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RATES AND MECHANISMS OF THE LOSS
OF FISSION PRODUCTS FROM URANIUM-GRAPHITE
FUEL MATERIALS

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INTRODUCTION

This paper presents evidence concerning the high-temperature loss of fission-product atoms from uranium-graphite fuel material. The results are in general agreement with previous work (1-9) and indicate that no single model can adequately describe the behavior of all fission-product elements.

Some of the variables that have been identified as affecting loss rates are: temperature, chemical specie or element, dimensions of the sample, concentration of the uranium, the method of manufacture of the fuel, and the porosity of the graphite.

Losses are governed by at least two different sets of rate-limiting processes. The rate of loss of Sr, Y, Cs, Ba, and the lanthanide elements is governed by diffusion through the graphite matrix and possibly by surface evaporation; and that of Ag, Cd, Sb, Te, and I by processes which have not been identified. The two sets of processes are distinguished experimentally by measurement of concentration gradients within a sample.

EXPERIMENTAL

Admixture Samples

Admixture fuel material was prepared by extrusion and graphitization of a mixture of uranium oxide, carbon, graphite and binder. Cylindrical samples were machined from the graphitized mixture. Most specimens were 0.230 inch diameter x 0.375 inch long and contained 2%, 5%, or 20% uranium by weight. Also used were samples, containing 5% uranium, which were 0.115 inch diameter x 0.375 inch or 0.355 inch diameter x 0.500 inch.

The particles of uranium were so small (1-2 microns) that most of the fission product atoms came to rest, at the end of their recoil paths, in the graphite matrix. The samples were stored in air which caused about 25% of the uranium carbide to revert to oxide.

Solution-Impregnated Samples

Solution-impregnated samples were prepared from 0.230 inch diameter AUC graphite cylinders and uranyl-nitrate solution. Following impregnation the samples were baked at 800°C to convert the uranium from the nitrate to the oxide. The samples averaged 5% uranium by weight with the uranium concentration near the surface being about twice the concentration near the center.

PROCEDURES

The general procedures for irradiation, heating and analysis of the samples were similar to those followed by Cowan and Orth (5, 7). Graphite tube furnaces with a 3-inch or longer hot zone were employed. Temperature measurements were made viewing the sample surface under black body conditions with an optical pyrometer. Appropriate corrections were applied to the temperature readings for absorption and reflection of light by the furnace window. The samples were heated in a flowing atmosphere of purified helium. The flow rate, at room temperature and one atmosphere of pressure, was a nominal 100 c.c. of He gas per minute. The samples were introduced into and removed from the furnace tube by momentary application of He pressure in the appropriate direction. The furnace tube ID was usually 0.020 inches greater than the sample diameter. The time required for the sample to come to temperature varied from several minutes at 1200°C to a few seconds at 2400°C.

The samples were irradiated in a thermal neutron flux to produce 10^{13} to 10^{14} fission events as required for the analyses. In most experiments the initial fission product concentration was based on measurement of the Mo^{99} remaining in the sample following the heating (5, 7). In a few experiments the initial gross radioactivity, compared to a standard, was used as a basis for computation of initial concentration. Concentrations of various fission products following heating were determined by standard radiochemical procedures. Results are reported as fission product concentration following heating divided by concentration prior to heating, $C(t)/C_0$. This ratio is referred to as "fraction remaining."

There are two main sources of experimental uncertainty: 1) the analysis of fission products and 2) the measurement of the temperature of the sample.

The uncertainties in analysis vary, depending upon the fraction remaining and the particular species being analyzed. Analyses of Sr, Y, Ba, Te, I, and the lanthanides are subject to a nominal error of $\pm 5\%$ for $C(t)/Co$. Errors for Ag, Cd, Sb, and Cs are somewhat larger, of the order of 8-10%. In experiments where the "fraction remaining" is small ($\leq 1\%$) the errors are larger, especially for the low yield fission products. This is more than compensated for by the fact that an error of 5% at 80% retention results in a greater error in the rate constant than an error of 10% at 1% retention.

Sufficient care was exercised in temperature measurements to ensure an accuracy of $\pm 15^\circ C$. Such an error can result in an error of more than 20% in the rate constant.

As an indication of reproducibility, values of fraction of Ba remaining, following 20 minutes at $1925^\circ C$, in four different experiments fell in the range from 0.24 to 0.31 (one size sample of admixture material).

RESULTS AND DISCUSSION

Temperature and Element as Variables

Typical variations in fission-product losses as a function of temperature from solution-impregnated material are illustrated in Fig. 1 for Cd, Cs, Sn, Sr, Sm, and Nd. Elements such as Zr and Mo are lost only very slowly even at $2400^\circ C$. There is a general correlation between the loss rate of an element and its melting or boiling point or its ability to form refractory carbides (1-9). Exceptions are the inert gases Kr and Xe, which are lost at rates comparable to Sr or Ba, and the non-metal elements Sb, Te and I which are lost more slowly than might be expected. Losses from admixture material vary in a similar manner as a function of temperature and element.

Fig. 1

Loss as a Function of Time

The losses of Ba and Te from admixture material, as a function of time, are shown in Fig. 2 and Fig. 3 and are indicative of differences in the processes governing their loss rates. The loss rate of Ba remains approximately proportional to the Ba concentration at all stages of loss. The loss rate of Te, initially equal to that of Ba, decreases rapidly following loss of a fraction of the Te. The shape of the curve for Ba is also typical for Sr, Y, Cs and the lanthanide elements. The curve for Te is also typical for Sb and I. The loss versus time behaviors of the low-melting elements Rb, Ag, Cd, In, Sn and the slowly lost refractories Zr, Nb, Mo, Tc, and Ru have not been well established. Ag, Cd, and Sn are lost rapidly even at 1200°C and in some respects behave similarly to Sb, Te and I. Loss rates of Zr, Nb, Mo and Ru are of the order of a fraction of 1% per minute at 2400°C.

Solution-Impregnated vs. Admixture

Loss rates from solution-impregnated samples are larger than loss rates from admixture samples. This is illustrated by the data in Table I, for samples which contain 5% uranium by weight. Results, for solution-impregnated samples, are in general agreement with the data reported by Doyle (4). However, we find that Sr behaves in a manner similar to Ba in so far as loss mechanisms are concerned.

Porosity of Graphite

Samples of solution-impregnated graphite were coated with pyrolytic carbon. The decrease of loss rates, illustrated qualitatively by data in Table II, depends on the thickness of the coat and may be attributed to the low porosity of pyrolytic carbon.

Uranium Concentration

Recent experiments using samples of 2%, 5% and 20% uranium admixture

Fig. 2

Fig. 3

TABLE I

Losses from Solution Impregnated and Admixture Samples
Heated at 1925°C for Ten Minutes

	Fraction Remaining	
	Solution Impreg.	Admixture
Ba ¹⁴⁰	0.27	0.55
Te ¹³²	0.18	0.56
Sr ⁸⁹	0.0033	0.028

TABLE II

Effects of Pyro-Carbon Coats on Losses of Sr, Cs, and Ba

Thickness of Coat (in.)	T (°C)	Time (min)	Fraction Remaining		
			Sr	Cs	Ba
0.001	1300	120	.91	.45	1.00
0.001	1550	120	.173	.16	.89
0.005	1550	120	.46	.60	1.03
0.003	2000	10	.048	.57	.73
none	1300	120	.98	.06	.99
none	1550	120	.151	~.005	.67

material indicate that uranium concentration is an important parameter for this type of material. The results are given in Table III. Most surprising is the increased loss rate of Ba from the 20% material in contrast with the generally smaller loss rates for Sr and the lanthanide elements. Loss of Te is apparently affected by uranium concentration although the effects at different temperatures do not seem to be consistent.

Concentration Gradients

The loss of any fission product atom from the interior of a solid material must involve the movement of that atom through the material to the surface. In a material such as graphite this movement may be along pores, through grains, along grain boundaries, etc., all of which can be described by the general term diffusion.

If the movement of the atoms to the surface, by whatever atomistic process, is rate-limiting, it follows that a concentration gradient will develop during loss. The gradient will be negative in the direction of flow, that is the concentration near the surface will be lower than the concentration near the center of the material.

That concentration gradients did develop during the loss of certain fission-product elements from admixture uranium-graphite but not for others was established experimentally. Values of concentration near the center and near the surface were measured following the heating of 0.230-inch-diameter and 0.355-inch-diameter admixture pins. A core was drilled out of the pins, and the core and remaining cylindrical shell were analyzed separately. Results of such experiments are given in Table IV. Concentrations are normalized to a value of 1.0 in the unheated samples. Core diameters were 0.125 and 0.250 inch for the 0.230 and 0.355 inch diameter pins, respectively. Gradients are large for Sr, Y, Cs, Ba, Ce, Nd and Eu and small for Ag, Cd, Sb and Te.

TABLE III

Effects of Uranium Concentration on Loss Rates from 0.230-Inch-Diameter Admixture Samples

Temp. °C	Time min.	Isotope	Fraction Remaining		
			2% U	5% U	20% U
1550	240	Sr	0.01		0.04
2400	4	Y	0.71	0.84	0.94
1550	240	Te	0.69		0.73
1925	40	Te	0.35	0.37	0.21
2400	4	Te	0.013	0.10	0.087
1550	240	Ba	0.72		0.39
1925	40	Ba	0.16	0.15	0.017
2400	4	Ba	0.04	0.03	0.0007
2400	4	Ce	0.56	0.65	0.84
1925	40	Nd	0.64	0.73	0.77
2400	4	Nd	0.41	0.55	0.71

TABLE IV
Concentration Gradients for Various Chemical Species

Isotope	Temp. °C	Time min.	Sample Diameter (inches)	Concentration		
				Core	Outer Shell	Whole Sample
Sr ⁸⁸	1925	10	0.230	0.030	0.017	0.021
		20	0.355	0.051	0.020	0.036
Y ⁹¹	2400	4	0.230	1.00	0.79	0.84
Ag ¹¹¹	1550	5	0.230	0.014	0.015	0.015
Cd ¹¹⁵	1550	5	0.355	0.33	0.34	0.034
Sb ¹²⁷	1925	20	0.355	0.25	0.20	0.23
		10	0.230	0.27	0.25	0.26
Te ¹³²	1925	20	0.355	0.55	0.52	0.53
Cs ¹³⁶	1550	5	0.230	0.78	0.48	0.57
		5	0.355	0.87	0.63	0.75
Ba ¹⁴⁰	1925	20	0.355	0.69	0.35	0.52
Ce ¹⁴⁴	2400	4	0.230	0.85	0.56	0.65
Nd ¹⁴⁷	1925	80	0.230	0.61	0.42	0.49
Eu ¹⁵⁶	1550	5	0.230	0.97	0.72	0.79

Size Effects

If the movement of atoms through the matrix is a rate limiting process, it follows that loss rates will depend on the dimensions of the sample. Losses from two sizes of admixture sample are presented for comparison in Table V. Losses of Sr, Cs, Ba and Ce differ for the two sizes; losses of Ag, Sb and Te do not differ significantly. The data for Cd, based on very low counting rates, were inconclusive.

Passage Through Unloaded Graphite

The evaporation of an atom from a surface on which it is absorbed requires energy and may, therefore, be a rate-limiting process. If evaporation is the only rate-limiting process then concentration will remain uniform during the process of loss and the loss versus time will follow a simple law, $C(t) = C \exp(-\alpha t)$. In a porous medium such as graphite one can imagine the evaporation occurring at some interior site followed by rapid gaseous diffusion through pores to the surface. However, if the evaporation step can occur only at the geometric surface, (and is the only rate-limiting process) then an initially non-uniform distribution of atoms within a sample will become uniform rapidly in comparison to the rate of loss. The existence of other rate-limiting processes, in addition to evaporation, will introduce variations from the ideal case described.

Experiments have been performed which show that evaporation of Ag, Cd, Sb and Te from the geometric surface of solid graphite is not a rate-limiting process in the loss of these elements. The samples consisted of a 0.115-inch-diameter admixture pin entirely enclosed in two tight-fitting, concentric AUC graphite capsules. Following heating, the pin and the two capsules were analyzed as three separate samples. The results are given in Table VI as

TABLE V
Effects of Sample Size on Loss Rates

Isotope	Fraction Remaining		
	0.230 inch DIA Sample	0.355 inch DIA Sample	
Sr ⁸⁹	0.74	0.92	5 min. 1550 °C
Ag ¹¹¹	0.015	0.015	
Cd ¹¹⁵	0.22	0.34	
Cs ^{136,137}	0.57	0.75	

Sb ¹²⁷	0.18	0.23	20 min. 1925 °C
Te ¹³²	0.50	0.53	
Ba ¹⁴⁰	0.24	0.52	
Ce ¹⁴⁴	0.81	0.88	

TABLE VI
Rates of Passage Through Unloaded AUC Graphite

Isotope	Time min.	Temp. °C	Concentration*		
			Admix Sample	AUC Case #1	AUC Case #2
Ag ¹¹¹	5	1550	8.8×10^{-3}	9×10^{-6}	3×10^{-6}
Cd ¹¹⁵	5	1550	0.44	4×10^{-5}	3×10^{-6}
Sb ¹²⁷	20	1925	0.31	1.8×10^{-4}	4×10^{-6}
Te ¹³²	20	1925	0.55	1.4×10^{-4}	1.2×10^{-5}
Sr ⁸⁹	5	1550	0.68	0.064	0.00064
	20	1925	0.0093	0.0106	0.004
Cs ^{134,137}	5	1550	0.72	0.0074	0.0031
Ba ¹⁴⁰	20	1925	0.21	0.10	0.0128
Ce ¹⁴⁴	20	1925	0.76	0.046	9×10^{-6}

* Normalized to 1.00 in the original sample; units cm⁻³.

concentrations following heating, normalized to a value of 1.00 in the unheated admixture pin. Initial fission product concentration in the AUC capsules was zero. The volumes of graphite in the pin and two capsules were 0.064, 0.36 and 0.99 cm³, respectively.

The results for Ag, Cd, Sb, and Te can be interpreted as indicating that the rate of passage of these elements through the graphite matrix and the geometric surface of the samples is rapid in comparison to the unknown rate-limiting processes. If this were not true then the concentration in the AUC graphite capsule would approach the decreasing concentration in the admixture sample. It should be noted that the results do not eliminate the possibility that evaporation from interior pore surfaces, or diffusion to the pore surfaces, are rate-limiting processes.

The results are not indicative of the relative rates of diffusion and evaporation of Sr, Cs, Ba and Ce but are in agreement with the gradient data which showed diffusion to be a rate-limiting process; they also show that diffusion of these elements through unloaded graphite occurs at approximately the same rate as diffusion through uranium-loaded graphite.

Diffusion Theory Application

Although there are many uncertainties involved in dealing with a poorly defined material, such as the admixture uranium-graphite fuel, it is nevertheless informative to attempt a mathematical description of the loss behavior. In this paper we restrict ourselves to concentration gradient data for Ba losses from 5% admixture samples. Since diffusion has been found to be a rate-limiting process, it is first assumed that it is the only rate-limiting process and that it is adequately described by the "Fick's Law" approximation. Solutions to the time dependent diffusion equation in cylindrical coordinates may be found in many texts, one of which is "The Mathematics of Diffusion" by

J. Crank, Oxford at the Clarendon Press, 1956. The particular solution is determined by the initial condition that $C(r, z, t = 0) = C_0$, and by the boundary condition that $C(\text{surface}) = 0, t > 0$. Comparisons of observations with theory are made in Table VII. The diffusion constants are based on "fraction-remaining" averaged over the entire sample. The theoretical concentration in the core is derived from the diffusion constant and the time of heating. The agreement is not entirely satisfactory.

The fact that observed gradients are invariably smaller than computed gradients may be due to the existence of a second rate-limiting process. The data for Ba were analyzed in terms of a model in which both diffusion and evaporation from the (geometric) surface of the material are rate-limiting. The differential equation remains the same; the surface evaporation appears as the boundary condition $\partial C / \partial r |_{(\text{surface})} = -\alpha C(\text{surface})$, which determines the particular solution. It is a property of the solution that one can choose a value of α so as to produce any desired value for the ratio of core retention to total retention, in the range of values from the ratio for pure diffusion ($\alpha \gg D/a$) to the ratio 1.0 for pure evaporation ($\alpha \ll D/a$). The particular value of $\alpha = 17.1 D$ was chosen to give a ratio intermediate between the experimental values at 1925°C and at 2400°C for the 0.230-inch diameter samples. Results are given in Table VIII. The fact that the same value of α allows correct prediction of the core to total concentration ratio for the 0.355-inch diameter sample is encouraging since the ratio of core volume total volume is quite different for the larger pin.

Activation Energies

Diffusion constants for Cs, Sr, Ba, Nd, Ce, and Y, based on the model in which diffusion is the only rate-limiting process, are plotted as a

TABLE VII

Barium Diffusion Constants, Assuming Diffusion in the Only Rate-Limiting Mechanism

Sample DIA inches	Temp. °C	Time min.	Fraction remaining	$\frac{D}{\text{cm}^2/\text{min}}$	$\frac{C(\text{core})}{C(\text{total})}$	
					Obs.	Computed
0.230	1925	10	0.47	4.1×10^{-4}	1.38	1.66
		20	0.26	4.9	1.40	1.81
		40	0.12	5.0	1.42	1.83
		80	0.024	5.0	1.42	1.83
	2400	1	0.30	8.8×10^{-3}	1.40	1.80
		2	0.14	8.9	1.50	1.83
		4	0.027	9.6	1.52	1.83
		8	0.0016	9.3	----	----
0.355	1925	20	0.52	3.5×10^{-4}	1.33	1.44

TABLE VIII

Barium Diffusion Constants, Assuming Diffusion and
Evaporation are Both Rate-Limiting; $\alpha = 17.1 \times D$

Sample DIA inches	Temp. °C	Time min.	Fraction Remaining	D	C(core)/C(total)	
				cm ² /min	Obs.	Computed
0.230	1925	10	0.47	9.8×10^{-4}	1.38	1.42
		20	0.26	9.6	1.40	1.46
		40	0.12	8.4	1.42	1.46
		80	0.024	7.8	1.42	1.46
	2400	1	0.30	1.74×10^{-2}	1.40	1.46
		2	0.14	1.54	1.50	1.46
		4	0.027	1.51	1.52	1.46
		8	0.0016	1.40	----	----
0.355	1925	20	0.52	7.2×10^{-4}	1.33	1.34

function of T^{-1} ($^{\circ}K^{-1}$) in Fig. 4. The points represent numerical averages for all data available at a given temperature and are biased due to the fact that in most experiments rare earth retentions were high and Sr, Cs, Ba retentions were low. Examination of the data for Ba in Table VII indicates that values of D tend to change as retention decreases. Activation energies derived from the slopes of the various curves, appear in Fig. 4. It should be noted that had the diffusion-evaporation model been used the diffusion constants would be about twice as large.

Conclusions

Most of the evidence presented in the paper is qualitative in nature and some of the interpretations will change as a result of future experiments. The conclusion, that diffusion through the graphite matrix is a rate-limiting process in the loss of some metallic fission products, is now well established. The hypothesis that evaporation is the second important rate-limiting process has not been confirmed, but this model fits the present data.

It has been shown that the rate-limiting step in the loss of Sb, Te and I is not diffusion through the matrix nor evaporation from the geometric surface. It has been suggested (1,2,4,6,8,9) that fission products which recoil into graphite grains or crystals will move slowly to pores and rapidly through pores to sample surface. This hypothesis is in accord with the observed two-component loss rates of Sb, Te and I. There are other hypotheses which also are in accord with observation. For example, it may be that the non-metals are strongly absorbed in uranium oxide (or carbide) and that the two-component behavior results from the competition between rapid escape and rapid absorption, the second component representing slow desorption from the uranium particles. This hypothesis can, and will, be tested.

Fig. 4

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FIGURE CAPTIONS

Fig. 1. Losses from solution-impregnated samples as a function of temperature;
(a) 120 min. at temperature, (b) 30 min. at temperature.

Fig. 2. Losses of Ba and Te from admixture samples as a function of time at
2400°C.

Fig. 3. Losses of Ba and Te from admixture samples as a function of time at
1925°C.

Fig. 4. Diffusion constants, based on the model in which diffusion is the
only rate-limiting process, as a function of temperature. Approximate
activation energies are: 40 kcal./mole for Cs, 60 kcal./mole for Sr,
and 70-75 kcal./mole for Ba, Nd, Ce and Y.

× - Cesium

⊗ - Strontium

▼ - Barium

◆ - Neodymium

■ - Cerium

● - Yttrium