^{28}}{3.8 \times 10^4}\right)} \\
 &= 3.88 \times 10^{-6} \text{ torr} \\
 &= 5.16 \times 10^{-4} \text{ N/m}^2
 \end{aligned}$$

D.2.3. Equilibrium Tritium in the Helium Coolant

$$\begin{aligned}
 \text{Equilibrium tritium} &= \frac{P_{\text{HT}}}{P_{\text{He}}} (\text{He inventory in g}) \times 9600 \\
 &= \frac{5.16 \times 10^{-4}}{5.065 \times 10^6} \times 3.642 \times 10^6 \times 9600 \\
 &= 3.5 \text{ Ci} = 1.295 \times 10^{11} \text{ dps}
 \end{aligned}$$

D.2.4. Tritium Discharged from the Plant

$$\begin{aligned}
 \text{Tritium discharged} &= \frac{2.44 \times 10^{17} \times 24 \times 365 \times 6 \times 9600}{6.023 \times 10^{23}} \\
 &= 204 \text{ Ci/yr} = 7.55 \times 10^{12} \text{ dps/yr}
 \end{aligned}$$

D.2.5. Tritium Concentration in Blowdown Water Leaving Plant

$$\begin{aligned}
 \text{Tritium concentration} &= \frac{204 \times 10^6}{19.8 \times 10^6 \times 60 \times 24 \times 365} \\
 &= 1.96 \times 10^{-5} \text{ } \mu\text{Ci/cm}^3 \text{ H}_2\text{O} \\
 &= 0.725 \text{ dps/cm}^3 \text{ H}_2\text{O}
 \end{aligned}$$

D.2.6. Tritium Removed by the Purification System

$$\begin{aligned}
 \text{Tritium removed} &= \frac{1}{2} \frac{P_{\text{HT}}}{P_{\text{He}}} \cdot \text{He} \\
 &= \frac{1}{2} \frac{5.16 \times 10^{-4}}{5.065 \times 10^6} \cdot \frac{6.4515 \times 10^{28}}{6.023 \times 10^{23}} \times 6 \times 9600 \\
 &\quad \times 24 \times 365 \\
 &= 2759 \text{ Ci/yr} = 1.0208 \times 10^{14} \text{ dps/yr}
 \end{aligned}$$

TABLE D-1
DATA FOR 1000-, 2000-, 3000-, AND 4000-MW(t) HTGRs

	1000 MW(t) ^(a)	2000 MW(t) ^(b)	3000 MW(t) ^(c)	4000 MW(t) ^(d)
Helium inventory, g	3.642×10^6	6.795×10^6	9.513×10^6	11.778×10^6
Helium pressure, N/m ²	5.065×10^6	5.065×10^6	5.065×10^6	5.065×10^6
Purification flow rate, molecules He/hr	6.4515×10^{28}	1.38×10^{29}	1.38×10^{29}	1.75×10^{29}
Hydrogen pressure in helium coolant, N/m ²	133	133	133	133
Average H ₂ permeability through steam generator tubes, cm ³ H ₂ /hr	8,118	22,232	33,347	44,463
Total water discharge from plant, cm ³ H ₂ O/min	19.8×10^6	49.33×10^6	66.38×10^6	98.9×10^6
Steam generator characteristics	See Table D-2	See Table D-3	See Table D-3	See Table D-4
Hydrogen permeation through steam generator (calculations)	See Table D-5	See Table D-6	See Table D-6	See Table D-7
Temperature profile of steam generator	See Fig. D-1	See Fig. D-2	See Fig. D-2	See Fig. D-3

(a) Data for Fort St. Vrain.

(b) Data for Delmarva.

(c) Data for St. Rosalie.

(d) Data from 4000-MW(t) project.

Fig. D-1. Mean temperature versus relative surface area distribution for Fort St. Vrain steam generator tubing

Fig. D-2. Mark II steam generator tube metal temperature distribution

Fig. D-3. Mark III steam generator tube metal temperature distribution

TABLE D-2
FORT ST. VRAIN STEAM GENERATOR MAIN STEAM AND REHEATER TUBES^(a)

Position	OD (in.)	Wall Thickness (in.)	Coil Tube Length (ft)	No. of Tubes	Heat Transfer Surface Area ^(b) (ft ²)	Fraction	Material	"Effective" Surface Area (ft ²)
Economizer	1.0	0.138	76.8	54	1085.8	0.34	T-2	929
Evaporator I	1.0	0.138	25.5	54	360.58	0.11	T-22	308
Evaporator II	1.0	0.225	23.4	54	330.47	0.11	T-22	249
Superheater I	1.0	0.225	24.3	54	343.44	0.095	T-22	258
Superheater II	1.0	0.205	49.8	54	704.12	0.22	Incoloy 800	547
Reheater	1.125	0.140	15.7	84	<u>389.13</u>	0.13	Incoloy 800	<u>338</u>
					3213.54 ^(c)			2629

(a) From Ref. 60.

(b) Heat transfer surface area is not the same as installed surface area. Lead-in and lead-out tubes have not been included since some are shielded from the coolant. For comparison the total installed surface area of one module is 3791 ft².

(c) Twelve steam generators = 38,562 ft².

TABLE D-3
MARK II STEAM GENERATOR MAIN STEAM AND REHEATER TUBES

Position	OD (in.)	Wall Thickness (in.)	Length (ft)	No. of Tubes	Surface Area (ft ²)	Fraction	Material	"Effective" Surface Area (ft ²)
Feed water leads	0.625	0.12	46.5	328	2,496	0.08	T-22	1,974
Economizer	1.000	0.117	119.5	328	5,131	0.18	T-22	4,504
		0.132-0.158	135.5		5,818	0.20	T-22	4,926
Evaporator	1.000	0.145						
Superheater I	1.000	0.223	42.5	328	3,650	0.11	T-22	2,756
Superheater II	1.000	0.191	16.5	328	1,417	0.04	Incoloy 800	1,125
Superheater III	1.125	0.215	66.5	328	6,424	0.20	Incoloy 800	5,098
Reheater	1.25	0.150	50.0	331	<u>5,416</u>	0.19	Incoloy 800	<u>4,736</u>
					30,352			25,119 ^(a)

(a) Total effective surface area = 100,476 ft² for the 2000-MW(t) HTGR (4 generators), 150,714 ft² for the 3000-MW(t) HTGR (6 generators), and 200,952 ft² for the 4000-MW(t) HTGR (8 generators).

TABLE D-4
MARK III STEAM GENERATOR MAIN STEAM AND REHEATER TUBES

Position	OD (in.)	Wall Thickness (in.)	Length (ft)	No. of Tubes	Surface Area (ft ²)	Fraction	Material	"Effective" Surface Area (ft ²)
Feed water leads	0.625	0.125	50	609	5,182	0.055	T-22	3,903
Economizer	1.00	0.110	126	609	20,089	0.250	T-22	17,794
Evaporator I	1.00	0.124	95	609	15,146	0.186	T-22	13,175
Evaporator II	1.00	0.144	44	609	7,015	0.084	T-22	5,948
Superheater I	1.125	0.239	41	609	7,354	0.080	T-22	5,649
Superheater II	1.125	0.198	45	609	8,071	0.092	Incoloy 800	6,549
Superheater lead out	1.125	0.198	30	609	5,381	0.062	Incoloy 800	4,366
Reheat 1	1.750	0.163	23	425	4,478	0.057	Incoloy 800	4,045
Reheat 2	1.750	0.180	23	425	4,478	0.056	Incoloy 800	4,000
Reheat 3	1.500	0.167	30	425	6,190	0.078		5,549
(+ shroud)	(1.855)	(0.2295)					Incoloy 800	
					84,358			70,978 ^(a)

(a) Four steam generators = $283,912 \text{ ft}^2 = 2.6377 \times 10^8 \text{ cm}^2$.

TABLE D-5
HYDROGEN PERMEATION THROUGH A FORT ST. VRAIN STEAM GENERATOR^(a)

Position	Material	Temp (°K)	Thickness (mm)	Effective Surface Area (cm ²)	Permeation Coefficient (at 133 N/m ² H ₂)	Fraction	H ₂ Permeation (cm ³ /hr)
Economizer	T-2	589	3.5	8.63 x 10 ⁵	5.5 x 10 ⁻⁴	0.085	32.6
		616			8.5 x 10 ⁻⁴	0.105	62.3
		644			1.3 x 10 ⁻³	0.150	136.1
Evaporator I	T-22	669	3.5	2.86 x 10 ⁵	1.8 x 10 ⁻³	0.110	138.2
Evaporator II	T-22	686	5.71	2.31 x 10 ⁵	2.15 x 10 ⁻³	0.105	96.59
Superheater I	T-22	719	5.71	2.4 x 10 ⁵	3.4 x 10 ⁻³	0.095	138.20
Superheater II	Incoloy 800	839	5.21	5.08 x 10 ⁵	2.8 x 10 ⁻⁴	0.085	11.20
		811			1.85 x 10 ⁻⁴	0.080	6.9
		783			1.1 x 10 ⁻⁴	0.055	2.8
Reheater	Incoloy 800	852	3.56	<u>3.14 x 10⁵</u>	3.6 x 10 ⁻⁴	0.045	11.1
		880			5.4 x 10 ⁻⁴	0.035	13.0
		908			8.0 x 10 ⁻⁴	0.050	<u>27.4</u>
						24.43 x 10 ⁵	

(a) Temperature distribution obtained from Ref. 60.

(b) Twelve steam generators = 8118 cm³/hr.

TABLE D-6
HYDROGEN PERMEATION THROUGH MARK II STEAM GENERATORS

Position	Material	Temp (a)		Thickness (mm)	Effective Surface Area (cm ²)	Permeation Coeff at 133 N/m ² H ₂	Fraction	H ₂ Permeation (cm ³ /hr)	Total (cm ³ /hr)
		(°F)	(°K)						
Feed water leads	T-22	400	477	3.048	1.8339 x 10 ⁶	9.5 x 10 ⁻⁵	0.04	29.09	63.39
		450	505	3.048	1.8339 x 10 ⁶	1.12 x 10 ⁻⁴	0.04	34.30	
Economizer	T-22	475	519	2.972	4.1844 x 10 ⁶	1.5 x 10 ⁻⁴	0.035	41.22	3125.19
		525	547	2.972		2.65 x 10 ⁻⁴	0.025	52.02	
		575	575	2.972		4.4 x 10 ⁻⁴	0.035	120.92	
		625	602	2.972		6.8 x 10 ⁻⁴	0.040	213.58	
		675	630	2.972		1.03 x 10 ⁻³	0.065	525.70	
Evaporator	T-22	725	658	3.683		1.55 x 10 ⁻³	0.095	933.01	
		775	686	3.683	4.5764 x 10 ⁶	2.30 x 10 ⁻³	0.085	1238.74	
Superheater I	T-22	825	714	5.664	2.5604 x 10 ⁶	3.0 x 10 ⁻³	0.08	988.83	
		875	741	5.664		4.0 x 10 ⁻³	0.045	741.62	
Superheater II	Incoloy 800	925	769	4.851	1.0452 x 10 ⁶	8.4 x 10 ⁻⁵	0.020	8.08	
		975	797	4.851		1.9 x 10 ⁻⁴	0.005	4.57	
		1025	825	5.461	4.7362 x 10 ⁶	2.6 x 10 ⁻⁴	0.13	144.44	
Superheater III	Incoloy 800	1065	847	5.461	4.7362 x 10 ⁶	3.4 x 10 ⁻⁴	0.07	101.70	
Reheater	Incoloy 800	975	797	3.810	4.3999 x 10 ⁶	1.9 x 10 ⁻⁴	0.055	64.01	2369.31
		1025	825	3.810		2.6 x 10 ⁻⁴	0.040	63.70	
		1075	852	3.810		3.6 x 10 ⁻⁴	0.045	99.23	
		1125	880	3.810		5.0 x 10 ⁻⁴	0.050	153.13	
					23.3364 x 10 ⁶		1.000		5557.89

(a) Temperatures are average over life of generator.

TABLE D-7
HYDROGEN PERMEATION THROUGH MARK III STEAM GENERATORS

Position	Material	Temp (°K)	Thickness (mm)	Effective Surface Area (cm ²)	Permeation Coefficient at 133 N/m ² H ₂	Fraction	H ₂ Permeation (cm ³ /hr)	Total (cm ³ /hr)
Feed water leads	T-22	450	3.175	3.626 x 10 ⁶	8 x 10 ⁻⁵	0.02	33	110
		469			9 x 10 ⁻⁵	0.02	37	
		489			9.5 x 10 ⁻⁵	0.02	40	
Economizer	T-22	516	2.794	16.531 x 10 ⁶	1.4 x 10 ⁻⁴	0.02	66	
		544			2.5 x 10 ⁻⁴	0.02	118	
		572			4.1 x 10 ⁻⁴	0.04	387	
		600			6.5 x 10 ⁻⁴	0.06	920	
		627			1.0 x 10 ⁻³	0.11	2,596	
Evaporator I	T-22	644	3.15	12.217 x 10 ⁶	1.3 x 10 ⁻³	0.185	5,034	11,724
Evaporator II	T-22	666	3.66	5.526 x 10 ⁶	1.7 x 10 ⁻³	0.085	2,603	
Superheater I	T-22	691	6.07	5.248 x 10 ⁶	2.3 x 10 ⁻³	0.025	625	
		719			3.2 x 10 ⁻³	0.055	1,912	
Superheater II	Incoloy 800	755	5.03	6.084 x 10 ⁶	6.4 x 10 ⁻⁵	0.035	29	
		783			1.1 x 10 ⁻⁴	0.030	42	
		811			1.85 x 10 ⁻⁴	0.030	73	
Superheater III	Incoloy 800	839	5.03	4.056 x 10 ⁶	2.8 x 10 ⁻⁴	0.065	290	
Reheat 1	Incoloy 800	780	4.14	3.758 x 10 ⁶	1.05 x 10 ⁻⁴	0.03	45	
		808			1.65 x 10 ⁻⁴	0.025	60	
		836			2.6 x 10 ⁻⁴	0.025	94	
		844			3.4 x 10 ⁻⁴	0.025	123	
Reheat 2		900			7.0 x 10 ⁻⁴	0.035	277	
Reheat 3 (+ shroud)	Incoloy 800	936	5.829	5.155 x 10 ⁶	1.1 x 10 ⁻³	0.075	933	5,326
							17,160	

APPENDIX E

TRITIUM RELEASES FROM LWRs

Since LWRs have been in commercial operation for a number of years, it is pertinent to briefly consider LWR experience with tritium. Where it is possible to identify mechanisms for tritium formation and migration that are similar to those for the HTGR, a better appreciation of the likely behavior of tritium in HTGRs can be obtained.

E.1. TRITIUM RELEASE FROM BWRs

The BWR core is a series of zircoloy-clad UO_2 fuel elements; reactivity control is maintained by a series of stainless steel clad boron carbide rods. The core is located in a reactor vessel situated in an air-ventilated chamber (dry well). The primary coolant (water) is converted to a steam/water mixture in the core; water is removed in steam separators and driers (less than 3% moisture) and the steam is then used to directly drive a turbine. After passage through the turbine, the steam is condensed and the condensate passes through filters, demineralizers, and heaters and then returns to the reactor. It has been stated (Ref. 61) that future BWRs will use a steam source that is independent of the primary coolant to eliminate radioactive release via the turbine steam seal. Tritium is produced (Ref. 62) in the fuel by fission, in the coolant from the neutron activation of naturally occurring deuterium, and in the control rods and structural materials from Li-6 and B-10 impurities. Any tritium released due to permeation of control rod or fuel element cladding will reside in the primary coolant and will be released via leakage or the condenser air ejector.

Two types of water are identified in a BWR based upon radioactivity and dissolved solids content:

1. "Clean" liquid waste (high radioactivity and low dissolved solids).
2. "Dirty" liquid waste (low radioactivity and high dissolved solids).

The "clean" liquid is filtered, demineralized, and recycled while the "dirty" waste is filtered and discharged.

The reactor building ventilation and the steam jet ejector are stated to be the main sources of tritium discharge to the stack. Possible paths of tritiated water in a hypothetical 1000-MW(e)/yr BWR based on a 1% fuel failure are shown in Table E-1. Table E-2 shows the reported tritium discharges from several BWR plants.

E.2. TRITIUM RELEASES FROM A PWR

The PWR core is zircaloy-clad UO_2 pellets; reactivity control is maintained by regulating the boron concentration (as H_3BO_3) dissolved in the primary coolant. Reactivity control is maintained either by dilution with demineralized water or by addition of boric acid. Future PWRs will regulate boron levels by temperature control of an ion-exchange resin to promote absorption or release of boron to the coolant. The secondary coolant is conventional except to avoid a buildup of dissolved salts in the steam generator, a regular discharge (blowdown) must be made.

Tritium will be generated by ternary fission in the fuel and from neutron activation of the boron solute in the primary coolant (Ref. 65). Additional sources are activation of Li-6 and H-2 in the coolant and from B-10 in fixed stainless-steel-clad burnable poison boron rods. Future PWRs are expected to use Ag-In-Cd alloys as a burnable poison (Ref. 64) so this source of tritium will be eliminated. The Westinghouse PWR design uses lithium for pH adjustment, which will activate under irradiation to produce tritium.

TABLE E-1
ESTIMATED RATE OF TRITIUM GENERATION AND RATE OF APPEARANCE IN
WASTE STREAMS OF A BWR(a)

Source	Estimated Rate [Ci/1000 MW(e)-yr]	
	Generation	Appearance in Waste Streams
Fission	2×10^4 (b)	2×10^2 (c)
Deuterium activation, $H-2(n,\gamma)H-3$	14	14
Boron activation ^(d) (control rods)	10^4	0

(a) From Ref. 63.

(b) Based on a thermal fission yield of 1.3×10^{-4} tritons/fission, 2.7×10^{21} fissions/MW(t)-day (i.e., 200 MeV/fission), and a thermal-to-electrical conversion efficiency of 33%.

(c) Assuming 1% defective cladding, about 200 Ci will appear in the primary coolant and the same amount as an upper limit may appear in spent fuel coolant.

(d) $B-10(n,2\alpha)H-3$ and $B-10(n,\alpha)Li-7$; $Li-7(n,n\alpha)H-3$.

TABLE E-2
AMOUNTS OF TRITIUM IN LIQUID DISCHARGES AT BWRs

Reactor	Cladding ^(a)	Ci/1000 MW(e)-yr			
		1969	1970	1971	1972
Dresden-1	Zr	61	31	122	325
Big Rock Point	Zr	590	1188	236	239
Humboldt Bay	Zr	114	141	190	302
LaCrosse	SS	--	1300	3900	4100
Nine Mile Point	Zr	--	46	36	73
Oyster Creek	Zr	128	55	48	120
Millstone 1	Zr	--	--	30	55
Dresden 2,3	Zr	--	--	123	90
Monticello	Zr	--	--	4.3	1.8×10^{-4}
Pilgrim 1	Zr	--	--	--	44 ^(b)
Quad-Cities 1,2	Zr	--	--	--	10 ^(b)
Vermont Yankee	Zr	--	--	--	0 ^(b)

(a) From Ref. 64.

(b) Plants operated less than 1 year.

Liquid wastes are separated into "clean" and "dirty" streams and each stream is processed through separate evaporators. An advanced PWR liquid radioactive waste system has been proposed where a separation is made between tritiated and nontritiated waste streams. Table E-3 shows the reported tritium discharge levels from several PWR plants. Figure E-1 gives the distribution of tritium measured at the Yankee Rowe PWR in 1971. Table E-4 gives estimated tritium generation rates from a 1000-MW(e) PWR.

Containment of tritium in the primary coolant for the life of the plant has been proposed, which implies that all leakages must be eliminated or collected and recycled. Since permeation of tritium through the steam generator tubes will occur, this would appear to be a rather ineffectual operation. PWRs operate with much thinner superheater tubes (5 mm) compared to the HTGR, and the surface area of the tubes is larger for PWRs than for HTGRs (for the same electrical output of the two plants) because the thermal efficiency of PWRs is lower. Therefore, tritium permeation of steam superheater tubes is more important in PWRs than in HTGRs.

Indefinite storage of secondary coolant leakage appears to be impracticable. For example, a leak of 10 gpm (c.f. HTGR specifications) would be 210 million gallons after 40 years.

Tritium releases in liquid effluents from PWRs are larger than from BWRs for the following reasons:

1. Production of tritium in PWRs is larger due to the use of H_3BO_3 for reactivity control and stainless steel cladding on fuel elements (only on the earlier reactors).
2. BWRs appear to discharge considerable amounts of tritium to the atmosphere.
3. Both the primary and the secondary coolants are contaminated in PWRs (BWRs have only a primary coolant), which increases the problem of containing the tritiated liquids.

TABLE E-3
TRITIUM FOUND IN PWR LIQUID DISCHARGES ^(a)

Plant	Fuel Cladding ^(b)	Tritium Released in Liquids [Ci/1000 MW(e)-yr]			
		1969(c)	1970(c)	1971(d)	1972(d)
Shippingport	Zr	517	38	NA	NA
Yankee-Rowe	SS-ZR ^(e)	8,900	3,100	10,000	10,200
Indian Point-1	SS ^(f)	5,300	--	4,800	4,050
San Onofre-1	SS ^(f)	11,000	13,000	11,800	10,400
Connecticut Yankee	SS ^(f)	11,800	16,600	11,800	11,400
Robert Ginna	Zr	74	398	477	400
Point Beach 1 & 2	Zr	--	--	690	1,500
Maine Yankee	Zr	--	--	--	174 ^(g)
Palisades	Zr	--	--	--	960
Robinson	Zr	--	--	420	685
Surry-1	Zr	--	--	--	100 ^(g)

(a) From Ref. 63.

(b) From Ref. 64.

(c) Calculated from data tabulated by the Environmental Protection Agency.

(d) Calculated from power production and release data.

(e) SS through 1970, Zr beyond.

(f) Tritium diffuses through stainless steel (see, for example, Ref. 66).

(g) Plants operated less than 1 yr.

Fig. E-1. Distribution of tritium in Yankee-Rowe PWR systems

TABLE E-4
ESTIMATED RATE OF TRITIUM GENERATION AND RATE OF APPEARANCE IN
WASTE STREAMS OF A PWR^(a)

Source	Estimated Rate [Ci tritium/1000 MW(e)-yr]	
	Generation	Appearance in Waste Streams
Fission	2×10^4 ^(b)	2×10^2 ^(c)
Burnable poison rods	1.2×10^3	1.2×10^3
Control rods	0	0
Soluble poison boron	5 to 10×10^2	5 to 10×10^2
Li-7 activation	14	14
Li-6 activation	8	8
Deuterium activation	1	1

^(a) From Ref. 63.

^(b) Based on a thermal fission yield of 1.3×10^{-4} tritons/fission, 2.7×10^{21} fissions/MW(t)-day (i.e., 200 MwV/fission), and a thermal-to-electrical conversion efficiency of 33%.

^(c) Assumes 1% cladding failure.

It is expected that HTGRs will release less tritium to the environment than either type of LWR. If a comparison is made between Tables E-2 and E-3 it is seen that the reported tritium discharge levels differ widely from one reactor site to another. Clearly the amount of tritium emitted in gaseous or liquid radioactive waste discharge depends upon the mode in which the reactor is operated. In order to minimize tritium discharges, all reactors should collect and recycle secondary coolant losses that contain very low concentrations of tritium.

Table E-5 reviews all operating and planned LWRs up to October 1974 and categorizes them in terms of the type of cooling water system employed. Most of the planned plants will use cooling towers instead of once-through cooling. The use of cooling towers would result in an extremely high concentration of tritium in future LWR effluents since only a small quantity of cooling water, which is used to dilute the tritiated water discharges, leaves the plant.

TABLE E-5
TYPE OF INSTALLED OR PROPOSED COOLING WATER SYSTEMS FOR U.S. COMMERCIAL NUCLEAR REACTOR PLANTS^(a)

Type of Cooling System	Completion Date Before 1975		Completion Date After 1974	
	PWR	BWR	PWR	BWR
Once-through (i.e., river, sea or ocean)	20	13	23	7
Reservoir	4	--	17	8
Canal	2	--	--	--
Spray canal	--	2	4	
Pond	--	--	1	
Cooling tower	--	1		
Mechanical tower (M)	--	1 ^(b)	57(21M) ^(c)	37(8M)

(a) Information obtained from Ref. 69.

(b) Monticello, Minneapolis, Minnesota (BWR, 548 MW, mechanical tower cooling).

(c) 57(21M) means 57 plants with tower cooling, 21 of which are mechanical.

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