OAK RIDGE NATIONAL LABORATORY LIBRARIES
3 4456 0550575 3

ORNL-TM-4744

Cy 160

Iodine Behavior in an HTGR

E. L. Compere
M. F. Osborne
H. J. de Nordwall

OAK RIDGE NATIONAL LABORATORY
CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.
UCN-7969
(3 3-67)

OAK RIDGE NATIONAL LABORATORY
OPERATED BY UNION CARBIDE CORPORATION • FOR THE U.S. ATOMIC ENERGY COMMISSION

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
Price: Printed Copy $5.45; Microfiche $2.25

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

ORNL-TM-4744
UC-77 — Gas-Cooled Reactor Technology

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

IODINE BEHAVIOR IN AN HTGR

E. L. Compere
M. F. Osborne
H. J. de Nordwall*

*Present address: Dragon Project, A.E.E. Winfrith, Dorchester, Dorset, England

FEBRUARY 1975

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

OAK RIDGE NATIONAL LABORATORY LIBRARIES
3 4456 0550575 3

CONTENTS

		Page
Abstract		1
1.	Introduction	2
2.	Regulatory and Derived Limits	3
3.	Formation of Fission Product Iodine and Its Release from Fuel	9
4.	Distribution of Iodine in the Primary Coolant System	14
5.	Surface Composition	20
6.	Adsorption Equilibria and Surface Capacity for Iodine	21
	6.1 Reversible Iodine Deposition and Exchange	26
	6.2 Removal of Iodine from the Primary Coolant as Metal Iodides	28
7.	Iodine Behavior Under Accident Conditions	31
8.	Discussion and Recommendations	38
9.	References	40
10.	List of Symbols	44
11.	Appendix: Derivation of Equation for Surface Requirement if Exchange Occurs Between Gas and Surface Phases	47

FIGURE LIST

Page

Fig. 1. HTGR system components controlling fission product transport to the environment 15

Fig. 2. Expected release of ^{131}I from an HTGR 19

Fig. 3. Temperature dependence of the oxidation of iron and chromium by ($H_2O + H_2 + CO + CO_2$) in equilibrium with carbon 22

Fig. 4. Adsorption of iodine on Fe_3O_4 vs concentration in gas 25

Fig. 5. Thermodesorption of iodine from iron powder into flowing helium, heated at 2°C/min 34

IODINE BEHAVIOR IN AN HTGR

E. L. Compere, M. F. Osborne, H. J. de Nordwall

ABSTRACT

The emission of iodine from nuclear power reactors as a result of normal operations or postulated accidents is regulated by requiring exclusion area boundaries such that the dose to any individual outside the area will be less than stipulated values. Application of the "as low as practicable" limit, proposed for light-water-cooled nuclear power reactor effluents, to the activity released from a typical reactor installation (here an HTGR), indicates that the release of ^{131}I should be as much below 13 mCi/year as is practicable using today's technology. Estimated values of primary coolant leak rate, and of the decontamination factor during passage through PCRV cracks and secondary containment, lead to a derived limit on the amount of iodine in the primary coolant gas. A consideration of the rates of removal from the primary coolant by purification and by deposition (plateout) on system surfaces, and of entry rates from failed coated particle fuel, indicates that some surface deposition is desirable. The metal surfaces of the system are expected to be oxidized. Permanent adsorption on Fe_3O_4 may be insufficient to sustain the needed deposition for the lifetime of the reactor, according to the experimental data presented. However, if iodine atoms exchange rapidly between gas and surface phases, the surface requirement is smaller and appears to be met. Formation and decomposition of volatile metal iodides around the circuit are possible, but concentrations may be too low for direct deposition to occur. In the case of postulated accidents, the iodine that is retained as deposits on primary system surfaces represents a major source of released iodine. It does not appear likely that regulatory limits would be exceeded by any accidents, provided prompt isolation of the secondary containment occurs. Even in the lack of such isolation, complete depressurization in the absence of an appreciable temperature rise in the steam generators should not cause doses at the exclusion area boundary due to release of surface-sorbed iodine to exceed limits stated in the Code of Federal Regulations, Title 10, Part 100.

1. INTRODUCTION

Iodine is one of the key elements for consideration in fission product release in high-temperature gas-cooled reactors (HTGRs) both during normal operation and during the period following the accidents considered in the course of safety analysis.

Few iodine compounds are highly stable under HTGR core conditions. Iodine, which is naturally gaseous, will be released by diffusion from imperfect or cracked fuel particles, and from particle coatings contaminated with uranium or thorium; it will then pass into the circulating coolant gas apparently without significant holdup by the core graphite. Although iodine will be removed by purification operations and by interaction with cooler system surfaces, any leakage of coolant will cause iodine to be transferred out of the primary system.

Iodine isotopes have relatively high fission yields, and a number of isotopes are of radiological significance since they decay with energetic beta and gamma radiations with half-lives of the order of hours or days. Elemental iodine and many iodine compounds are comparatively volatile and soluble in water, and consequently susceptible to rapid transfer, biological uptake, and concentration by a variety of pathways. Localization in the thyroid causes this organ to be the critical point of human attack.

The fuel for HTGRs consists of UC_2 or UO_2 (and also fertile ThC_2 and ThO_2), in the form of very small kernels that are covered with a layer of porous carbon and then encased in impermeable spherical coatings of pyrolytic carbon and silicon carbide. Matrix rods containing these particles are held in cylindrical channels of graphite blocks which also contain coolant channels. A large array of such blocks, surrounded by graphite reflector blocks and supplied with control rods, constitutes the reactor core. The helium coolant flows under high pressure down through the core and into steam generators, where its temperature is reduced from about 732°C to about 315°C. Circulators then return this gas to the core, a small fraction passing continuously through a purification system which removes essentially all fission products and chemical impurities. The

core, steam generators, and circulators are contained within a steel-lined prestressed concrete reactor vessel (PCRV), which, in turn, is enclosed within a secondary containment structure. The exhaust from the secondary containment structure passes through only HEPA filters before being released. The secondary containment vent is closed rapidly under emergency conditions, and a charcoal "kidney" filter becomes operative 1 hr later. The secondary containment is capable of holding the entire gaseous contents of the primary system.

The reference system for this study is a 2000-MW(th) power station reactor such as that described in a recent PSAR (Docket 50-450).[1]

The purposes of this report are to consider the restraints imposed by USAEC regulations on emissions of iodine from HTGRs, to identify the distribution pathways leading to such emissions, to consider the system parameters and chemical characteristics that control the emission rate, and finally, to identify those factors which might require attention to avoid exceeding the stipulated limits. In addition, some experimental data are included to help in defining iodine transfer functions.

2. REGULATORY AND DERIVED LIMITS

The USAEC regulations with regard to maximum population dose lead to derived limits for emissions from all reactors, and thence to derived limits on iodine content in an HTGR primary system. The regulations requiring exposures to be "as low as practicable" require that exposures be kept substantially lower than these maximum values. The relationships of system parameters necessary to remain within such limits by adequate margins are, therefore, of interest. The regulations are set forth in the Code of Federal Regulations, Title 10, Part 100 (10 CFR 100), which establishes minimum distance for the exclusion area boundary after consideration of doses resulting from releases associated with hypothetical accidents, and in 10 CFR 50, Appendix I (proposed),[2-5] which requires emissions to be "as low as practicable" and limits the average annual dose that could be received outside the exclusion area from releases occurring as a result of continued operation within technical

specifications. The broader limitations of 10 CFR 20 also apply, particularly with respect to exposure of personnel within the exclusion area.

Because iodine must pass into the gaseous primary coolant of a HTGR prior to release, the major effects are almost certainly associated with gas effluents. The dose limitations of the regulations can be related to plant emission by consideration of atmospheric transfer after release to points beyond the exclusion area boundary, the ensuing possible transfer by dominant pathways to individuals, and the resulting dose accumulation by an individual possibly exposed in this way for the particular period involved.

According to 10 CFR 100, the exclusion area boundary must be located at such a distance that no individual so excluded would receive, as a result of any accident, a thyroid dose exceeding 300 rem from radioiodine. The relationship between emission and inhalation dose is:

$$\text{dose} = R_V \left(\frac{\chi}{Q}\right) Br\ E,$$

where

R_V = release, Ci,

χ/Q = atmospheric dispersion factor, (sec/m^3),

Br = effective intake rate of air, (m^3/sec),

E = thyroid dose resulting from the intake of 1 Ci of the nuclide.

For ^{131}I, a dose of 1.47×10^6 rem would result from the inhalation of 1 Ci by a standard adult.[6-8] The breathing rate under accident conditions is taken as 5×10^{-4} m^3/sec.[9]

It is useful to define dose as follows:

$$\text{dose} = D_L\ f/M,$$

where

D_L = dose limit,

f = fraction of total thyroid dose contributed by the nuclide and pathway under consideration,

M = safety margin (an accident safety margin at least above 10 will be considered necessary).

It follows that

$$R_v \left(\frac{\chi}{Q}\right) = \frac{f}{M} \times \frac{300}{5 \times 10^{-4} \times 1.47 \times 10^{6}} = 0.4 \frac{f}{M} .$$

The dispersion factor, $\frac{\chi}{Q}$, to be used is determined by the heights of release and intake, the distance, and the wind speed and stability class; χ is the concentration in air, in curies per cubic meter, at a given point; and Q is the release rate, in curies per second. The dispersion factor is somewhat site-specific. For example, for the reference power station, with ground level release and intake, at a range of 450 m, at an assumed wind velocity of 3 m/sec and stability category "D", a (χ/Q) value of 1.17×10^{-4} sec/m^3 was obtained for the worst sector. A general estimate of $\chi/Q = 1 \times 10^{-3}$ sec/m^3 was used for unspecified HTGRs by de Nordwall and Bell,[10] consistent with a conservatively higher stability category, "F", and lower wind velocity (1 m/sec) at a range of 500 m. We have used the latter value. The limiting plant release, R_v, is then (400) (f/M) Ci of ^{131}I.

The primary system source inventory can be related to a release in terms of loss fraction from the primary system and the secondary system, L_P and L_S, to the environment. Hence the limiting primary system inventory, $(N_P)_{max}$, in curies, is given by

$$(N_P)_{max} = 400(f/M)/(L_P \cdot L_S).$$

The secondary containment of the reference power station is designed to be closed promptly by an accident signal, so that gaseous escape under these conditions would amount to less than 0.25% per day. Thus the loss factor for the secondary containment is less than 2×10^{-4} in 2 hr. A loss of 0.0002 of any plausible primary system inventory should not approach the (400) $(\frac{f}{M})$ Ci limit. Accident doses could exceed the limit of 10 CFR 100 only if closure of the secondary system did not occur. Even then, as will be developed below, the fractional release (L_P) from the primary system to the secondary containment might of necessity be low enough that the limit could not be exceeded.

Operation within technical specifications will be regulated by 10 CFR 50, Appendix I (proposed),[2-5] which requires that the potential

average annual dose to the thyroid of any individual from radioiodine by all actual pathways should not exceed 15 mrem per year and should be "as low as practicable" below this limit. (This is specifically applicable only to light-water reactors at present.)

It has been established that the dominant isotope is ^{131}I, and that the dominant pathway is air-grass-actual cow-milk-child.[3,7] Thus a 2-year-old child drinking 1 liter milk per day would receive a dose of 3620 mrem per year when the average ^{131}I concentration in the air is 1 pCi/m^3. Appropriate factors for the various iodine isotopes are shown in Table 1. The limiting air concentration at the nearest effective point of deposition is then 15 (f/M) (3620) = 0.0042 $(\frac{f}{M})$ pCi $^{131}I/m^3$. A value of M = 1 may be used here because the air concentration should be repeatedly subject to determination. At the present stage of the "as low as practicable" rule, the air concentration is to be evaluated at the location of the "nearest actual cow" in the pathway rather than the "fencepost cow."[11]

The iodine concentration in air at a given distance is related to the average plant release rate by the atmospheric dispersion factor for the sector. The median site boundary distance for 35 plants[11] was found to be about 750 m (range, 120 to 1700 m), and the median χ/Q was about 8×10^{-6} (Ci/m^3)/(Ci/sec) (range, 10^{-4} to 7×10^{-7}). We shall use the conservative value of $\chi/Q = 1 \times 10^{-5}$ (Ci/m^3)/(Ci/sec), employed by de Nordwall and Bell[10] without considering whether or not it applies to the nearest actual cow or one hypothetically tied to a fence at the exclusion area boundary of a hypothetical reactor.

The limiting release rate is, then:

0.0042×10^{-12} (f/M)/(1×10^{-5}) = 4.2×10^{-10} (f/M) Ci/sec = 0.013 (f/M) Ci/year.

A decontamination factor of 100 is assumed for the combination of secondary containment and PCRV concrete for the reference power station.[1] Therefore, the leakage rate of the primary coolant system must be less than 4.2×10^{-8} (f/M) Ci/sec. If the rate of helium leakage is taken to be 0.01% per day (leakage rate constant, 1.2×10^{-9} sec^{-1}), the maximum permissible ^{131}I content of the primary coolant gas must be:

Table 1. Thyroid dose factors for selected pathways

	^{129}I, 1.6×10^7 y	^{131}I, 8.06 d	^{132}I, 2.28 h	^{133}I, 20.8 h	^{134}I, 52.3 m	^{135}I, 6.7 h
Thyroid dose rate for unit air concentration, (mrem/y)/(pCi/m^3)						
Inhalation[a, b, c, d]						
2-yr-old, breathing 5.6 m^3/d	16.5	12.5	0.835	5.51	0.424	2.00
Adult, breathing 20 m^3/d	29.6	10.6	0.414	2.70	0.209	0.985
Milk[a, c, d, e]						
2-yr-old, child, consuming 1 liter/d	4640	3620	4.58	262.	0.911	31.2
Adult, consuming 1 liter/d	2330	448	0.330	18.7	0.0655	2.28
Thyroid dose/plant emission by dominant pathway						
Normal operation - (mrem/y)/(Ci/y vented):						
Child, milk, $\bar{\chi}/Q = 1 \times 10^{-5}$	1470	1150	1.45	83.	0.29	10.
Accident, rem/(Ci vented):						
Adult, inhalation, $\chi/Q = 1 \times 10^{-3}$						
Breathing rate, 5×10^{-4} m^3/sec	1.4	0.49	0.018	0.12	0.009	0.044

[a]See ref. 7(a).

[b]See ref. 6 and associated note.

[c]See ref. 8.

[d]See ref. 7(b) (1-year-old child).

[e]See ref. 3.

$4.2 \times 10^{-8} (\frac{f}{M})/1.2 \times 10^{-9} = 36$ (f/M) Ci.

This corresponds to 1.33×10^{18} (f/M) atoms of ^{131}I. If mingled with 4227 kg of helium at 47.6 atm, the partial pressure of ^{131}I is 1.0×10^{-10} atm at unit (f/M).

Various other estimates of leakage rates and decontamination factors have been made by other investigators. For example, leakage rates have been taken as 100% per year,[12] with no subsequent decontamination; however, a coolant content of 5×10^{-5} Ci of ^{131}I was indicated, resulting from the implicit assumption of very rapid deposition on surfaces from the primary coolant gas.

Audebeau[13] and co-workers assumed a leakage rate of 0.2% per day and no further decontamination (factor = 1) in assessment of the effects of fuel quality control on iodine release from HTGRs. A "plateout coefficient" (understood to represent the ratio of the amount of iodine on surfaces to that in gas) of 10^3 was assumed, resulting in a coolant inventory of 0.68 Ci in their model.

The potential exposure of workers in the secondary containment is estimated as follows: The indicated maximum permissible leakage rate into the secondary containment system of 4.2×10^{-10} (f/M) Ci/sec is diluted by the containment purge at a rate of 8.5 m^3/sec. The ^{131}I concentration in the secondary containment is thus calculated to be 4.9×10^{-11} Ci/m^3, well below the occupational (40-hr week) limit of 9×10^{-9} Ci/m^3 (or μCi/mℓ) given by 10 CFR 20, Appendix B, Table I, Column 1. At an occupational breathing rate of 30 m^3 per 24-hr day, an exposure for 13 weeks (40-hr weeks) to such a secondary containment atmosphere is calculated to develop a thyroid dose of 0.047 rem per quarter, which is well below the whole-body occupational limit of 1.25 rem per quarter and is thus deemed tolerable.

The relationship between the plant emission of the various iodine isotopes and the thyroid dose by the dominant pathways is shown in Table 1. It is clear that, under both normal and accident conditions, ^{131}I is the greatest contributor to the dose, and that the air-grass-cow-milk-child is dominant under normal operation.

Methyl iodide can be ignored because (1) no significant amount of this compound should be formed under reactor conditions, (2) it is not taken up readily by grass and thus is not involved in the milk pathway, (3) no decontamination (except the PCRV factor) has been invoked in which its action would differ from molecular I_2, and (4) its effect by inhalation should be the same as I_2.

The dose effects of unit release of ^{129}I on a curie basis are about the same as (actually slightly greater than) for ^{131}I. However, the long half-life (1.6×10^7 years) of ^{129}I will cause any release to have very low curie values. Consequently, the effects of release of ^{129}I from a single reactor will be quite minor relative to the effects of other iodine isotopes, and will be neglected in this report.

3. FORMATION OF FISSION PRODUCT IODINE AND ITS RELEASE FROM FUEL

The fuel and fertile material for an HTGR consists of small ceramic kernels (UO_2, UC_2, ThO_2, or ThC_2) surrounded by a carbon buffer layer and contained within an impervious coating (pyrolytic carbon, possibly over a layer of SiC), small fractions of which may be or become cracked during the fuel lifetime. The coated particles are embedded in a carbon matrix to form fuel rods. These rods are contained in circular channels in the prismatic graphite fuel elements that make up the core.

For a particular region, characterized by composition and age (and thus relative power and temperature), the fission rate (determined by power density) and appropriate yield determine the generation or birth rate (B) of a given nuclide or its precursors. It then becomes desirable to obtain a value for the fractional release (F) and release rate (R), at steady state for short-lived isotopes and on a time-dependent basis for long-lived or stable isotopes.

Most fission product atoms come to rest within the ceramic kernel, and some are transferred by recoil into the carbon buffer surrounding the kernel. (A relatively small amount of fissionable material also may exist as a manufacturing impurity in the particle coating. This is usually

minor and will be ignored.) Because diffusion of iodine through pyrolytic carbon coatings is very slow ($D \sim 10^{-14}$ cm^2/sec at 1250°C), fission product iodine is entirely retained within intact particles, and its release will depend on the fraction of particles that are cracked and on the release characteristics of such particles. The fission product must first move by diffusion to the surface of the grain of material in which it came to rest. Subsequent evaporation can release a gaseous atom from the cracked particle.

The release rate and fractional release of fission product atoms by diffusion from solids in which they come to rest with uniform distribution was described by Booth,[14] using as a model a sphere having a surface/volume ratio equal to the total area of the surfaces to which the atoms diffuse, divided by the total volume of the solid phases in which they are formed. Loss by diffusion from the solid region under consideration is then characterized in terms of a diffusion rate coefficient,

$$D' = D/a^2,$$

where

D = diffusion coefficient of the isotope atom in the solid,

a = the radius of the equivalent sphere.

Various expressions derived from diffusion theory for such a model, giving the steady-state or transient release/birth ratio (R/B) and the fraction of atoms external to the sphere (F) for radioactive or stable species, during steady irradiation or after irradiation ceases, have been summarized by Belle.[15]

For a short-lived nuclide with decay constant λ at steady state,

$$R/B = \frac{3}{\sqrt{\lambda/D'}} \left(\text{Coth} \sqrt{\lambda/D'} - \frac{1}{\sqrt{\lambda/D'}}\right) \approx 3 \sqrt{D'/\lambda}$$

and

$$F = R/B \approx 3 \sqrt{D'/\lambda},$$

where

F = fraction of isotope atoms external to the sphere.

For a stable (or very long-lived) isotope (if $D't < 1/\pi^2$),

$$R/B \approx \frac{6}{\sqrt{\pi}} \sqrt{D't} - 3\,D't$$

and

$$F = \frac{4}{\sqrt{\pi}} \sqrt{D't} - \frac{3}{2}\,D't\ .$$

The same value of D' should apply for isotopes or similar atoms within a given particle at a given temperature, permitting adjustment for half-life. Thus, xenon relationships can be used for iodine, and possibly tellurium - insofar as it diffuses as a monoatomic nonreacting gas; xenon values may be estimated from those observed for krypton using known mass and size relationships for diffusion. Temperature dependence of release behavior is usually attributed to its effect on the diffusion coefficient; this should be true, but only as long as the release mechanism is constant.

There may be an appreciable variation between different sets of fuel particles. Thus Flowers,[16] using Zumwalt's data[17] for the diffusion coefficient of xenon in UC_2, and release data for bare particles in in-pile loop experiments Pluto V and VI, estimated a value of 2.8 μm for a. However, in unrelated experiments reported by Burnette, Bell, and Baldwin,[18] the release of 4.4-hr ^{85m}Kr at 1100°C from bare particles with an R/B of 0.005 leads to an estimated value of 15 μm for a. Consequently, estimates of release rates should be related to measurements on the particular fuels or fuel types where possible.

The behavior of ^{85m}Kr in a variety of fuel particles and rods was used by Burnette, Bell, and Baldwin[18] to study factors affecting fission product release. They concluded that the dominant factor in release of gaseous fission products at normal fuel temperatures was the diffusion of recoil atoms from the buffer matrix of cracked particles, and that kernel release, while appreciable at normal operating temperatures, would become dominant only at considerably higher temperatures. This conclusion should be also valid for iodine isotopes.

The following procedure was used by de Nordwall and Bell[10] to obtain the effective average R/B for a given nuclide, for example, ^{131}I.

Experimentally determined values are available[1] at 1100°C for as-manufactured fuel rods and rods containing imperfect or cracked fuel particles, showing R/B for krypton and xenon isotopes as a function of their half-lives or decay constants. The value for an iodine isotope of a given half-life is taken to be equal to that of xenon of the same half-life. An average cracked fraction for the core was estimated for both BISO and TRISO fuels in terms of fast fluence, taking into account the changing proportions of fission in these fuels with age. A core consisting of one-fourth each of 0.5-, 1.5-, 2.5-, and 3.5-year-old elements gave an average cracked fraction of 0.268% when weighted according to the fraction of power in the respective segments (0.30, 0.25, 0.23, 0.22).

The uncracked fraction of fuel was assigned the R/B for as-loaded fuel, reduced two and one-half times to allow for reduction from the 1100°C test temperature to the 880°C average core temperature. The cracked fraction was assigned the value of R/B observed at 1100°C without temperature adjustment, multiplied by the effective cracked fraction.

Applying these methods to the reference reactor, an effective core average cracked fraction of 0.268% was used, and the effective ^{131}I R/B was estimated to be 1.7×10^{-4}. We used this R/B value for ^{131}I and set the values for other short-lived iodine isotopes as proportional to the square root of their half-lives.

It was more difficult to estimate release values for the effectively stable iodine isotopes, since a steady state is not reached and different reload segments must be taken into account. The effect of burnup on release characteristics is not well understood. PSAR calculations conservatively assume complete release of these isotopes by all cracked particles. If we use the R/B value for ^{131}I to estimate a combined diffusion rate coefficient, D', for both matrix and kernel, we can use this value to estimate the R/B and fractional release for the respective core reload segments at selected times after the initial reactor startup.

The release rate and released atom inventory of the various iodine isotopes estimated in this way are shown in Table 2. These are also the entry values to the primary coolant. The stable isotopes, although lowest

Table 2. Estimated inventory of iodine nuclides released into the primary coolant system for a 2000-MW(th) reactor

80% service factor for "stable" isotopes; 0.27% cracked particles

Iodine nuclide	127	129	131	132	133	134	135
Half-life	stable	1.6×10^{7} y	193.5 h	2.28 h	20.8 h	0.88 h	6.7 h
Yield, %[a]	0.411	1.358	3.140	4.495	6.290	6.412	5.371
Atoms/Ci		2.7×10^{25}	3.7×10^{16}	4.4×10^{14}	4.0×10^{15}	1.7×10^{14}	1.3×10^{15}
Release rate (1 y), atoms/sec	2.0×10^{14}	6.8×10^{14}	3.2×10^{14}	5.0×10^{13}	2.2×10^{14}	4.6×10^{13}	9.5×10^{13}
(eqb), atoms/sec	3.7×10^{14}	1.2×10^{15}	3.2×10^{14}	5.0×10^{13}	2.2×10^{14}	4.6×10^{13}	9.5×10^{13}
Inventory of released atoms							
At 1 y, atoms	4.3×10^{21}	1.4×10^{22}	3.2×10^{20}	6×10^{17}	2.4×10^{19}	2×10^{17}	2.7×10^{18}
At 3 y, atoms	1.8×10^{22}	6.1×10^{22}	3.2×10^{20}	6×10^{17}	2.4×10^{19}	2×10^{17}	2.7×10^{18}
At 40 y, atoms	3×10^{23}	1.0×10^{24}	3.2×10^{20}	6×10^{17}	2.4×10^{19}	2×10^{17}	2.7×10^{18}

[a] 60% ^{233}U fissions, 40% ^{235}U fissions.

in yield, become the most abundant of the iodine atoms entering the primary coolant; therefore, their rate of release controls the chemical behavior of iodine in the primary system.

At the end of 1 year's operation, for example, the inventory of iodine atoms released into the primary system is calculated to be about 1.9×10^{22} atoms; in three years, it is about 8×10^{22} atoms, etc. At steady state, the calculations indicate that the system would contain about 8600 Ci of ^{131}I, along with somewhat smaller but appreciable quantities of the other radioactive iodine nuclides. The entry rate of iodine into the primary coolant system is estimated to be (at 1 year) 1.6×10^{15} atoms/sec; of these atoms, 20% are ^{131}I. The entry rate of stable isotopes increases as they build up in the fuel element; just prior to replacement, the total iodine entry rate is calculated to be 2.3×10^{15} atoms/sec, 14% of which are ^{131}I.

The calculation of release by kernel and buffer as separate entities in terms of such factors as time, temperature, fluence, and composition is preferable; however, it has not been attempted because the required information has not been assembled.

Uncertainties in R/B are particularly related to the fraction of cracked particles present in high-temperature zones as fuel life is extended. It has been suggested[18] that, at temperatures above 1200 to 1300°C, release by bulk diffusion from grains becomes much more rapid than that occurring at lower temperatures along grain boundaries or from the buffer matrix. At sufficiently high temperature and fast fluence or burnup, particle cracking also increases. Details of these effects are not considered in this report.

4. DISTRIBUTION OF IODINE IN THE PRIMARY COOLANT SYSTEM

The pathways of iodine in an HTGR from fuel to the environment have been described by de Nordwall and Bell.[10] The major avenues of transport are shown in Fig. 1. It is evident that the primary coolant gas is central in any consideration of release of iodine to the environment. The major

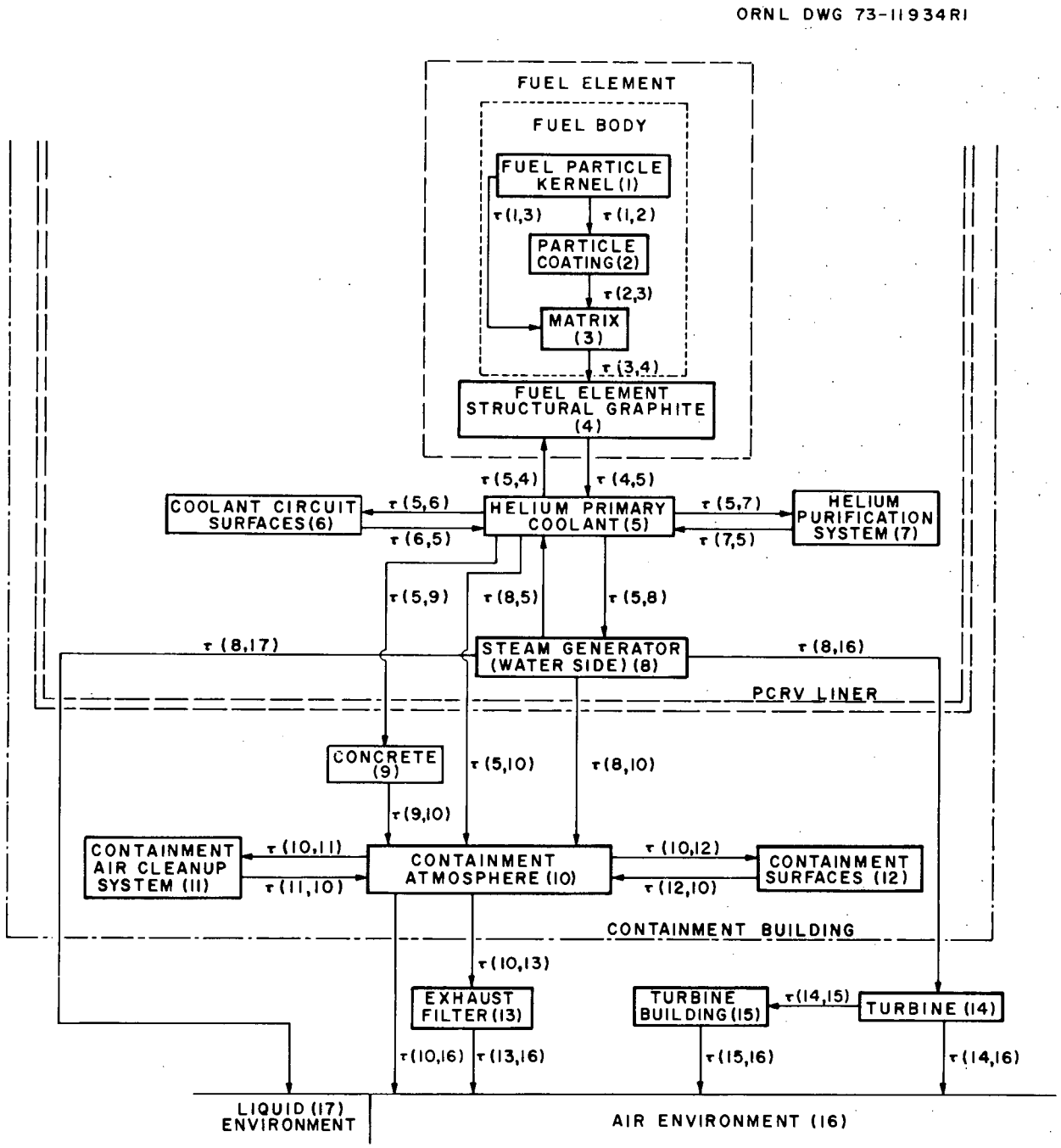

Fig. 1. HTGR system components controlling fission product transport to the environment.

transport path from the primary system is that resulting from slight helium leakage. Generally, this helium must pass through cracks or other apertures in the PCRV and thence into the purged secondary containment. It is then released to the environment by way of the purge gas from the secondary containment.

Iodine atoms entering the primary coolant system are rapidly circulated with the heated helium coolant gas through the steam generators and back through the core. Any of several forms of iodine removal by system surfaces may occur. Part of the circulating stream is passed through a helium purification system. Some parameters recently listed[1] for a typical power station reactor were given as follows:

Power: 2000 MW(th)
Plant load factor: 80%
Primary helium inventory for mixing: 4227 kg (9320 lb) at 47 atm
Coolant circulation rate: 910 kg/sec (2006 lb/sec)
PCRV leak rate: 0.01% per day
Helium purification plant flow rate: 0.261 kg/sec (2070 lb/hr)

These values provide the following rate constants for the removal of iodine from the primary coolant gas:

Decay (^{131}I)	$\lambda = 0.995 \times 10^{-6}\ sec^{-1}$,
Purification	$r_P = 6.17 \times 10^{-5}\ sec^{-1}$,
PCRV leak	$r_L = 1.16 \times 10^{-9}\ sec^{-1}$,
Surface deposition (plateout)	$r_S = \frac{910}{4227} \ln \frac{100}{100-Z} \approx 0.0022Z,\ sec^{-1}$.

In the above, Z is the percent removed per pass by plateout. The combined removal rate constant obtained from the above,

$$\Sigma(r,\lambda) = 6.27 \times 10^{-5} + r_S,$$

is evidently strongly affected by the surface deposition rate.

At steady state the amounts of a given iodine nuclide in the gas, N_G, or on the surface, N_S, are given by:

$$N_G = J/\Sigma(r,\lambda)$$

$$N_S = N_G \frac{r_S}{\lambda} = \frac{Jr_S}{\lambda\ \Sigma(r,\lambda)},$$

where

J = the entry rate of the nuclide into the primary coolant, taken as equal to the release rate from fuel (as discussed earlier).

The leak rate, L^*, from the primary system is, therefore,

$$L^* = N_G r_L = \frac{Jr_L}{\Sigma(r,\lambda)}.$$

Insofar as radioactive nuclides are concerned, the above expression is also true if rapid reversible partitioning of iodine nuclides between gas and surface phases occurs (such that $N_S = F_P N_G$, where F_P is the "plateout factor") and if we use $F_P\lambda$ in place of the term r_S.

However, the surface quantity of stable nuclides here also becomes fixed, instead of steadily increasing as it would for irreversible deposition. Consequently, a statement of plateout per pass, or plateout factor, for a single isotope may not discriminate between irreversible and reversible deposition. We shall later consider various factors involved in a reversible dynamic adsorption model.

Based on the relationships given above, an ^{131}I entry rate of 3.2×10^{14} atoms/sec (8.6×10^{-3} Ci/sec) to the primary system, with no surface deposition, would result in an ^{131}I content of 140 Ci for the primary system gas at steady state. This is higher than the derived limiting content of 36 Ci. Clearly, some surface deposition (more than 0.1% per pass) is desirable. As discussed later, deposition has been found to occur at ample rates (up to 40% per pass) in reactors where the surfaces had not become covered with iodine. Large amounts of iodine will enter the primary system and will be deposited on primary system surfaces during the lifetime of power reactors. It is, in consequence, necessary to evaluate the nature of surface deposition and the capacity of system surfaces for fission product iodine. The nature of the deposition could strongly affect the rate of removal under accident conditions.

Surface deposition or plateout may occur by (1) reaction with metal surfaces to produce a volatile iodide and subsequent permanent deposition

of the reaction product at some point in the system, or (2) adsorption on surfaces.

If the conditions for the first possibility--formation, vapor transport, and permanent deposition of a volatile iodide--are fulfilled, then it is certainly possible for the plateout to continue indefinitely. If, on the other hand, plateout involves the localization of iodine on the surface by adsorption (or reaction), the system iodine pressure will rise, as the system surfaces become loaded, until it is limited only by the purification plant removal. At this point, if the attachment of iodine to the surface is essentially permanent, the incoming radioactive iodine isotopes will not be adsorbed and their concentration in the coolant could become undesirably high. In this case, other options to control iodine release would have to be exercised.

If a fairly rapid exchange of iodine occurred between gasborne and adsorbed phases, a sufficient surface should provide ample holdup to permit adequate decay of radioactive iodine.

Limitation on the environmental release of iodine discussed earlier was shown to correspond to ^{131}I partial pressures in the coolant of $\sim 1 \times 10^{-10}$ atm (at $f/M \sim 1$), or a total iodine partial pressure of 5×10^{-10} atm based on entry composition. Normal operation is not expected to approach these limits by wide margins because of rapid surface deposition. Such a dependence on surface deposition, along with the possibility of limited surface capacity, makes this a key factor in iodine behavior. Phenomena related to gas and surface behavior of iodine species are, consequently, important.

Figure 2 shows the expected distribution of ^{131}I in an HTGR under normal conditions, assuming that (1) the surface deposition is conservatively set equivalent to 30% per pass, and (2) that no surface deposition occurs. In the "normal" case, the emission from the plant vent would be about 0.00005 Ci/year, corresponding to a maximum dose of 0.06 mrem/year to a child's thyroid. If no deposition occurred, the plant release could increase to 0.05 Ci/year, corresponding to a dose of 60 mrem/year to a child's thyroid. It is evident from these calculations that surface

ORNL DWG 74-7333RI

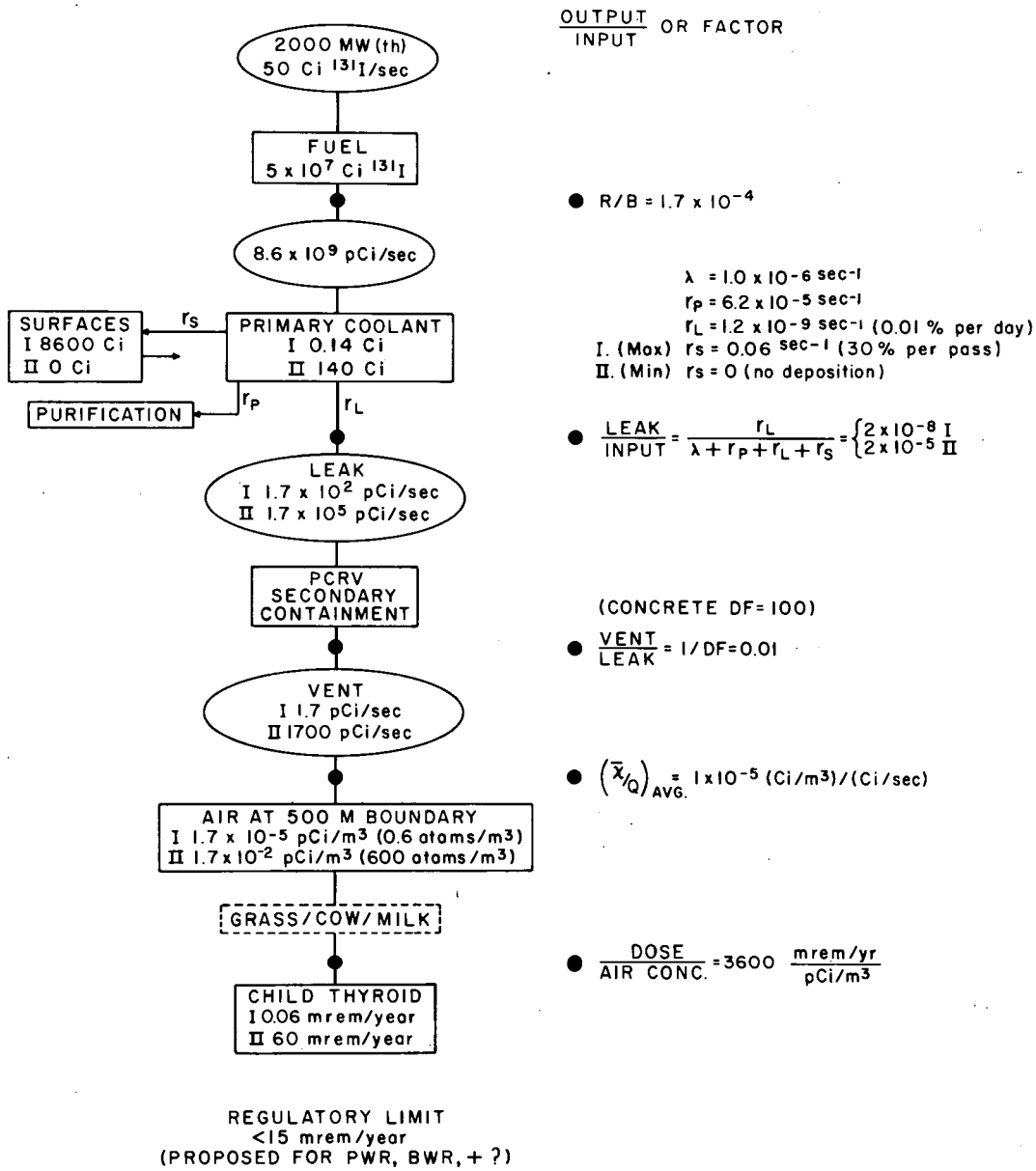

Fig. 2. Expected release of ^{131}I from an HTGR.

deposition could be important; however, if it were not adequate, other measures available to the designer (e.g., fuel quality improvement, suitable filtration of vent streams, etc.) provide useful alternatives.

5. SURFACE COMPOSITION

The major materials of the primary coolant circuit that could, in some manner, contribute to iodine plateout are heat exchanger surfaces, core and reflector graphite surfaces, and system walls.

Interaction between graphite and iodine is not considered in detail in this report. However, a rough calculation based on the equation for the adsorption of iodine on graphite presented by Castleman and Salzano,[19]

$$Q' = 3.2 \times 10^{-4}\ p^{1/2}\ T^{-1/4}\ \exp\ (20000/R'T),$$

where

Q' = quantity adsorbed, ppm,
T = absolute temperature,
R' = gas constant,
p = iodine partial pressure, torr

indicates that, at 400°C and a partial iodine pressure of 10^{-10} atm, 0.054 μg of iodine per gram of graphite might be adsorbed if all internal surfaces were involved. This is equivalent to 1.2×10^{22} atoms on 45,400 kg graphite. Adsorption is significantly less at higher temperatures. This would appear to be about an upper limit for the cooler reflector graphite and indicates that (1) adsorption on graphite, although not trivial, is not expected to be the dominant removal mechanism,[20] and (2) studies to verify the appreciable extrapolations of the above equations are of value. At a later date we will report data obtained recently that appear to be consistent with the above estimate.

Iodine in the HTGR primary coolant may react with bare metal surfaces to form metal iodides, but this reaction must compete with possible oxidation of the surface by impurities in the helium, largely the result of slight water ingress. In the set of exploratory thermochemical calculations described below, it was assumed that an impurity concentration corresponding to 10 (or 20) ppm of H_2O with a total coolant pressure of

50 atm existed in the circuit prior to equilibration with graphite at the temperatures considered.

Subject to this assumption, results of thermochemical calculations[21-23] which are presented graphically in Fig. 3 indicate that oxidation of iron to Fe_3O_4 can occur up to about 400°C, whereas Cr_2O_3 can form at all temperatures of interest. At temperatures up to about 500°C, iron can be oxidized in the presence of Cr_2O_3 to produce $FeCr_2O_4$. Increasing the hydrogen/oxygen ratio by a factor of 10 would reduce the temperature below which Fe_3O_4 is stable by about 50°C, but would apparently have little effect on Cr_2O_3 or $FeCr_2O_4$ formation. An increase in water content or a reduction in the hydrogen/oxygen ratio slightly increases the temperature below which Fe_3O_4 is stable. Radiation reactions or other sources of hydrogen, such as oil leaks (not evaluated) might cause the gas to become more reducing. In Fig. 3, the proportionate excess or deficiency of free and combined hydrogen relative to free and combined oxygen in the gas phase is expressed in terms of a ratio

$$R^* = (P_{H_2} + P_{H_2O})/(P_{H_2O} + P_{CO} + 2P_{CO_2}),$$

such that $R^* = 1$ if the only source of hydrogen or oxygen is water.

Based only on thermal equilibrium considerations, there are apparently few, if any, combinations of metal composition and temperature in the primary system which would not be susceptible to metal oxide formation, particularly if enough time were available to permit sufficient chromium to diffuse to the metal surface in alloys containing low proportions of chromium. It is recognized that manganese, which is present in the alloys to the extent of 1% or less, also forms relatively stable oxides.

6. ADSORPTION EQUILIBRIA AND SURFACE CAPACITY FOR IODINE

Some experimental data for the adsorption of iodine on iron have been reviewed elsewhere.[24] Iodine partial pressures as low as 1×10^{-9} atm at 400°C were used, with an observed iodine loading of iron surfaces of 3.8 μg/cm^2 in one case[25] and 0.5 μg/cm^2 in another.[26] Occupation of 4×10^{14} sites/cm^2, which would, as explained later, couple as many single iodine atoms to

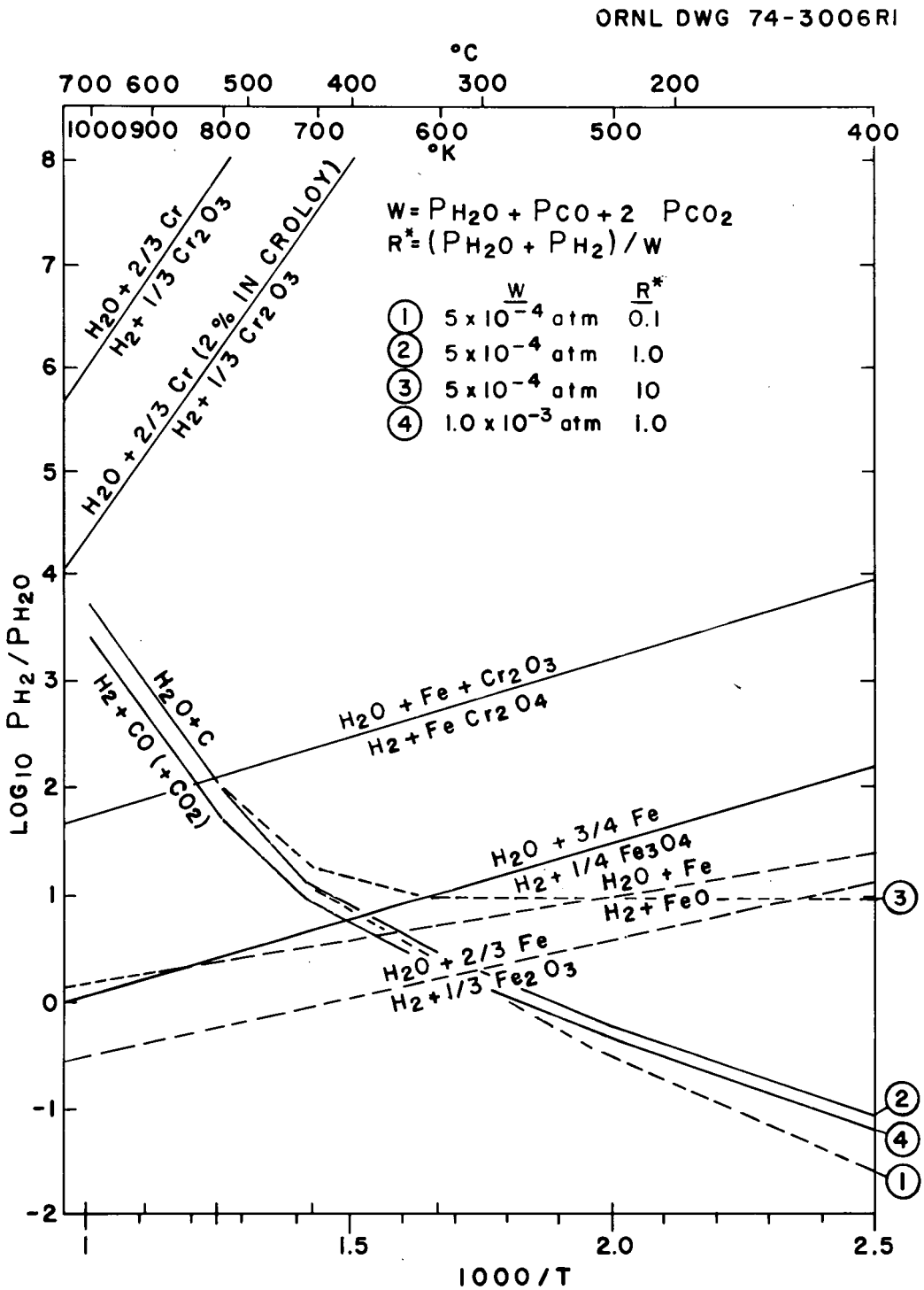

Fig. 3. Temperature dependence of the oxidation of iron and chromium by (H_2O + H_2 + CO + CO_2) in equilibrium with carbon.

specific iron atoms as possible, would result in an iodine loading of 0.08 $\mu g/cm^2$; on the other hand, close packing of iodine atoms (2.2-Å radius) would correspond to 0.12 $\mu g/cm^2$. Thermochemical calculations--reported in a later section--indicate that the vapor pressure of solid FeI_2 at 400°C is 2×10^{-6} atm. Thus the experiments cited above indicate that more than a monolayer exists on metallic iron at 10^{-9} atm, but that considerably less than full reaction to produce a solid FeI_2 phase has occurred. Data at the needed iodine pressure levels of 10^{-10} atm and below are not available.

Because sufficient moisture (equivalent to 10 ppm) is anticipated to cause the formation of oxide on iron at 400°C and below, oxide rather than metal surfaces may predominate, and adsorption on such surfaces is of particular interest. It was noted by Bull[27] that iodine vapor at 10^{-5} to 10^{-4} atm reacted uniformly at 400°C with the external surface of oxide on low-carbon steel, produced by oxidation in air at 900°F for 20 min. The reaction was interpreted as an interaction of the oxide at the outer surface with iodine to form FeI_2 and an iron-deficient oxide. Additional iron in the steel is then oxidized and diffuses into the oxide layer. In other work (reported internally), Bull and Neill found no reaction between iodine and Fe_3O_4.

A study of the adsorption of iodine on Fe_3O_4 at temperatures and iodine partial pressures applicable to the steam generator region of an HTGR is reported below.

The determination of the adsorption coefficient of iodine on Fe_3O_4 was conducted[21] using the bithermal equilibration method described elsewhere.[28] Determinations at a particular sample temperature generally used iodine source vapor pressures of 10^{-11}, 10^{-10}, 10^{-9}, 10^{-8}, and 10^{-7} atm. The first sample consisted of Fe_3O_4 prepared by Sweeton and Baes;[29] measurements were made at 200 and 300°C. A second sample of high-purity Fe_3O_4, obtained from the Rocky Mountain Research Company, was used for determinations at 250, 350, 400, and 450°C. The first sample had a surface area (BET) of 0.16 m^2/g and a crystallite size of 222 Å. The second sample had a surface area of 0.25 m^2/g and a crystallite size of 216 Å.

The vapor pressure of iodine at low temperatures was obtained by interpolation from values listed by Honig and Hook.[30] The partial pressure of iodine at the sample was calculated by taking into account the dissociation of I_2 into I atoms, which become dominant at the higher temperatures and lower pressures, and of course the thermal transpiration effect.[24, 25]

The temperature in an HTGR circuit (and correspondingly the dissociation of I_2) varies while the pressure of helium remains effectively constant. For this reason, the function $(P_I + 2P_{I_2})$, which will be called the iodine burden and denoted by P_{burden}, is a more useful abscissa against which to plot isotherms showing the amount of iodine adsorbed on unit surface than P_I or P_{I_2}. Such a plot is shown in Fig. 4.

The data in Fig. 4 appear to approach a limiting value of adsorption in the vicinity of 1.8×10^{14} to 2.0×10^{14} atoms/cm^2, suggesting that this may represent monolayer saturation.

A closely packed monolayer of iodine atoms (ionic radius, 2.2 Å) would result in about 6×10^{14} sites/cm^2. However, chemisorption implies specific bonds to particular substrate atoms; consequently, the capacity would appear to be related to the spacing of iron atoms, possibly divalent iron, in the Fe_3O_4 surfaces that are less closely spaced. A Fe_3O_4 unit cell (a_o = 8.394 Å) contains eight molecules arranged in an inverse spinel structure: $Fe^3(Fe^2Fe^3)O_4$.[31] The Fe^2 ions on this structure are indicated to be arranged in pairs with a spacing of approximately 3.0 Å between the two; thus they are positioned too closely to hold an iodine atom on each. The least distance between adjacent pairs is apparently about 4.9 Å; with this spacing there would be no more than about 2.8×10^{14} such sites per cm^2, and quite possibly less, depending on which planes make up the surface.

The chemisorption of iodine on all exposed atoms of elemental iron (bcc, a_o = 2.8664 Å) is not possible in any simple plane. The closest feasible regular spacing of iodine chemisorption sites appears to be on alternate iron atoms in the (110) plane, permitting about 4.1×10^{14} sites/cm^2.

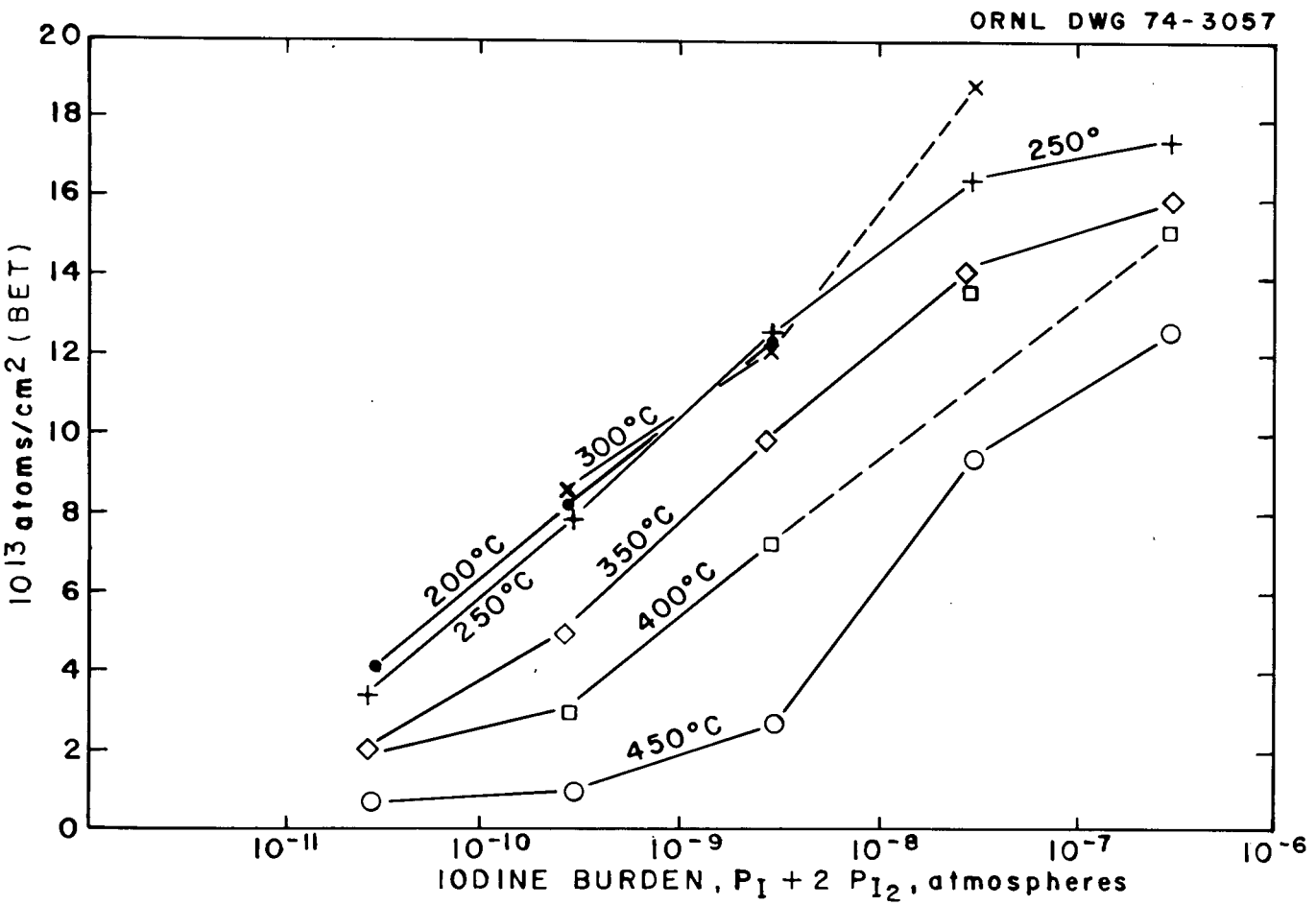

Fig. 4. Adsorption of iodine on Fe_3O_4 vs concentration in gas.

The data shown in Fig. 4 may be extended at a given temperature to lower pressures, using a Temkin expression of the form

$$\ln P = - C' + \ln [\theta/(1 - \theta)] + B'\theta,$$

where

P = iodine burden, atm,

θ = fractional coverage.

Assuming the presence of 2×10^{14} sites/cm^2, the constants B' and C' at the respective temperatures are:

Temperature (°C)	B'	C'
200-300	6.26	23.71
350	5.90	22.12
400	7.81	22.06
450	9.36	22.49

In Table 2, the inventory of iodine released into the primary coolant system was estimated to be 1.9×10^{22} atoms at the end of the first year. At a partial pressure of 5×10^{-10} atm (previously indicated to be an upper limit) and at temperatures of 200 to 300°C the capacity of Fe_3O_4 surfaces for iodine is about 8×10^{13} atoms/cm^2 (see Fig. 4). Thus these data imply that if permanent adsorption on Fe_3O_4 were the only deposition mechanism, the sites on about 2×10^8 cm^2 of microscopic surface would be needed within a year. The superficial area of steam generator surface below such temperatures is of this magnitude. (The roughness factor is unknown.)

Since the expected life of the reactor is 40 years, other means of removing ^{131}I and other shorter-lived iodine isotopes from the primary helium require consideration.

6.1 Reversible Iodine Deposition and Exchange

The existence of an adsorption equilibrium implies concurrent evaporation along with deposition, resulting in an exchange of isotopes between gas and surface phases. If the rates are adequate, the surface area needed

to provide enough holdup for sufficient decay of radioactive species to occur could be considerably less than that required if adsorbed atoms were more or less permanently fixed to adsorption sites. The partial pressure of stable iodine at steady state would be a function of the rates of entry and rates of removal by the purification plant. The ensuing partial pressure would establish the fractional surface coverage; this coverage and the available surface area would then determine the average residence time, while the residence time would determine the reduction by decay of the content of radioactive iodine in the system (and consequently the gas).

A simple model[21] for steady-state isothermal adsorption of a single radioactive species and a single stable species leads to the following expression for the area needed to maintain the concentration of iodine isotopes in the coolant at a given level. This expression is derived in the Appendix.

$$An = \left[\frac{C_1^\circ}{C_1} - 1\right] \left[1 + \frac{r_P}{\lambda_1}\right] \left[1 + \frac{\lambda_1}{e}\right] \left[\frac{V}{k_2} + \frac{J_2}{r_P}\right] ,$$

where

A = system microscopic area [BET], cm^2,

n = number of adsorption sites on unit microscopic area, sites/cm^2,

C_1° = radioactive isotope concentration in gas in absence of adsorption, atoms/cm^3,

C_1 = radioactive isotope concentration in gas, atoms/cm^3,

r_P = rate constant for removal from primary system to purification system, sec^{-1} [6.17×10^{-5}],

λ_1 = isotope decay constant, sec^{-1} [1×10^{-6}],

e = surface evaporation rate constant, sec^{-1} (assume $e \gg \lambda$),

V = gas system volume, cm^3 [9.7×10^8],

k_2 = Langmuir coefficient in concentration units [$\theta = k_2C(1 - \theta)$] for stable nuclides [$4.8 \times 10^{-11}$, based on Fig. 4],

J_2 = ingress rate of stable species, atoms/sec [9×10^{14}].

Values in brackets apply to the system discussed earlier, where also (as shown in the Appendix)

$$\frac{C_1^o}{C_1} = \frac{N_{G1}^o}{N_{G1}} = 140/36 \sim 3.9,$$

in which

N_{G1}^o, N_{G1} = amount of gasborne radioactive nuclide in the absence of adsorption, or with adsorption and exchange.

We then calculate

$An = 6.3 \times 10^{21}$ sites.

If the value of n is 2×10^{14} sites/cm^2 [Fig. 4], then

$A = 3 \times 10^7$ cm^2 [BET].

Since the superficial area in the steam generators, particularly the economizer and evaporator regions, will be somewhat greater than 10^8 cm^2, it appears that iodine removal by adsorption on Fe_3O_4 with relatively rapid exchange could be marginally sufficient to ensure an iodine pressure below 10^{-10} atm. Exchange rates have not been directly measured for iodine on Fe_3O_4; however, relatively rapid exchange was reported by the General Atomic Company[20] for iodine at 400°C on mild steel surfaces loaded with iodine at relatively high iodine pressures ($\sim 10^{-7}$ atm).

6.2 Removal of Iodine from the Primary Coolant as Metal Iodides

It is possible that metallic areas will be available (particularly if H_2/H_2O is high for any reason) and that, consequently, gasborne iodine could react with metals to form volatile iodides. Condensation of these iodides on the cooler parts of the circuit would provide an unlimited sink for iodine that would require consideration in the analysis of accidents involving fission product redistribution.

The thermodynamic data assembled by Hoinkis[24] have been used to calculate the equilibrium compositions at various temperatures for a constant iodine burden of 2×10^{-10} atm, assuming that elemental iron is always present. The results are presented in Table 3.

Table 3. Composition of equilibrium vapor at fixed iodine burden, in the presence of elemental iron

	Temperature (°K)		
	1000	673	500
Vapor pressure $FeI_2(s)$, atm	2.5×10^{-2}	2.1×10^{-6}	7.22×10^{-11}
I burden = $\Sigma(N_I)_i \cdot P_i$, atm (assigned)	2.0×10^{-10}	2.0×10^{-10}	2.0×10^{-10}
Fe burden = $\Sigma(N_{Fe})_i \cdot P_i$, atm	3.9×10^{-16}	1.49×10^{-12}	7.76×10^{-11}
P_I, atm	2.00×10^{-10}	1.97×10^{-10}	1.98×10^{-11}
P_{I_2}, atm	1.14×10^{-17}	8.95×10^{-14}	1.25×10^{-11}
P_{FeI_2}, atm	3.9×10^{-16}	1.49×10^{-12}	7.74×10^{-11}
$P_{Fe_2I_4}$, atm	4.7×10^{-29}	7.3×10^{-20}	3.15×10^{-14}
P_{FeI_3}, atm	1.3×10^{-23}	2.6×10^{-17}	1.34×10^{-13}

Steady circulation with equilibrium at all points around the circuit, and with metallic iron available at all points, will result in a Van Arkel type of process, in which iron will react to form gaseous iron iodides as the iodine-bearing gases are cooled, and iron will be precipitated[24,32] as the gases are heated. Also, as the temperature approaches 500°K, the partial pressure of FeI_2 will exceed the vapor pressure and deposition of this compound could occur.

We have indicated above that Fe_3O_4 should exist in the system at temperatures below 400°C (673°K). If elemental iron were available to the gas only above 400°C, the iron burden at this temperature would limit the partial pressure of FeI_2 at lower temperatures, and the temperature of the gas would have to decrease to about 456°K (183°C) before condensation of FeI_2 could occur. (In this and other discussions the burden, in atmospheres, of a given atom is defined as the sum of the partial pressures of each gasborne species containing it, multiplied by the number of the given type of atoms in the species. At constant system pressure, it is independent of temperature and reactions in the gas phase unless additions or removal from the gas phase occur.)

Two factors militate against deposition by condensation. First, we do not believe that metal surface temperatures will fall as low as 183°C, and possibly not as low as 227°C, except in the area behind the thermal barrier, which is effectively inaccessible. Second, the reaction rates with high-temperature surfaces would have to be faster than is thought likely, so that equilibrium concentrations might not develop around the circuit. Data supporting iron iodide transport at higher iodine pressures ($\sim 10^{-8}$ to 10^{-7} atm) have been presented by the General Atomic Company.[20]

In addition to iron, the metal alloys of HTGR primary coolant circuits contain nickel, chromium, and manganese, as well as small proportions of other elements. These are also capable of forming volatile iodides, principally the diiodides. Calculations related to the behavior of iron have been reported by Hoinkis,[24] and Milstead et al.;[25] calculations for chromium have been reported by Osborne;[28] and the stability and volatility of various metal iodides have been discussed by Rolsten.[32] We have calculated

equilibrium constants[21] on a common basis for the formation of FeI_2, NiI_2, CrI_2, and MnI_2, as gases and condensed phases at 500°K and 1000°K, using thermodynamic data presented by Brewer.[33,34] These values and their difference, which is the logarithm of the vapor pressure (in atmospheres) of the condensed metal diiodide, are shown in Table 4.

The values indicate unambiguously that in cases where manganese is available to form the iodide it will be the dominant condensed or vapor species (despite low concentration in the alloys); the associated log K value is much the highest. This is consistent with Rolsten's[32] statement that the high stability of manganese iodide will prevent the production of manganese by the iodide process.

Because HTGR coolant systems are likely to contain much more oxygen (as H_2O, CO, and CO_2) than iodine, it is likely that both manganese and chromium will (where available at the surface) be bound as oxides. The equilibrium behavior of such complex metal-iodine-gas systems has yet to be evaluated.

7. IODINE BEHAVIOR UNDER ACCIDENT CONDITIONS

The retention on system surfaces of some fraction of the radioactive iodine entering the primary coolant was shown in an earlier section to be necessary in order to keep the corresponding concentration in the gas low enough to ensure that plant releases during normal operation would not exceed values derived from regulatory limits. In the representative example presented in Fig. 2, about 8600 Ci ^{131}I could be present on surfaces, and no more than 36 Ci in the gas ($N_S/N_G = F_P > 240$). Values of $F_P > 20,000$ have been measured in operating HTGRs[35,36] with relatively clean circuits, indicating that this condition is adequately fulfilled. Surface iodine is thus a major accident source term. In assessing the release of iodine during an accident, one must therefore pay careful attention to the rate at which deposited iodine can become gasborne due to evaporation, chemical reaction, or the inherent mobility of the surface itself, as in the case of a dust film. To date, we have been concerned with desorption and desorption plus chemical reaction.

Table 4. Logarithms of equilibrium constants for the reaction $M(s) + 2I(g) = MI_2(s \text{ or } g)$

Compound	(1) log K (solid)		(2) log K (gas)		(3) log VP = (2)-(1) (atm)	
	500°K	1000°K	500°K	1000°K	500°K	1000°K
FeI_2	23.23	6.02[a]	12.72	5.15	-10.51	(-0.87)[a]
NiI_2	18.47	2.79	6.28	1.74	-12.19	-1.05
CrI_2	26.59	7.54	10.07	4.08	-16.52	-3.46
MnI_2	35.78	12.53[a]	24.04	10.50	-11.74	(-2.03)[a]
$2I = I_2$			21.11	5.76		

[a] Liquid.

The kinetics of the desorption of iodine from Fe_3O_4 into vacuum was studied as a function of temperature and iodine loading conditions by Hoinkis,[37] who used a temperature-ramp technique, in which the iodine remaining adsorbed was measured as the temperature was steadily increased. He concluded that the vacuum desorption process followed first-order kinetics, and that adsorbed iodine atoms were distributed between sites of different desorption energies (generally between 1.5 and 2.5 eV). An explicit rate equation, however, was not directly stated.

The paragraphs below describe four scouting experiments[21] made by using portions of a sample of iron powder on which iodine had been adsorbed at 400°C to a surface concentration of 7.4×10^{14} atoms I/cm^2 (BET). [The iron powder had a specific surface area of 0.14 m^2/g (BET).]

Isothermal desorption into flowing helium containing 3% H_2O was examined at 250°C by placing one-fourth of the iron sample (about 0.4 g) in a 1-in-diam heated tube and passing the helium-steam mixture (at 1 atm) over the sample in the tube at 1 std liter/min. After 5 hr, about 13% of the original iodine had been desorbed.

Three desorption experiments were conducted using the temperature-ramp technique. In two of these experiments, a He-3% steam mixture was passed over a separate portion of the above iron sample, while the temperature was increased steadily at the rate of 2°C/min; flows of 2.2 std liters/min and 4.5 std liters/min, respectively, were used. Pure helium ($<$ 10 ppm H_2O) flowing at 2.2 std liters/min and the same rate of temperature increase (2°C/min) were used in the third temperature-ramp experiment. The amount of iodine remaining on the specimen at any time (or temperature) was determined by in-situ gamma spectrometry. A graph of the course of desorption in the respective experiments is shown in Fig. 5. The course of each desorption experiment was consistent with first-order kinetics.

First-order desorption rate coefficients (k', sec^{-1}) obtained by differentiating the curves are shown in Table 5 for temperatures of 250, 400, and 550°C, along with the value obtained from the isothermal experiment. In comparison, Neill[38] reported that, at 400°C, iodine at a surface concentration of about 8×10^{15} atoms/cm^2 on bright steel was desorbed

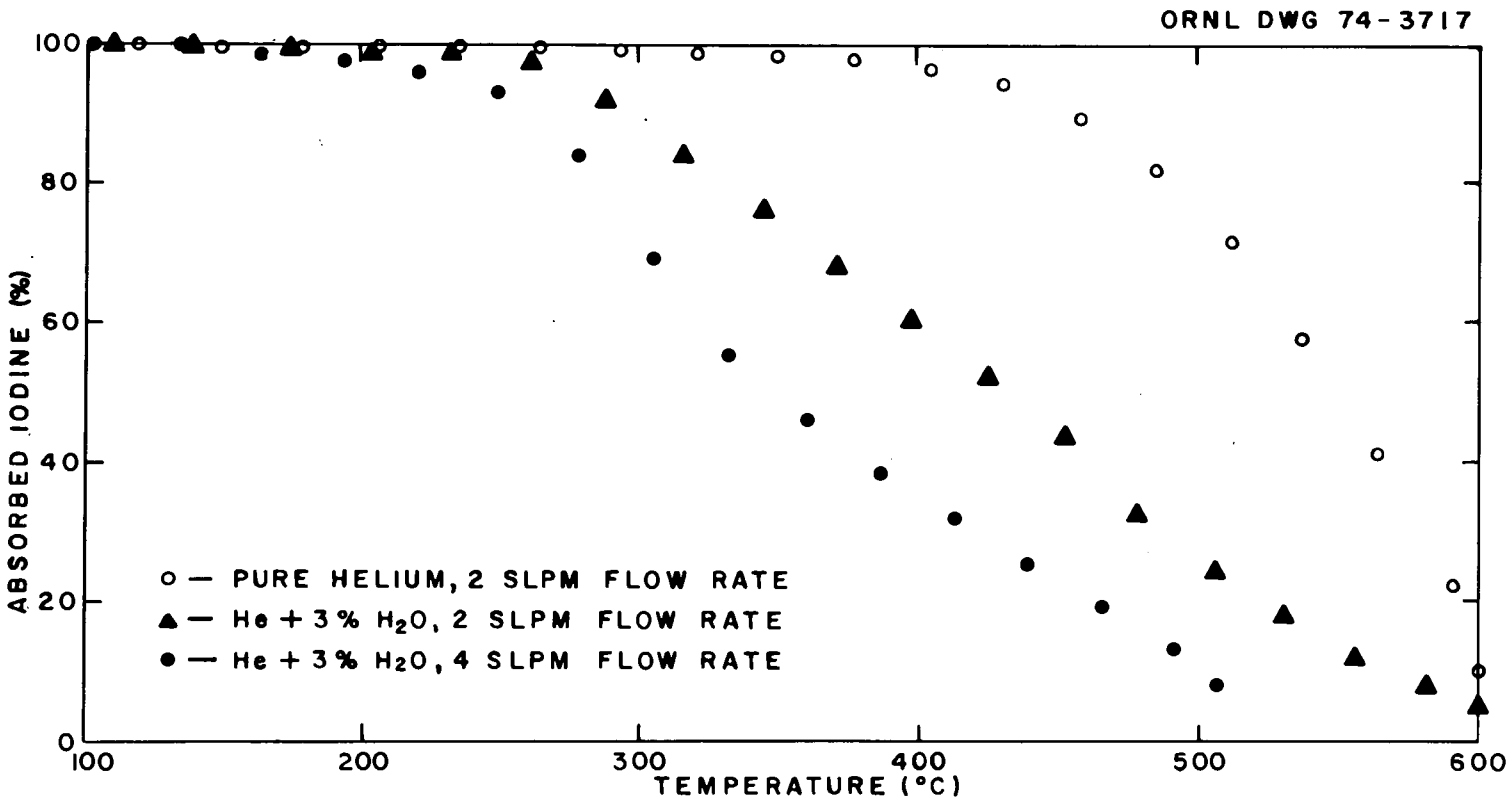

Fig. 5. Thermodesorption of iodine from iron powder into flowing helium, heated at 2°C/min.

Table 5. Desorption of iodine from iron into flowing moist or dry helium

k' = first-order desorption rate coefficient, sec^{-1}

Z' = partition coefficient (atoms/liter)/(atoms/cm^2)

Type	Helium flow rate (std ℓ/min)	Fraction H_2O	Coeff.	Temperature (°C) 250	400	550
Isothermal	1.0	0.03	k'	8×10^{-6}	-	-
			Z'	0.14		
Ramp	2.4	0.03	k'	2.0×10^{-5}	1.5×10^{-4}	5×10^{-4}
			Z'	0.16	0.9	2.6
Ramp	4.3	0.03	k'	4×10^{-5}	2×10^{-4}	1.1×10^{-3}
			Z'	0.16	1.2	2.5
Ramp	2.2	0	k'	2×10^{-6}	3×10^{-5}	4×10^{-3}
			Z'	0.016	0.19	2.0

under vacuum with an initial rate constant of about 7×10^{-5} sec^{-1}; this is about twice what we observed for dry flowing helium. However, evaporation into vacuum and into a flowing gas stream may not be limited by the same factors.

It may be seen that the desorption rate coefficients (k') were proportional to flow in the experiments using moist helium. This suggests that desorption may depend on partition between the surface and gas phases. A partition coefficient, Z' (atoms/liter)/(atoms/cm^2), may be obtained as follows:

$$Z' = \frac{k' \; A}{F^*} \; \frac{273.1}{T} \quad ,$$

where

F^* = flow, std liters/sec,
T = temperature, °K,
k' = first-order rate coefficient at T, sec^{-1},
A = area (BET) of the sample, cm^2.

Values of Z' for the various experiments and conditions are also shown in Table 5. As seen, the values of Z' at a given temperature are consistent for the experiments conducted in moist helium.

If we assume that the desorption rate into pure helium can be similarly treated, the partition coefficients are less than for moist helium at 250°C and at 400°C, thereby indicating decreased desorption under given conditions.

An equilibrium partition ratio, Z'_{eq}, can be calculated at 400°C for the static equilibration conditions under which the sample was prepared by depositing iodine on the sample surfaces. The following relationship is used:

$$Z'_{eq} = \frac{6.02 \times 10^{23} \times P}{SR'T} = \frac{6.02 \times 10^{23} \times 2.5 \times 10^{-8}}{7.4 \times 10^{14} \times 0.082 \times 673} = 0.37 \; \frac{\text{atoms/liter}}{\text{atoms/cm}^2} ,$$

where

S = original surface concentration of the sample (7.4×10^{14} atoms/cm^2),
P = iodine pressure at the sample ($\sim 2.5 \times 10^{-8}$ atm after thermal transpiration and dissociation),
T = temperature of the sample (400°C or 673°K),
R' = gas constant.

Comparison of the static value with the experimental value for 400°C in the experiment carried out with dry helium, $Z' = 0.19$, shows that the results are in fairly close (i.e., by a factor of 2) agreement--the kinetic value indicating a little less release than is implied by the static value. The closeness of agreement indicates that the experiment with dry helium probably depended predominantly on partition equilibrium. This was quite possibly true for the moist experiments also, but mass transfer analysis (not attempted) appears desirable.

It may be shown that if a substance is partitioned between gas and surface phases with a partition ratio of F_P (atoms on surfaces/atoms in gas), and the gas is isothermally bled off (depressurized), then

$$(F_P + 1) \ln \left(\frac{N_P^o}{N_P} \right) = \ln \left(\frac{P^o}{P_1} \right),$$

where

N_P^o, N_P = initial and final numbers of atoms in the system,

P^o, P_1 = corresponding system pressures.

By this mechanism, all the gas in the system at any moment contains the concentration of iodine that would be in equilibrium with the surface at the time, unhindered by transfer rates.

By definition,

$$F_P = \left(\frac{A}{V}\right)/Z' ,$$

where

A = microscopic surface area of the system on which iodine is adsorbed,

V = effective volume of the gas in the system.

In order to estimate the effects of full depressurization in an HTGR (with unoxidized surfaces), we assume a metal area of 2×10^8 cm^2 holding iodine and an effective volume equal to that occupied by 4227 kg (9320 lb) of helium at 47.6 atm (P_o) (i.e., $V = 0.95 \times 10^6$ liters at 250°C, etc.). Therefore we calculate the fraction lost at the various temperatures to be:

	250 °C	400 °C	550 °C
Dry helium	0.0003	0.005	0.056

The complete release to the environment of the order of 1% of the primary coolant circuit inventory of ^{131}I may be required to exceed the limits stipulated by 10 CFR 100. This material is likely to have been deposited in the cooler region of the steam generator. The above values suggest that, in a dry system in which iodine is adsorbed on unoxidized metal, a heatup of these regions would have to occur before a potentially intolerable release of ^{131}I would occur, even in the case of complete depressurization followed by all gas being entirely released to the environment. This may also be the case (as indicated by similarly calculated values) in the moist system; however, mass transfer effects may require consideration.

8. DISCUSSION AND RECOMMENDATIONS

The iodine dose received by an individual under accident conditions should remain, by acceptable margins, below the limits stated in 10 CFR 100 if the secondary containment vent closes as designed, regardless of the primary system inventory. Even if the closure did not operate effectively, inherent desorption characteristics appear to have the capability for limiting the release adequately, provided (1) the inventory of iodine deposited on primary system surfaces is within expected limits, and (2) these surfaces do not undergo significant heatup during the accident. The inhalation of released ^{131}I is the dominant pathway.

The release of fission products held in the fuel was not considered. However, an appreciable temperature rise (which, in turn, requires time) is thought to be necessary before this effect would provide a source greater than that provided by fission products deposited on primary system surfaces.

The plant emission during normal operation must be "as low as practicable," and certainly less than about 13 mCi/year to remain within the proposed limits of 10 CFR 50, Appendix I, of 15 mrem/year; ^{131}I in the air-grass-cow-milk-child pathway is dominant in such releases.

In relating the plant emission to the primary coolant gas inventory, the assumption of some decontamination (DF = 100) of leaks passing through PCRV concrete and through the secondary containment was accepted. A leak rate of the primary coolant of 0.01% per day was also assumed. The use of these assumptions leads to a maximum permissible ^{131}I partial pressure in the primary coolant of 1×10^{-10} atm. Actually, it will doubtless be orders of magnitude lower if deposition on primary system surfaces occurs as expected.

Estimates of the release of the iodine isotopes from fuel particles to the primary system can be correlated with the release of noble gases from the particles, and hence can be related to empirical determinations available for these. Nevertheless, extension for application to long-lived or stable iodine isotopes requires more detailed consideration of the release model, as it is affected by particle composition, fluence, temperature, cracking, and other factors. The release rate of the essentially stable iodine will determine the amount of adsorbed iodine. It is important that a significant capacity of surface deposition of iodine be operative in the system; without such removal, the purification plant alone could not keep the inventory of ^{131}I in the primary coolant gas as low as required.

The surfaces are expected to be covered with oxide (Fe_3O_4, $FeCr_2O_4$, Cr_2O_3), provided the expected moisture level is present in the gas (equivalent to 10 ppm of H_2O). The adsorption of iodine on Fe_3O_4 was indicated to be sufficient to keep the gas concentration within the necessary limits for normal operation, provided the adsorption was reversible. For the expected conditions, deposition of vapor-borne iron iodide should not occur, and the possible transport and deposition of chromium and manganese iodides would be inhibited by the probable reaction of moisture with surface atoms. The rates of desorption or exchange with oxidized surfaces were not considered; nor were the adsorption equilibria for graphite or for unoxidized iron.

In subsequent work it will be desirable that various factors mentioned above be made explicit. This will allow distributed rather than combined regions and parameters to be properly considered.

9. REFERENCES

1. Summit Power Station, Units 1 and 2, Delmarva Power and Light Co., Preliminary Safety Analysis Report Docket 50-450 (1973 and 1974 to date).

2. Code of Federal Regulations, Title 10, Part 50, Appendix I, presently proposed only for light-water reactors. As originally stated for light-water reactors the limit was 5 mrem/year; however, the Regulatory staff has recently recommended a limit of 15 mrem/year to the AEC [Nuclear News, p. 40 (April 1974)].

3. AEC Regulatory Guide 1.42, "Interim Licensing Policy on as Low as Practicable for Gaseous Radioiodine Releases from Light-Water-Cooled Nuclear Power Reactors" (June 1973).

4. Final Environmental Statement Concerning Proposed Rule Making Action: Numerical Guides for Design Objectives and Limiting Conditions for Operation to Meet the Criterion "As Low as Practicable" for Radioactive Material in Light-Water-Cooled Nuclear Power Reactor Effluents, WASH-1258 (3 Vol.), Directorate of Regulatory Standards, USAEC (July 1973).

5. The Safety of Nuclear Power Reactors (Light-Water-Cooled) and Related Facilities, WASH-1250, USAEC (July 1973).

6. T. J. Burnett, "Reactors, Hazard and Power Level," Nucl. Sci. Eng. 2, 382-93 (1957). However, a value of 15% retention of inhaled ^{131}I was used rather than the currently assumed 23% retention.

7.(a) J. K. Soldat, N. M. Robinson, and D. A. Baker, Models and Computer Codes for Evaluating Environmental Radiation Doses, BNWL-1754 (February 1974).

(b) J. K. Soldat, F. P. Brauer, J. F. Cline, J. E. Fager, B. Klepper, W. H. Ricard, B. E. Vaughan, and D. G. Watson, The Radioecology of Iodine-129: An Interim Report, BNWL-1783 (September 1973).

8. C. E. Easterly, ORNL Health Physics Division, personal communication.

9. D. H. Slade (ed.), Meteorology and Atomic Energy - 1968, TID-24190 (July 1968), p. 366.

10. H. J. de Nordwall and W. E. Bell, "Fission Product Control in HTGR Plants," paper presented at the American Nuclear Society Topical Meeting, Gas-Cooled Reactors, HTGR and GCFBR, May 7-10, 1974, Gatlinburg, Tenn.; CONF-740501, pp. 439-62.

11. J. M. Graf and P. O. Strom, "Siting Considerations for Radioactivity in Reactor Effluents During Normal Operation," paper presented at the American Nuclear Society Conference on Nuclear Power Plant Siting, Portland, Ore., Aug. 25-28, 1974; Trans. Am. Nucl. Soc. 19 (Suppl. 1), 19-21 (1974).

12. H. Bonka and K. Brussermann, Iodine Release from Nuclear Power Plants and Reprocessing Plants as Well as Contamination of the Environment in the Future, Jul-997-RG (August 1973).

13. J. P. Audebeau, R. L. R. Lefevre, and M. S. T. Price, "Quality Management for HTR Fuels," paper presented at the British Nuclear Energy Society Conference, London, Oct. 15-19, 1973; (to be published in the Proceedings).

14. A. H. Booth, A Method of Calculating Fission Gas Diffusion from UO_2 Fuel and Its Application to the X-2-f Loop Test, CRDC-721 (September 1957).

15. J. Belle, Uranium Dioxide. Properties and Nuclear Applications, p. 490, USAEC, Washington, D. C., 1961.

16. R. H. Flowers, The Relation of Fission Product Release Limitations to the Design and Operation of a Large HTR Station, AERE-R-6575 (D.P. Report-719, Part 7) (1970).

17. L. R. Zumwalt, P. E. Gethard, and E. E. Anderson, Fission Product Release from Single Crystal UC_2 Particles, GA-4267 (1963).

18. R. D. Burnette, W. E. Bell, and N. L. Baldwin, Fission Product Retention Characteristics of HTGR Fuel, paper presented at the British Nuclear Energy Conference, London, Oct. 15-19, 1973; (to be published in the Proceedings).

19. A. W. Castleman, Jr., and F. J. Salzano, Current Studies of Fission Product Behavior at BNL, BNL-7423 (September 1963).

20. "Sorption of Iodine on Metal Surfaces (Dynamic Method)," pp. 143-55 in Public Service Company of Colorado 330 MW(e) High-Temperature Gas-Cooled Reactor Research and Development Program, Quarterly Progress Report, Sept. 30, 1967, GA-8270.

21. E. L. Compere and M. F. Osborne, "Iodine Adsorption and Desorption Studies," GCR Programs Annu. Progr. Rep., Dec. 31, 1973, ORNL-4975 (in press).

22. O. Kubachewski, E. Ll. Evans, and C. B. Alcock, Metallurgical Thermochemistry, 4th ed., Pergamon, New York, 1967; see especially Table E.

23. D. R. Stull, JANAF Thermochemical Tables, Thermal Research Laboratory, Dow Chemical Company, Midland, Mich., 1964.

24. E. Hoinkis, A Review of the Adsorption of Iodine on Metal and Its Behavior in Loops, ORNL-TM-2916 (May 1970).

25. C. E. Milstead, W. E. Bell, and J. H. Norman, "Deposition of Iodine on Low Chromium-Alloy Steels," Nucl. Appl. Technol. 7, 361-66 (1969).

26. D. L. Gray and F. H. Neill, "Fission Product Deposition Experiment," pp. 113-15 in GCR Program Semiannu. Progr. Rep., Sept. 30, 1967, ORNL-4200.

27. W. E. Bull, "Interaction of Iodine with an Oxidized Steel Surface," p. 85 in GCR Program Semiannu. Progr. Rep. Mar. 31, 1968, ORNL-4266.

28. M. F. Osborne, "Iodine Adsorption and Desorption," pp. 168-72 in GCR Programs Annu. Progr. Rep., Dec. 31, 1972, ORNL-4911.

29. F. H. Sweeton and C. F. Baes, Jr., "The Solubility of Magnetite and Hydrolysis of Ferrous Iron in Aqueous Solutions at Elevated Temperatures," J. Chem. Thermodyn. 2, 479-500 (1970).

30. R. E. Honig and H. O. Hook, RCA Rev. 21, 360-68 (September 1960).

31. H. Krebe, Fundamentals of Inorganic Crystal Chemistry, translated by P. H. L. Walter, pp. 266-67, McGraw-Hill, London, 1968.

32. R. F. Rolsten, Iodide Metals and Metal Iodides, Wiley, New York, 1961.

33. L. Brewer, G. R. Somayajulu, and E. Brackett, "Thermodynamic Properties of Gaseous Metal Dihalides," Chem. Rev. 64, 111-21 (1964).

34. G. N. Lewis and M. Randall, Thermodynamics, 2nd ed., revised by K. S. Pitzer and L. Brewer, McGraw-Hill, New York, 1961.

35. P. R. Rowland, W. E. Browning, and M. Carlyle, Behavior of Iodine Isotopes in a High Temperature Gas Reactor Coolant Circuit, D.P. Report 736 (November 1970).

36. H. J. de Nordwall, F. F. Dyer, J. O. Kolb, and W. J. Martin, "An Interim Report on Fission-Product Release During Operation of the Second Peach Bottom Core," paper presented at the British Nuclear Engineering Society Conference, London, Oct. 15-19, 1973) (to be published in the Proceedings).

37. E. Hoinkis, "Surface Interactions of Iodine with Fe_3O_4," Vacuum 22(11), 525-30 (1973).

38. F. H. Neill, Adsorption and Desorption of Iodine on Mild Steel, ORNL-TM-2763 (April 1970).

The following uncited references are also of interest:

(a) M. J. Haire and D. W. McEachern, Gaseous Radioactivity Levels in the Primary Coolant of an HTGR, GA-A 12946 (Oct. 1, 1974).

(b) F. E. Vanslager, Proposed Analysis and Interpretation of the Fort. St. Vrain Plateout Probes, GAMD-9768 (August 1970).

(c) F. P. O. Ashworth, "Retention and Control of Fission Products in a High Temperature Gas-Cooled Reactor," J. Brit. Nucl. Energy Soc. 12, 421-22 (October 1973).

10. LIST OF SYMBOLS

English Alphabet

a = radius of equivalent sphere in Booth model of release; $a = 3 \times$ effective (volume/surface)

a_o = lattice parameter

A = system microscopic surface area

B = rate of generation or birth of nuclide in fuel (steady state)

B' = coefficient in Temkin adsorption isotherm

Br = effective intake rate of air: emergency, 5×10^{-4} m^3/sec; occupational, 10 m^3/8 hr; average, 7300 m^3/yr

C = concentration of nuclide in coolant

C^o = concentration estimated for no adsorption

C' = coefficient in Temkin adsorption isotherm

D = diffusion coefficient

D' = diffusion rate coefficient = D/a^2

DF = decontamination factor of region = (amount entering/amount leaving)

D_L = regulatory dose limit

e = surface evaporation rate constant for adsorbed species

E = thyroid dose resulting from intake of 1 Ci of given nuclide

f = fraction of total thyroid dose contributed by nuclide and pathway under consideration

f' = fraction of gas atoms of given element striking surface that are adsorbed

F = fractional release: atoms of species outside sphere/atoms inside and outside

F_P = plateout factor, atoms of species on surfaces/atoms in gas

F^* = flow rate across sample

J = entry rate of nuclide into primary coolant

k' = first-order desorption rate constant

k_i = Langmuir adsorption coefficient, in concentration units, from $\theta_i = k_i C_i (1 - \theta)$

K = equilibrium constant

L_P = fractional release of primary system inventory to secondary containment in an accident

L_S = fractional release of secondary system inventory to environment in an accident

L^* = leak rate of nuclide from primary system

M = safety margin; ratio of Regulatory limit to estimated dose

n = number of adsorption sites on unit microscopic area

N_G = amount of nuclide in primary coolant gas

N_P = amount of nuclide in primary coolant system

N_S = amount of nuclide on surfaces of primary coolant system

p = partial pressure of element, torr

P = pressure, atm

Q = rate of release of nuclide from plant vent

Q' = quantity of iodine adsorbed on graphite, ppm (Salzano equation)

r_L = first-order rate coefficient for gas leakage from primary coolant system

r_P = first-order rate coefficient for flow to purification plant as fraction of primary system contents

r_S = first-order rate coefficient for surface deposition (plateout)

R = release rate of nuclide from fuel or fuel particle

R' = gas constant

R^* = 1/2 ratio (hydrogen/oxygen)

R_v = release of nuclide in plant vent, Ci

S = amount of nuclide adsorbed on unit microscopic surface area

t = time (since beginning of irradiation and diffusion)

T = absolute temperature, °K

V = effective volume to contain system gas at given temperature and pressure

VP = vapor pressure of condensable compound

W = partial pressure of water equivalent to gaseous oxygen-containing species

Z = percentage removed per pass by plateout

Z' = partition coefficient, conc. in gas/conc. on surface

Greek Alphabet

α = average velocity of atoms of given species directed toward surface

$\Theta_i;\Theta$ = fraction of sites that are occupied by nuclide or by element

λ = decay constant

σ = area of unit adsorption site

$\tau_{(i,j)}$ = transfer function of given nuclide from region i to region j

χ = nuclide concentration in air at given location

11. APPENDIX:

DERIVATION OF EQUATION FOR SURFACE REQUIREMENT IF EXCHANGE OCCURS BETWEEN GAS AND SURFACE PHASES

We shall consider the number of surface sites required for a given gas-phase concentration to result if radioactive and stable species enter the gas region, interchange by adsorption on a surface and evaporation from it, and are removed in a gas purge stream from the system.[21]

For purposes of simplification, we shall consider an isothermal system in which a single stable species and a single radioactive isotope of the same element interact with the surface in a manner such that the sorption behavior can be described by a Langmuir-type adsorption isotherm. In this system, isotope i is assumed to enter the coolant at a steady rate J_i, and the coolant is passed through a purification plant at a constant rate. Detailed species balance requires that the time rate of change in the total number of atoms of species i, (dN_i/dt), be described by the relation

$$(dN_{S_i}/dt) = J_i - N_{S_i}\lambda_i - VC_i\lambda_i - VC_i r_P \ , \qquad (1)$$

where

N_i = total number of atoms of species i in the primary system,

N_{S_i} = number of atoms of species i adsorbed on the surface,

λ_i = rate constant for radioactive decay

C_i = concentration in atoms per unit volume,

V = gas volume of the system,

r_P = system rate constant for species removal by coolant purification (and any leakage).

Similarly, the time rate of change in the number of atoms of species i located on surfaces, $dN_{S_i}/dt)$, is given by

$$(dN_{S_i}/dt) = An\sigma\alpha f'(1 - \theta)C_i - An\theta_i\lambda_i - An\theta_i e, \qquad (2)$$

where

A = total microscopic system area (i.e., the BET surface area),

n = number of adsorption sites per unit microscopic area,

σ = surface area per unit site,

Θ_i = fraction of sites occupied by species i atoms,

$\Theta = \Sigma_i \Theta_i$ = total fraction of occupied sites,

α = average velocity of atoms directed toward the sorption surface,

f' = fraction of species i atoms which strike a vacant sorption site and are actually sorbed,

e = fraction of sorbed atoms which evaporate per unit time.

Under steady-state conditions, Eq. (2) reduces to yield a Langmuir-type isotherm of the form

$$\Theta_i = k_i(1 - \Theta)C_i, \tag{3}$$

where

$$k_i = \sigma\alpha f'/(\lambda_i + e). \tag{4}$$

It will be useful to express the adsorption effect by comparing the gas concentration under adsorption conditions with the steady-state concentration (C_i^o) that would exist if no sorption occurred. The steady-state concentration if no sorption occurs ($N_{Si} = 0$) is obtained from Eq. (1) as

$$C_i^o = J_i/V(\lambda_i + r_P). \tag{5}$$

We now measure the adsorption effect by comparing the gas-phase concentration of species 1 (C_1) with this value:

$$\frac{C_1^o}{C_1} = 1 + \frac{Ank_1\lambda_1(1 - \Theta)}{V(\lambda_1 + r_P)} . \tag{6}$$

For a stable species (for which we employ the subscript 2), Eq. (5) becomes

$$C_2 = J_2/V\ r_P, \tag{7}$$

and if we further assume that $\Theta \sim \Theta_2$,

$$(1 - \Theta) = 1/(1 + k_2 C_2), \tag{8}$$

and if we note that $k_1/k_2 = e/(\lambda_1 + e)$ from Eq. (4)], the surface requirement takes the mathematical form

$$A\ n = \left[\frac{C_1^o}{C_1} - 1\right] \left[1 + \frac{r_P}{\lambda_1}\right] \left[1 + \frac{\lambda_1}{e}\right] \left[\frac{V}{k_2} + \frac{J_2}{r_P}\right], \tag{9}$$

where subscript 1 now refers to the radioactive species.

This equation can be solved if the evaporation rate constant e is known or is much larger than λ_1. If $e \gg \lambda_1$, then $k_1 \approx k_2$, and prompt exchange occurs.

A useful variation uses the relationship

$$\frac{N_{G1}^o}{N_{G1}} = \frac{VC_1^o}{VC_1} = \frac{C_1^o}{C_1} \tag{10}$$

to obtain:

$$A\ n = \left[\frac{N_{G1}^o}{N_{G1}} - 1\right] \left[1 + \frac{r_P}{\lambda_1}\right] \left[1 + \frac{\lambda_1}{e}\right] \left[\frac{V}{k_2} + \frac{J_2}{r_P}\right], \tag{11}$$

where

N_{G1}^o, N_{G1} = amount of gasborne radioactive nuclide if no adsorption occurred, and if adsorption with exchange does occur.

ORNL-TM-4744
UC-77 — Gas-Cooled Reactor Technology

Internal Distribution

1. J. L. Anderson
2. C. F. Baes
3. S. J. Ball
4. E. C. Beahm
5. R. L. Beatty
6. A. L. Boch
7. E. G. Bohlmann
8. R. A. Bradley
9. R. E. Brooksbank
10. K. B. Brown
11. J. P. Callahan
12. D. A. Canonico
13. S. Cantor
14. C. E. Clifford
15. T. E. Cole
16. C. F. Coleman
17-37. E. L. Compere
38. A. L. Compere
39. J. A. Conlin
40. J. H. Coobs
41. D. Costanzo
42. W. B. Cottrell
43. G. E. Creek (consultant)
44. F. L. Culler
45. F. C. Davis
46. F. E. Dearing
47. B. C. Duggins
48. F. F. Dyer
49. C. E. Easterly
50. W. P. Eatherly
51. R. L. Egli
52. R. B. Evans
53. G. G. Fee
54. D. E. Ferguson
55. Uri Gat
56. R. W. Glass
57. W. R. Grimes
58. P. A. Haas
59. J. W. Hill
60. R. M. Hill, Jr.
61. F. J. Homan
62. J. D. Jenkins
63-101. P. R. Kasten
102. R. J. Kedl
103. W. J. Lackey
104. T. B. Lindemer
105. R. A. Lorenz
106. A. L. Lotts
107. R. E. MacPherson
108. J. C. Mailen
109-115. A. P. Malinauskas
116. W. J. Martin
117. W. R. Martin
118. M. T. Morgan
119. F. H. Neill
120. K. J. Notz
121. L. C. Oakes
122-126. M. F. Osborne
127. G. W. Parker
128. R. L. Pearson
129. H. Postma
130. R. H. Rainey
131. P. L. Rittenhouse
132. P. Rubel
133. G. Samuels
134. J. P. Sanders
135. H. C. Savage
136. D. Scott
137. C. D. Scott
138. J. D. Sease
139. J. H. Shaffer
140. R. L. Shepard
141. J. W. Snider
142. I. Spiewak
143. R. S. Stone
144. R. A. Strehlow
145. J. R. Tallackson
146. M. Tobias
147. D. B. Trauger
148. J. E. Van Cleve
149. V. C. A. Vaughen
150. T. N. Washburn
151. J. R. Weir
152. R. P. Wichner
153. R. G. Wymer
154. G. D. Whitman

155. Ken Davis (consultant)
156. J. C. Frye (consultant)
157. C. H. Ice (consultant)
158. E. A. Mason (consultant)
159. R. B. Richards (consultant)
160-161. Central Research Library
162. Document Reference Section
163-174. Laboratory Records
175. Laboratory Records, RC
176. ORNL Patent Office

External Distribution

177. Research and Technical Support Division, ERDA, ORO
178. Director, Reactor Division, ERDA, ORO
179-180. Director, Reactor Research and Development, ERDA, Washington, D.C. 20545
181-323. Given distribution as shown in TID-4500 under Gas-Cooled Reactor Technology category

☆U. S. GOVERNMENT PRINTING OFFICE: 1974-748-189/153