RELEASE OF FISSION PRODUCTS ON THE IN-PILE MELTING OR BURNING OF REACTOR FUELS

R. P. Shields
W. E. Browning, Jr.
C. E. Miller, Jr.
B. F. Roberts

Reactor Chemistry Division, Oak Ridge National Laboratory , Oak Ridge, Tennessee

In-pile experiments are being conducted to study the release of fission products during simulated reactor accidents. Two types of experiments have been performed in the Oak Ridge Research Reactor to simulate reactor accidents in which fuel elements are destroyed by melting or burning. One type consisted of melting or vaporizing a miniature stainless-steel-clad UO_2 fuel element in a helium atmosphere. In the other type, a miniature fuel element composed of spheroidal particles of uranium carbide coated with pyrolytic carbon and embedded in a graphite matrix was burned in air. In each case, fission and gamma heat raised the temperature of the fuel element high enough to cause destruction. The details of design and operation of these experiments have been described previously.[1,2]

UO_2 Melting Experiments

In a typical in-pile meltdown experiment a miniature UO_2 fuel element clad in stainless steel is placed in a helium filled container of stainless steel, Fig. 1 which is lined with ceramic thermal insulation. This assembly is moved to a position close to the top of the lattice of the Oak Ridge Research Reactor to build up traces of fission products in the UO_2 specimen. At the end of irradiation period the assembly is lowered into a position where fission and gamma heat cause the specimen to melt. Helium gas sweeping over the specimen carries gas-borne fission products to suitable filters and traps where they are separated and collected. After the specimen is withdrawn from the flux, the furnace, filters, traps, and associated tubing are removed from the reactor. These parts are then cut up in a hot cell, examined, and analyzed for fission products.

Eleven experiments have been run, the first two of which were mainly for testing equipment although fission product release information was gained. The conditions for the next seven were identical, that is, 6% enriched UO_2, 400 cm^3 per min helium flow and the same time at the melting position. The inherent variation in the reactor neutron flux, however, caused a spread in the maximum temperature and resulted in partial melting in some cases and complete melting in others. The flow of helium sweep gas was increased from 400 to 800 cm^3/min for Experiment 10 and 4000 cm^3/min for Experiment 11; otherwise, the conditions were the same as in the preceding UO_2 meltdowns.

UNCLASSIFIED
ORNL-LR-DWG 49981R

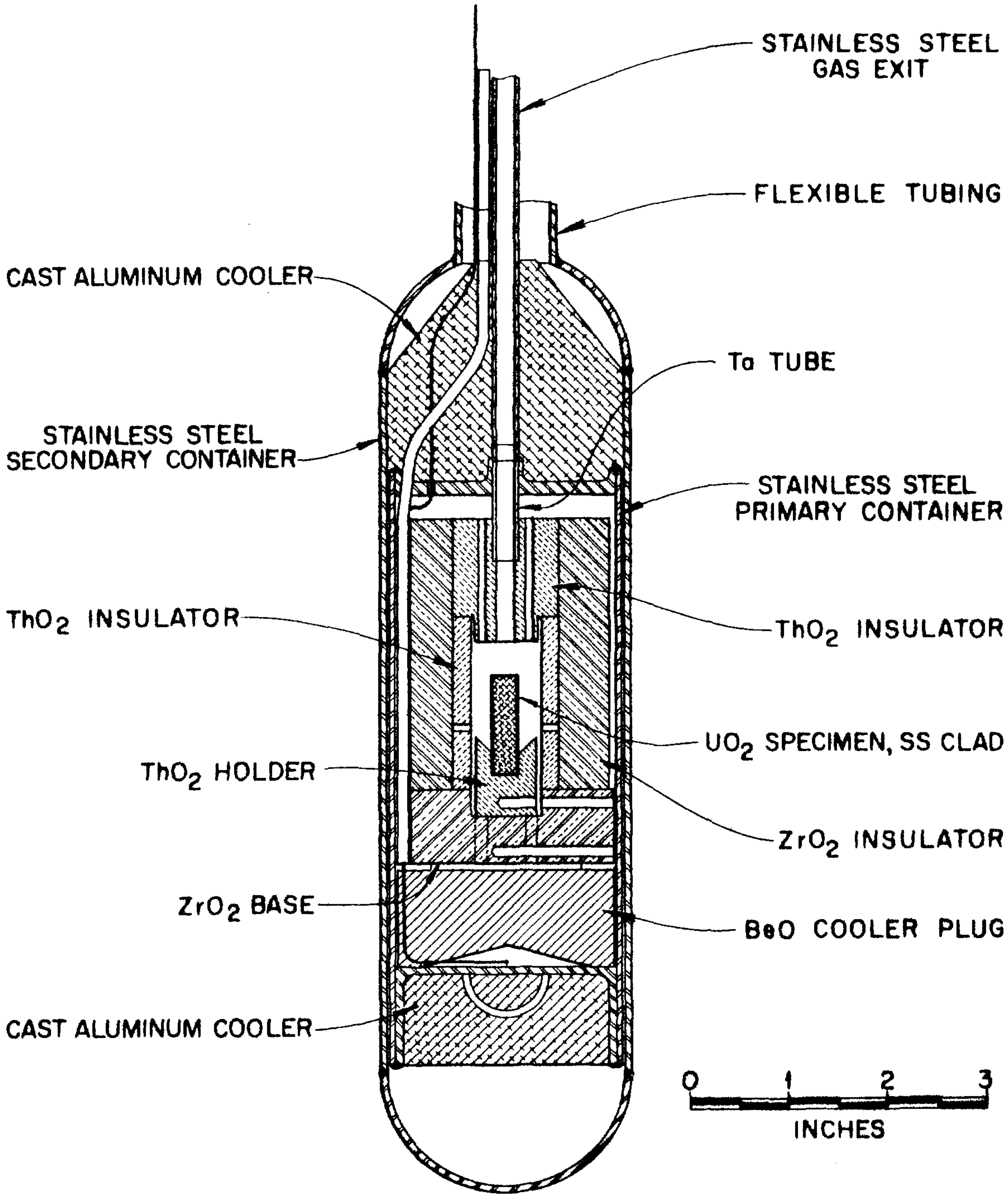


FIGURE 1

Reactor Furnace; for Fuel Element Meltdown Experiments.

The analytical results of the experiments through Number 10 have been discussed in detail[3,4] and the physical appearance of the UO_2 after the melting is described in references (1, 5). The results summarized in Tables 1 and 2 show the percentages of the various fission products released from the fuel residues and holder and the percentages of the isotopes which escaped from the high temperature zone of the furnace. Each value is based on the total amount of that fission product found throughout the experimental assembly. The data in Table 1 except for Experiment 7, show, in general, that nearly all of the I, Te, and Cs and more than half of the Sr, Zr, Ru, Ba, and Ce were released from the fuel. One-third to one-half of the UO_2 was released and the fission products contained in this UO_2 were considered to be released from the fuel. Fission product release was generally greater in Experiment 2 which had apparently reached a higher maximum temperature and which was irradiated unclad.

The values given in Table 2 are release values from the high temperature zone of the furnace. This zone consists of the volume enclosed by and including the ZrO_2 thermal insulation. The temperature of this zone during the period in which the UO_2 was molten was 1000°C or greater. In Experiment 2 strontium and barium were swept out of the furnace in the form of gaseous krypton and xenon by the helium during irradiation of the unclad fuel. The Ba^{140}, for example, was found in the charcoal trap where it would be expected if it had been carried as Xe^{140}. Comparing the release of fission products from the high temperature zone (Table 2) with that released from the fuel (Table 1), there was a slight decrease in the release of I, Te, and Cs, and a considerable decrease in the release of Sr, Zr, Ru, Ba, Ce, and U. Release of these latter fission products and uranium from the high temperature zone was generally less than 3%. This decrease in release values from fuel to high temperature zone is considered significant since during an actual reactor accident temperatures corresponding to those of the high temperature zone would probably occur only within the reactor containment.

The consequences of the increased helium flow in Experiments 10 and 11 appear to be a reduction in the release of the less volatile fission products caused by a reduction in temperature, and an increase in the release of these products from the high temperature zone because of the higher velocity of the sweep gas.

Characterization Studies of Released Fission Products

The distribution of fission products and uranium among the various regions in each experiment is being analyzed and interpreted in terms of the fractionation processes which govern the behavior of these materials. Fractionation refers to any alterations of the radionuclide composition occurring during the experiment which results in a sample composition different from that predicted for normal fission yields. Similar fractionation studies have been reported by Freiling in the study of debris from nuclear detonations.[6] Fractionation occurs because of differences in characteristics of the fission products leading to differences in release or deposition mechanisms. A study of fractionation, then, should lead to a better understanding of both the mechanisms and the characteristics. As an example of the type of data analysis which is being used in the fractionation studies, the ratio of Ba^{140}/Zr^{95} vs Sr^{89}/Zr^{95} is plotted in Fig. 2 for Experiment 7. The equation of the line empirically determined is shown. In this plot the abscissa may be regarded as a measure of the intensity of the volatilization conditions to which each sample, represented by a point on the plot, has been exposed. Since Sr^{89} is more volatile than Zr^{95}, points to the right represent samples with increasing amounts of volatilized Sr^{89}, for example, samples from cooler regions, while points to the left represent samples progressively depleted in Sr^{89}. The ordinate is a measure of the degree to which Ba^{140} volatilized for each volatilization condition on the abscissa.

Table 1. Material Released from the Fuel in UO_2 Melting Experiments (%)

Sample length, 1. in; diameter, 0.210 in; sample molten 5 min except Experiment 2, 10 min; helium flow, 400 cc/min, except Experiments 10 and 11, 800 and 4000 cc/min

Expt.	Sr^{89}	Zr^{95}	Ru^{106}	I^{131}	Te^{132}	Cs^{137}	Ba^{140}	Ce^{144}	UO_2
2	99.8	87.3	88.0				99.7	93.0	50.0
3	93.0	86.9	51.2				96.1	85.2	42.7
4	76.6	55.5	82.8	99.6			94.1	58.9	44.5
5	57.3	42.9	90.8	99.4	98.4	97.2	55.4	44.6	34.5
6	54.6	60.1	59.8	99.0	91.4	98.6	51.7	48.7	46.8
7	5.21	0.908	10.9	96.0		96.5	14.0	2.50	0.710
8	43.7	58.1	57.4	98.7	97.6	98.0	70.0	43.4	36.0
9	71.3	71.5	93.1	99.7	99.1	98.8	71.2	70.3	70.5
10	68.8	57.7		97.3	95.9	94.9	72.5	59.3	55.8
11	18.3	12.2	48.4	97.7	99.4	96.3	26.3	7.58	5.08

Table 2. Material Released from High Temperature Zone[a] of the Furnace in UO_2 Melting Experiments (%)

Expt.	Sr^{89}	Zr^{95}	Ru^{106}	I^{131}	Te^{132}	Cs^{137}	Ba^{140}	Ce^{144}	UO_2
2	20.1	0.115	2.84				14.5	0.508	4.08
3	1.24	0.110	0.614				0.732	1.78	0.0520
4	2.90	0.0465	6.60	94.5			0.941	0.651	0.773
5	1.44	0.0200	5.22	87.0	79.2	79.0	2.30	0.328	0.233
6	0.911	0.0896	1.32	94.3	48.8	81.9	0.547	0.0675	0.291
7	0.866	0.0370	2.15	49.7	11.5	74.1	0.576	0.322	0.00894
8	1.28	0.0508	1.73	95.4	81.4	87.5	0.824	0.244	0.0197
9	0.974	0.123	4.022	79.70	89.34	58.14	1.118	0.302	0.0128
10	2.119	2.819		89.46	71.45	79.73	2.837	1.003	0.289
11	2.93	0.568	0.198	89.0	69.5	86.4	8.01	1.24	1.64

[a] High-temperature zone includes fuel material and thermal insulation; minimum temperature, 1000°C.

Unclassified
ORNL-LR-DWG 75996

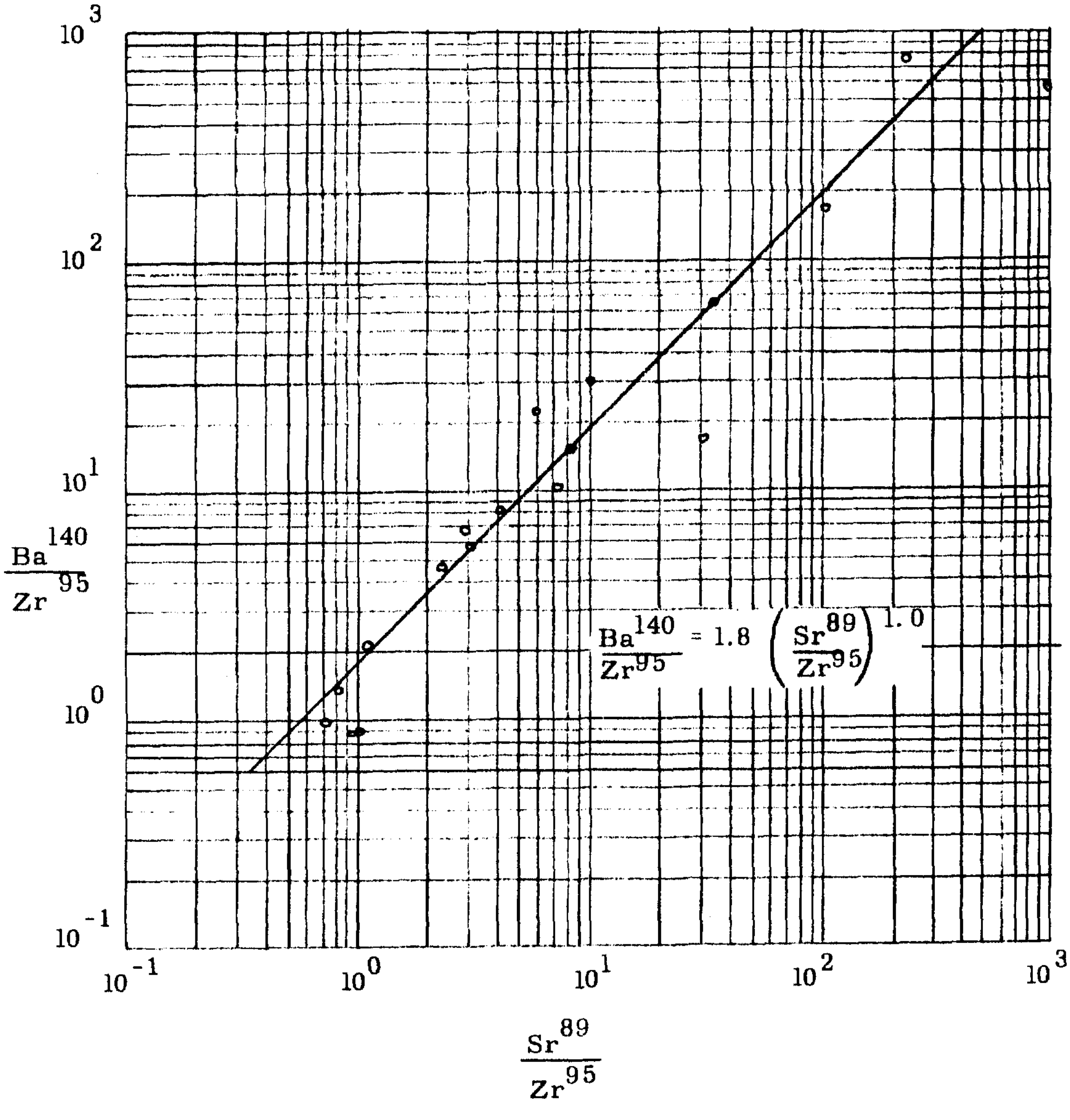


Figure 2 - Fractionation of Ba^{140} vs Sr^{89}

This plot indicates that Ba^{140} and Sr^{89} behave similarly and are both more volatile than the reference Zr^{95}. In a similar plot for Ru from Experiment 7, the slope is greater than unity, indicating that the Ru was more volatile than the Sr. In Experiment 8 the slope for Ru was unity indicating that its volatility was nearly the same as Ba^{140}. The difference in the slope probably represents a difference in the release mechanism since the fuel in Experiment 7 did not melt extensively while that in Experiment 8 did. One result of the fractionation studies is the conclusion that in several of these experiments, ruthenium follows the stainless steel cladding as the cladding melts into a puddle and subsequently vaporizes to other areas of the assembly. The mechanism for this is not yet known. However, it is anticipated that this work should lead to the formulation of models which explain the observed distributions and which may provide a basis for predicting the behavior, especially that in a controlled system of accident released fission products under various conditions. A knowledge of fractionation mechanisms will aid in the recognition of the relative importance of the various factors which define a reactor accident.

The characterization of released fission products by the diffusion tube method is being continued. Early results of this method were previously reported.[3]

In-Pile Burning of UC_2-Graphite Fuel

Three experiments have been conducted in the Oak Ridge Research Reactor at ORNL in which fuel specimens consisting of pyrolytic-carbon-coated uranium carbide particles embedded in a graphite matrix were burned at temperatures up to approximately 1400°C. In two of these experiments, fission and gamma heat produced a sufficiently high temperature for a large portion of the fuel to burn during the 15-min. period in which air was supplied as the sweep gas. The method of running the experiment and the results of the first experiment were described previously.[3] The specifications for the specimen and pertinent experimental conditions are listed below:

Fuel Specimen	
Particles	Uranium Carbide spheres 175-250μ Laminar pyrolytic-carbon coating 75-100μ thick
Matrix	Graphite
Manufacturer	Minnesota Mining and Manufacturing Company
Dimensions	0.6-in. bushing, 0.5 in. long with 0.25-in. axial hole
Uranium content	8 to 10 wt. % natural uranium
Burning Conditions	
Initial temperature	890°C
Combustion temperature	Up to 1400°C
Air flow rate	400 cm^3/min
Burning duration	15 min

As the graphite matrix burned, some of the fuel particles fell away from the unburned fuel. Metallographic examination of these particles and those in the unburned fuel showed that the damage to particles ranged from none to complete destruction of the coating and oxidation of the uranium carbide; however, it was not possible to determine the percentage of particles which belong in these categories. Some of the particles which remained in the unburned fuel also showed cracks. In Experiment 1, a count of the damaged and undamaged particles in the exposed surface of the fuel showed that about 45% of the particles had at least one crack in the coating. Experiment 2 was discarded without obtaining radiochemical analyses because the low uranium content of the specimen made a comparison with the other burning experiment impossible.

The results of Experiment 3, for the most part, confirmed the conclusions from Experiment 1. In the first experiment,[3,7] 58% of the specimen burned as compared with 41% in the third. In the third experiment, most of the uranium carbide in the specimen was concentrated on one side, and this side burned very little; 93% of the uranium found by analyses was in the unburned fuel.

The release of Sr, Zr, Ba, Ce, and U from the high-temperature zone of the furnace was very low, but large fractions of I, Te, and Cs were released. Forty percent of the Ru was released from the furnace in Experiment 1 and 5.7% in Experiment 3. The loss of ruthenium in the first experiment was probably due to the formation of volatile oxides. A large fraction of some of the fission products was probably retained inside those particles with undamaged pyrolytic-carbon coatings, especially those in the unburned fuel. Determination of the release of krypton and xenon was omitted to avoid collecting oxygen in liquid-nitrogen cooled charcoal absorbers. The following conclusions, based on Experiments 1 and 3, can be made:

1. Strontium, barium, zirconium, and cerium were retained where they are formed.

2. The unburned fuel retained 88 to 97% of the iodine associated with the uranium of the unburned fuel.

3. The following were released from the high temperature zone of the furnace: 15 to 25% of the I, 15 to 25% of the Te, and 35 to 40% of the Cs.

4. The release of ruthenium varied between 5 and 40%.

5. An appreciable amount of Cs (10% of total), Ru (1%), and I (1.5%) penetrated the filter, but Te was retained by the filter.

6. The fragments which fell away from the specimen during burning contained the same percent of carbon as the unburned fuel.

7. The side of the specimen with the least amount of uranium carbide burned more rapidly than other portions.

The results of both melting and burning in-pile experiments show that, although large fractions of the fission products were released from the fuel, they were almost entirely retained inside the high temperature zone of the furnace with the exception of iodine, cesium, and tellurium; if oxygen is present, ruthenium is also released. The noble gases appear to be released completely. These results suggest that for the conditions tested, effective retention of many fission products may be expected by high temperature surfaces near the hot zone in reactor accidents. Of the fission products released from the high temperature zone, significant fractions were carried as particles as small as 20 to 30A° in diameter. This work is being continued with emphasis being placed on the effects of the conditions of reactor accidents on the amounts and forms of released fission products.

Table 3. Fission Products and Uranium from In-Pile Burning Experiments

	Material Found (Percentage of Total in Assembly)								
	Sr^{89}	Zr^{95}	Ru^{106}	I^{131}	Te^{132}	Cs^{137}	Ba^{140}	Ce^{144}	U
Unburned fuel[a]									
Experiment 1	50.6	58.2	27.0	59.7	47.6	38.1	51.7	54.8	61.9
Experiment 3[b]	75.4	83.9	87.0	82.4	76.1	39.1	84.9	85.3	93.9
Outside of fuel residue[c]									
Experiment 1	13.8	3.7	48.2	28.9	42.7	51.3	14.5	9.05	2.12
Experiment 3	13.1	5.04	8.81	16.5	23.2	54.5	6.96	6.98	0.877
Retained in furnace									
Experiment 1	98.8	99.5	59.3	73.2	64.9	63.0	99.5	93.8	99.6
Experiment 3	98.7	98.7	94.3	85.6	85.7	58.4	99.3	97.1	99.8

[a] 58.6% of the sample was burned in Experiment 1 and 41% in Experiment 3.

[b] Experiment 2 was not analyzed because of low uranium content in the specimen.

[c] Fuel residues include the unburned portion of the specimen, fuel particles and powder, and the floor of the combustion furnace.

References

1. W. E. Browning, Jr., et al., Nuclear Safety Program Semiannual Progress Report June 30, 1962, ORNL-3319, pp. 29-38.

2. W. E. Browning, Jr., et al., Reactor Chemistry Division Annual Progress Report January 31, 1962, ORNL-3262, pp. 172-76.

3. W. E. Browning, Jr., et al., Nuclear Safety Program Semiannual Progress Report December 31, 1962, ORNL-3401, pp. 27-35.

4. W. E. Browning, Jr., et al., Nuclear Safety Program Semiannual Progress Report June 30, 1963, ORNL-3483, pp. 22-26.

5. W. E. Browning, Jr., et al., Reactor Chemistry Division Annual Progress Report January 31, 1963, ORNL-3417, pp. 236-243.

6. E. C. Freiling, Science 3, 1991-8 (1961).

7. W. E. Browning, Jr., et al., Gas-Cooled Reactor Monthly Progress Report September 1962, ORNL-3372, pp. 256-59.

DISCUSSION AND COMMENT

Variations of release in steam atmosphere would be expected. The variations in release mechanisms and particle sizes would probably occur when oxygen would be introduced. There are no future plans for carbide fuels. A later paper will describe diffusion tube separation of particles produced by melting fuels. Release in a water environment will be studied at a later date.

Session Chairman: The paper "Current Studies of Fission Product Behavior at BNL," by A. W. Castleman, Jr., and F. J. Salzano will be delivered by Mr. Lee Gemmell of that Laboratory's Health Physics Division. We regret that neither of the authors can be present; however, Mr. Gemmell is an able proxy.

CURRENT STUDIES OF FISSION PRODUCT BEHAVIOR AT BNL

by

A. W. Castleman, Jr. and F. J. Salzano
Brookhaven National Laboratory
Upton, New York

INTRODUCTION

Programs are under way at Brookhaven National Laboratory to study the behavior of fission products released from reactor fuel materials. Major emphasis has been placed on fission-product iodine because of the physiological hazard associated with the I^{131} isotope.

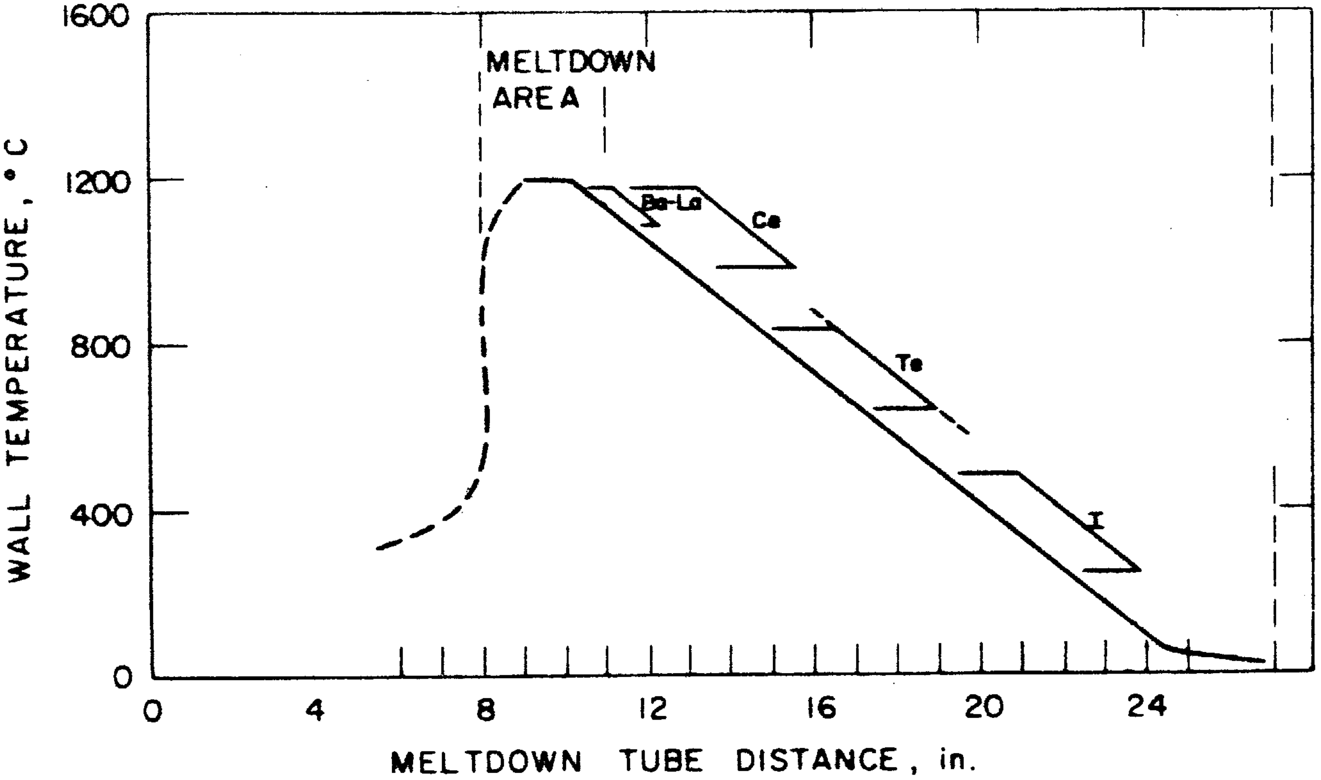
A complete reactor safety analysis, considering either a slow or rapid release of fission products, requires a knowledge of the chemical and physical states of the fission products during release, the extent of their release, and an understanding of their chemical interactions with the reactor environment.

RELEASE OF FISSION PRODUCTS FROM URANIUM AT HIGH TEMPERATURES

An extensive research effort has been carried out at BNL and other laboratories in the last few years for the purpose of studying fission product release rates from fuel elements. However, the subject is complex and not yet sufficiently understood. The purpose of the BNL work is, first, to develop a fundamental understanding of the fission product release mechanism; and second, to investigate the various factors which govern their physical and chemical behavior during and after release. It is expected that a detailed study of release from various reactor fuels under inert, oxidizing, and reducing conditions will provide data which can be used to predict fission product behavior in systems which have not been experimentally investigated.

The studies reported here are concerned with fission product release from metallic U and a U -3.5% Mo alloy into inert (He), oxidizing (air), and reducing environments. The experimental techniques have been previously described.(1,2) The fission products released into He and air were separated by condensing them (or their compounds) at different temperatures in a quartz tube, whose temperature decreased with length. The release of iodine into He and air from samples heated to temperatures between 1150° and 1250°C was studied in detail. Recently, preliminary results were obtained at temperatures up to 1800°C. These results are reported herein.

Most of the iodine released from U into He at temperatures between 1150° and 1250°C was in some combined form as evident from its deposition temperature zone shown in Fig. 1. (The condensation zone of other fission products is shown for com-



FISSION PRODUCT DEPOSITION URANIUM-He

Figure 1

parison.) Elemental iodine is quite volatile and would not condense at such high temperatures (250° to 350°C). This is also borne out by the work of Hölemann and Braun(3) who studied the adsorption of microgram quantities of iodine on quartz surfaces in the temperature range 150° to 1000°C. Using their values, less than 3% of the iodine which deposited at 300°C could be attributed to adsorption, even assuming rapid equilibrium with the quartz surface. The iodine condensation was found to depend only on temperature, as evidenced by the fact that quartz, gold, and stainless steel surfaces behaved the same.

The released iodine from both metallic U and a U -3.5% Mo alloy was found to be identical in nature. This is consistent with thermodynamic estimates which show that molybdenum iodides are unstable under the conditions of a fuel meltdown. The above iodine release results were the same for fuels irradiated over the range of 3.0×10^{14} to 5.4×10^{19} nvt, showing that within this range there was no concentration dependence.

Two possible explanations could be offered for the observed iodine behavior:

1. Chemical combination with uranium.
2. Chemical combination with another fission product.

Considering the second, no other fission product was consistently associated with the iodine in its deposition zone. If the released iodine had formed a compound with some other fission products, CsI would be the most likely possibility, on the basis of free energy of formation values and on relative concentrations. The chemical activity of the Cs, however, is so low compared to that of the uranium, that the iodine is converted almost quantitatively to a uranium iodide. About 90% of the released Cs deposited in the temperature range 600° to 800°C, while the quantity deposited in the iodine zone was a function of run-time and gas-flow rate. Undoubtedly, some reaction between the iodine compound and Cs occurs in the cell after release from the fuels with the higher burnups. The iodine deposit was found to be unstable in air at 250° to 350°C, elemental iodine being slowly released. CsI is quite stable in air at these temperatures; uranium iodides, however, are unstable in air and would release elemental iodine to a flowing air stream as observed.

On the basis of these results, as well as thermodynamic and kinetic considerations, the released species is uranium iodide, probably UI_2. Approximately the right concentration of U was found in the deposition zones, but a definite ratio of U/I has not yet been established.

Preliminary results at 1800°C show that considerably more elemental iodine is released than at 1250°C. This would be expected, since the uranium iodides are less stable at the higher temperature.

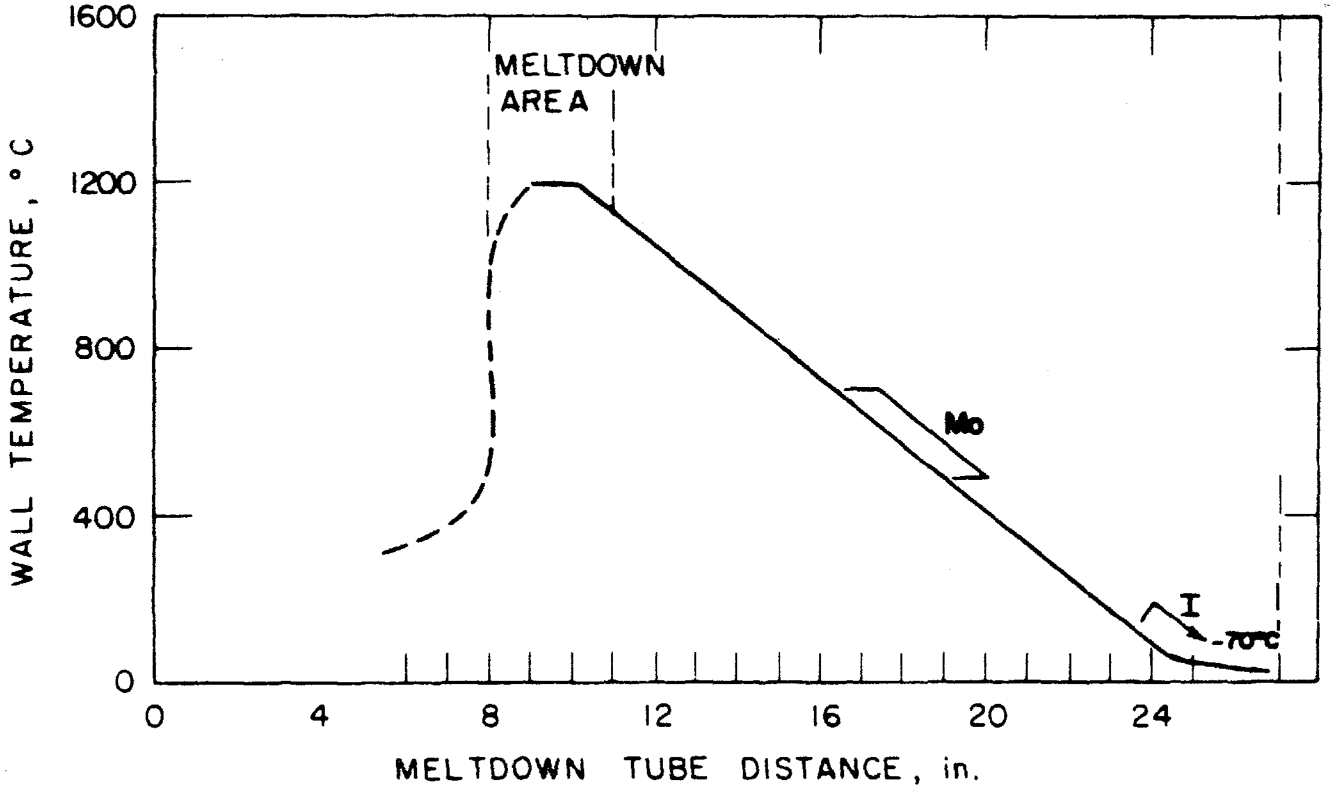
The deposition behavior of fission products released into air is shown in Fig. 2. In contrast to the He results, elemental iodine rather than a uranium iodide is released from U heated to 1200°C in air. These results are summarized in Table I.

Iodine Reactions

Atmosphere	Reaction	Temperature
He	$U + 2I \longrightarrow UI_2$	1200°C
	$UI_x(\text{ads.}) + O_2 \longrightarrow UO_2I_2 + I_2$ $UO_2I_2 \longrightarrow UO_2 + I_2$	ambient
Air	$3U(I) + 4O_2 \longrightarrow U_3O_8 + I$	1200°C

Table I

Another series of experiments was undertaken to study the chemical state of iodine released from U into steam at temperatures between 1000° and 1320°C. Since hydrogen is evolved during the oxidation of the U, the fission products are re-



FISSION PRODUCT DEPOSITION URANIUM-AIR

Figure 2

leased into a reducing medium. Some of the competing reactions associated with the iodine release are shown below.

(1) $U(F.P.) + 2H_2O \rightarrow UO_2 + 2H_2 + F.P.$

(2) $H_2 + 2I \rightleftarrows 2HI$ (Vapor phase)

(3) $I_2 + H_2O \rightleftarrows HIO + I^- + H^+$ (Aqueous phase)

(4) $3IO^- \xrightarrow{\Delta} IO_3^- + 2I^-$ (Aqueous phase)

Reaction (1) is the over-all reaction which liberates H_2 and fission products. The reaction between H_2 and iodine is shown in reaction (2). Although HI is relatively unstable with respect to molecular iodine and hydrogen, it is quite stable with respect to atomic iodine which is released from the U in steam. HI is very soluble in water and readily dissolves upon formation. Some elemental iodine dissolves in water according to reaction (3), but this is separated as elemental iodine and not collected as iodide ions in the analytical procedure.

Typical results of the release from metallic U at 1200°C are shown in Table II. Greater than 90% of the released iodine was collected as iodide ions. Essentially no difference in the iodine chemical state was found by varying the fuel temperature within the range 1000° to 1320°C. The pH of the water initially charged to the release cell was varied between 5.9 and 6.8; however, this had no apparent effect on the chemical state of the released iodine. The chemical state of the iodine is evidently a function of residence time after release, and depends primarily on subsequent chemical reactions, i.e., the

Table II

Iodine Release - Steam, Uranium System (1200°C)

Species	Average Percent
I°	8.7
I^-	90.9
IO_3^- IO_4^-	0.4

hydrogen-iodine reaction kinetics. Less than 1/2% of the iodine was collected as IO_3^-, which is formed by the high temperature disproportionation of IO^- [reactions (3) and (4)].

BEHAVIOR OF IODINE ON GRAPHITE

Graphite is used as a moderator and fuel-matrix material in power reactors. In advanced types of high-temperature gas-cooled reactors it performs both functions. In such reactors, certain fission products, including iodine, will be released even during normal operation. These will be, to a certain extent, adsorbed on the fuel and any other graphite components. Therefore, it is important to understand and be able to predict the behavior of iodine in contact with graphite, i.e., the adsorption behavior and possible reactions with the bulk graphite.

Some preliminary results of the behavior of iodine on a reimpregnated graphite have been reported.(4) The adsorption of iodine was studied by using I^{131} tracer with a scintillation scanning probe. The techniques and procedure used in the present study are the same as those previously described.(4) The purpose of this report is to present a summary of the final results and conclusions.

The object of the study was to measure the adsorption of iodine on TSX graphite, a high-purity material. Initial studies(5) indicated considerable variation in the adsorption behavior of iodine on what was thought to be similar graphites. The adsorption behavior of iodine on this pure polycrystalline graphite was investigated over the temperature range of interest (100° to 800°C) in reactor systems. Moreover, certain variables, in addition to temperature and pressure, which could affect the adsorption behavior of iodine were studied. The other variables were (a) outgassing temperature, (b) heat treatment, and (c) contact with water vapor at 900°C. Since it has been established by several investigators(6-9) that there is no reaction of pure iodine and bulk graphite at temperatures up to 1000°C, one is only concerned with adsorption phenomena. Iso-

Table III

TABLE OF EXPERIMENTS

BEHAVIOR OF IODINE ON TSX GRAPHITE

1 Sample	2 Surface Area by Nitrogen M^2/g	3 Surface Area by Iodine Adsorption at 100°C M^2/g	4 Outgassing Temperature °C	5 Treatment	6 Experimental Procedure
C	0.38	0.24	2000	Outgassed at 2000°C. Exposed to air and reoutgassed in the equilibration capsule at 900°C	800°C Isotherm measured 500°C One point obtained at 1 mm Hg 100°C Isotherm measured
D	0.33	0.36	2000	Outgassed at 2000°C. Exposed to air and reoutgassed in the equilibration capsule at 900°C	800°C Isotherm measured 500°C Isotherm measured 100°C Isotherm measured
E	0.28	0.22	900	Outgassed in the equilibration capsule at 900°C	800°C Isotherm measured 500°C Isotherm measured 100°C Isotherm measured 200°C Isotherm measured
F	0.31	0.24	900°C	Equilibrated with 23 mm Hg H_2O vapor at 900°C, then outgassed at 900°C	800°C Isotherm measured 500°C Isotherm measured 200°C Isotherm measured 100°C Isotherm measured
G	Not measured	0.23	200°C	Outgassed in the equilibration capsule at 200°C	100°C Isotherm measured 200°C Isotherm measured

therms were measured at 100°, 200°, 500°, and 800°C over the pressure range 0.010 to 15 mm Hg.

RESULTS

A series of five graphite samples was studied. For the purpose of discussion they are given the letter designations C, D, E, F, and G. The surface area of each sample, as measured with nitrogen at -195°C, is given in Table III, along with the outgassing temperature and sample treatment.

The data obtained on iodine adsorption at 800°C for samples C, D, E, and F are shown in Fig. 3. The largest adsorption took place on sample C which was heated to the highest temperature, 2000°C (2150°C maximum), while the least adsorption took place on sample E which was heated to the lowest temperature, 900°C. The results from samples D and F, which were outgassed at 2000°C (2030°C maximum) and treated with water vapor at 900°C, respectively, fell between those from C and E.

The data obtained at 800°C can be adequately expressed by the Freundlich equation

$$Q = Kp^n$$

where Q is the quantity of iodine adsorbed in ppm, p is the pressure in mm Hg, and K and n are constants which depend on temperature and the nature of the adsorbing surface. In the table shown in Fig. 4, are listed the values of K and n obtained. As K decreases the value of n increases.

The data obtained on the adsorption of iodine at 500° and 200°C are shown in Fig. 4 and 5. The same co-ordinates are plotted as in Fig. 3. At these temperatures, the data no longer give a linear relationship. The isotherms are not similar in shape and show abrupt changes in slope. A consistent feature of the data is the relative positions of the adsorption isotherms, i.e., that sample which gave the highest adsorption at 800°C also showed the highest adsorption at 500° and 200°C. Neither the 500° nor the 200° data can be fitted by any of the common isotherm equations. From Table III, it can be seen that

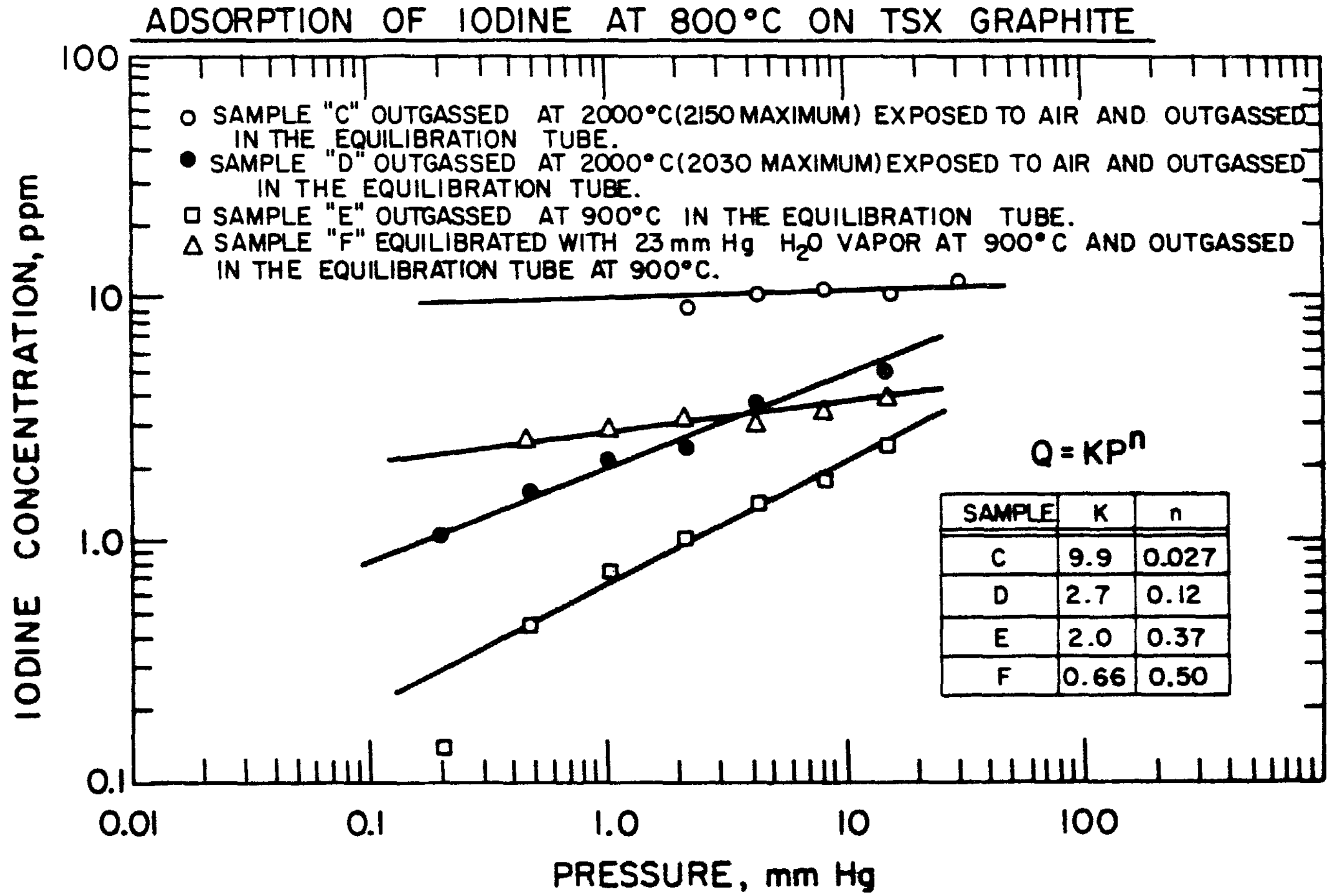

ADSORPTION OF IODINE AT 800°C ON TSX GRAPHITE
○ SAMPLE "C" OUTGASSED AT 2000°C (2150 MAXIMUM) EXPOSED TO AIR AND OUTGASSED IN THE EQUILIBRATION TUBE.
● SAMPLE "D" OUTGASSED AT 2000°C (2030 MAXIMUM) EXPOSED TO AIR AND OUTGASSED IN THE EQUILIBRATION TUBE.
□ SAMPLE "E" OUTGASSED AT 900°C IN THE EQUILIBRATION TUBE.
△ SAMPLE "F" EQUILIBRATED WITH 23 mm Hg H_2O VAPOR AT 900°C AND OUTGASSED IN THE EQUILIBRATION TUBE AT 900°C.
$Q = KP^n$
SAMPLE | K | n
C | 9.9 | 0.027
D | 2.7 | 0.12
E | 2.0 | 0.37
F | 0.66 | 0.50
IODINE CONCENTRATION, ppm
100
10
1.0
0.1
0.01
0.1
1.0
10
100
PRESSURE, mm Hg

Figure 3

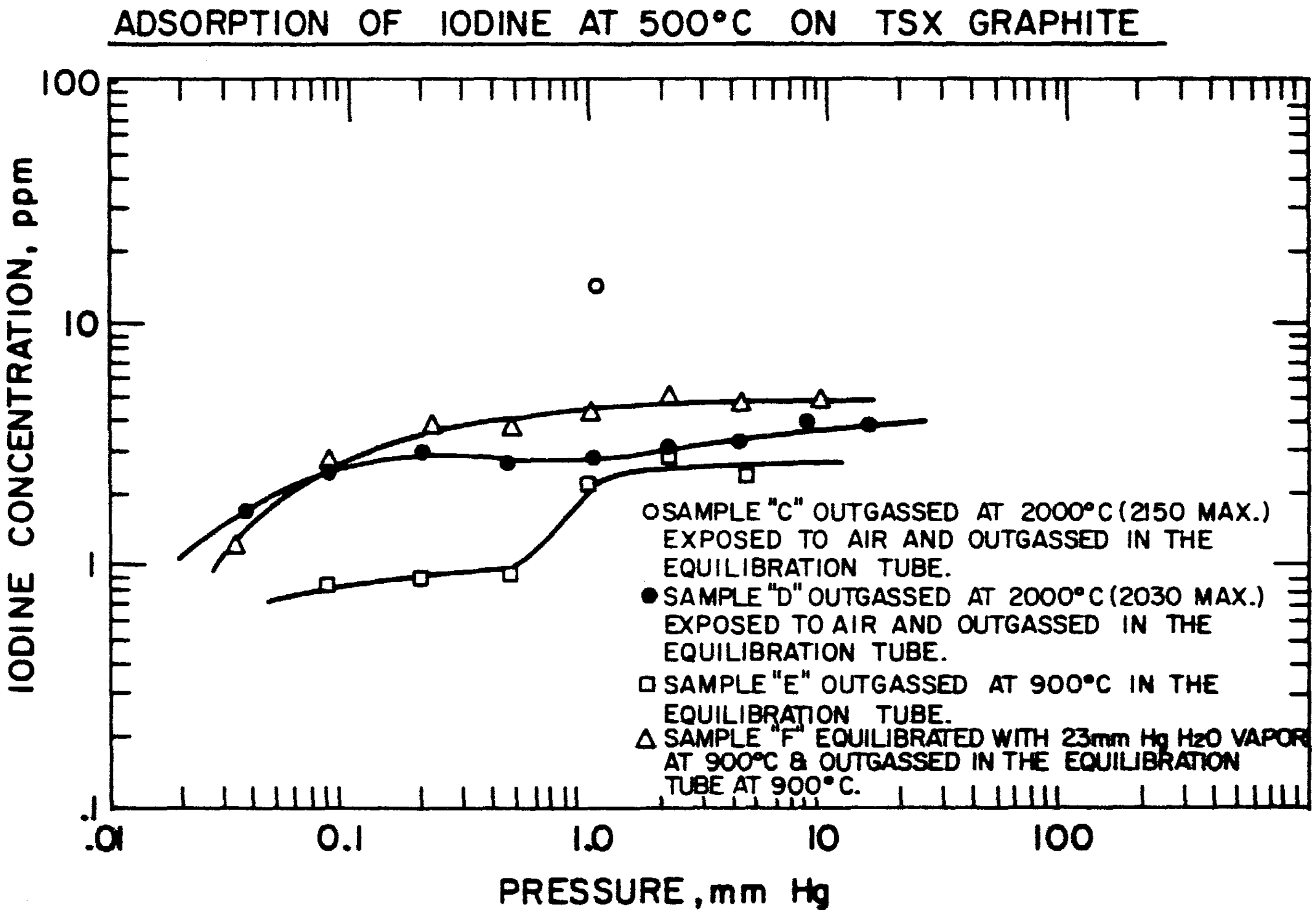

ADSORPTION OF IODINE AT 500°C ON TSX GRAPHITE
IODINE CONCENTRATION, ppm
100
10
1
.1
.01
0.1
1.0
10
100
PRESSURE, mm Hg
○ SAMPLE "C" OUTGASSED AT 2000°C (2150 MAX.) EXPOSED TO AIR AND OUTGASSED IN THE EQUILIBRATION TUBE.
● SAMPLE "D" OUTGASSED AT 2000°C (2030 MAX.) EXPOSED TO AIR AND OUTGASSED IN THE EQUILIBRATION TUBE.
□ SAMPLE "E" OUTGASSED AT 900°C IN THE EQUILIBRATION TUBE.
△ SAMPLE "F" EQUILIBRATED WITH 23mm Hg H2O VAPOR AT 900°C & OUTGASSED IN THE EQUILIBRATION TUBE AT 900°C.

Figure 4

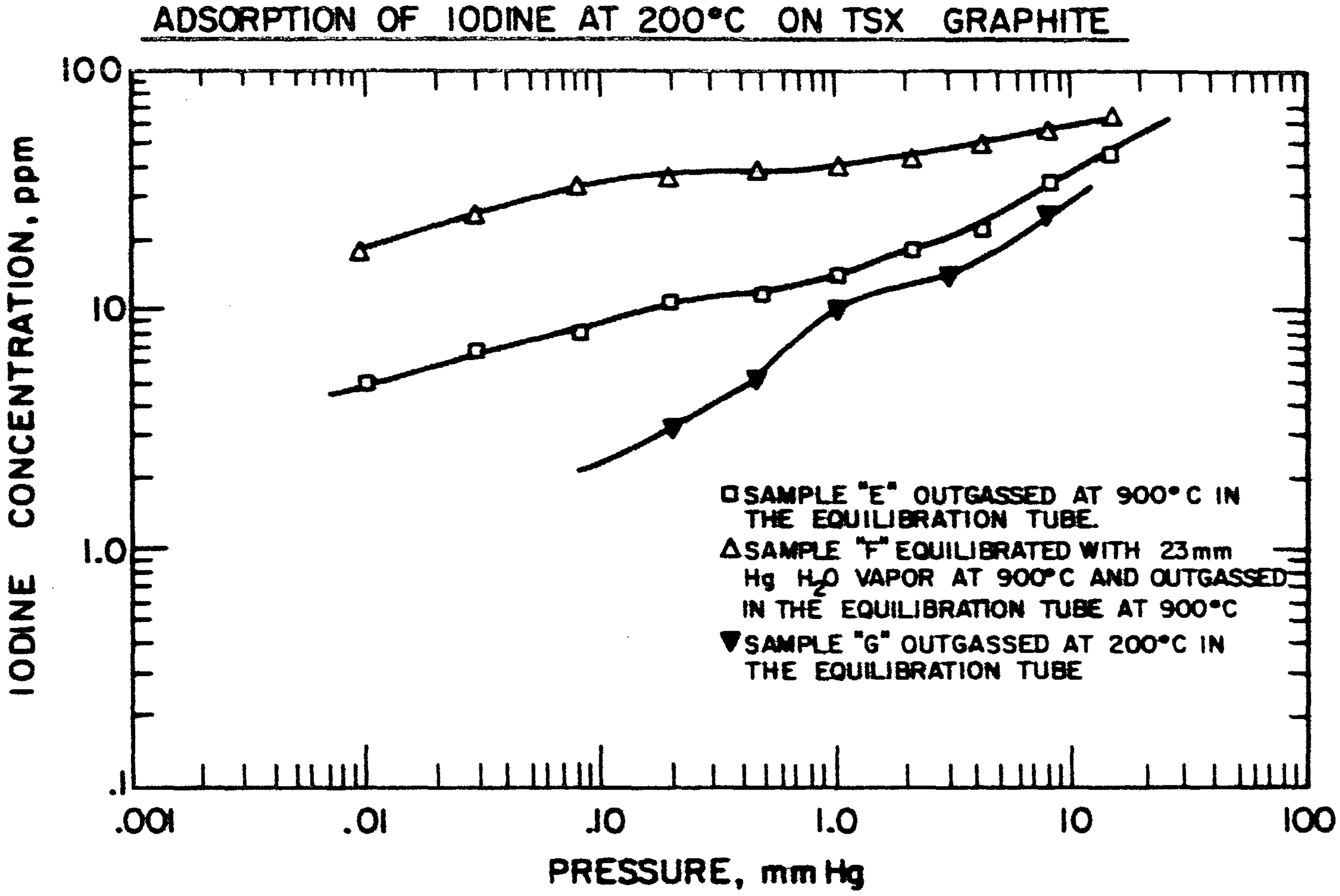

ADSORPTION OF IODINE AT 200°C ON TSX GRAPHITE
IODINE CONCENTRATION, ppm
100
10
1.0
.1
.001
.01
.10
1.0
10
100
PRESSURE, mm Hg
□ SAMPLE "E" OUTGASSED AT 900°C IN THE EQUILIBRATION TUBE.
△ SAMPLE "F" EQUILIBRATED WITH 23 mm Hg H_2O VAPOR AT 900°C AND OUTGASSED IN THE EQUILIBRATION TUBE AT 900°C
▼ SAMPLE "G" OUTGASSED AT 200°C IN THE EQUILIBRATION TUBE

Figure 5

there is no relation between surface area and iodine adsorption, since the surface areas of the samples were similar.

The data obtained at 100°C are shown in Fig. 6. They fall into two distinct isotherm groups, which appear to merge at about a pressure of 2 mm Hg. At low pressures, the isotherms differ by an order of magnitude. The samples outgassed at 2000°C and the sample treated with the water vapor are included in the higher isotherm, while the samples outgassed at 200° and 900°C are included in the lower isotherm.

Utilizing B.E.T. theory,(10) it is possible to calculate the monolayer coverage on the graphite and therefore its surface area. The surface area values obtained for all the samples are shown in the third column of Table III and show excellent agreement with each other, and with the exception of sample D, are within 5% of the mean. These values compare well with the surface area values obtained with nitrogen at -195°C which are listed in the second column of the table.

DISCUSSION

The adsorption of iodine on graphite at 200°, 500°, and 800°C was found to vary with outgassing temperature, heat treatment, and contact with water vapor at 23 mm Hg. None of the above treatments was found to affect appreciably the surface area of the graphite. There was no relation between surface area and the quantities of iodine adsorbed. These facts, and the fact that the iodine could not be completely removed by reducing the partial pressure to zero, indicate that iodine is wholly or partially chemisorbed at these temperatures. P. Connor et al.(11) have investigated the adsorption of iodine on a graphite powder up to 400°C and found evidence for at least partial chemisorption in the fact that adsorption of hydrogen reduces the subsequent adsorption of iodine by approximately a stoichiometric amount.

More direct evidence for chemisorption would be the magnitude of the heat of adsorption. Calculated values of the

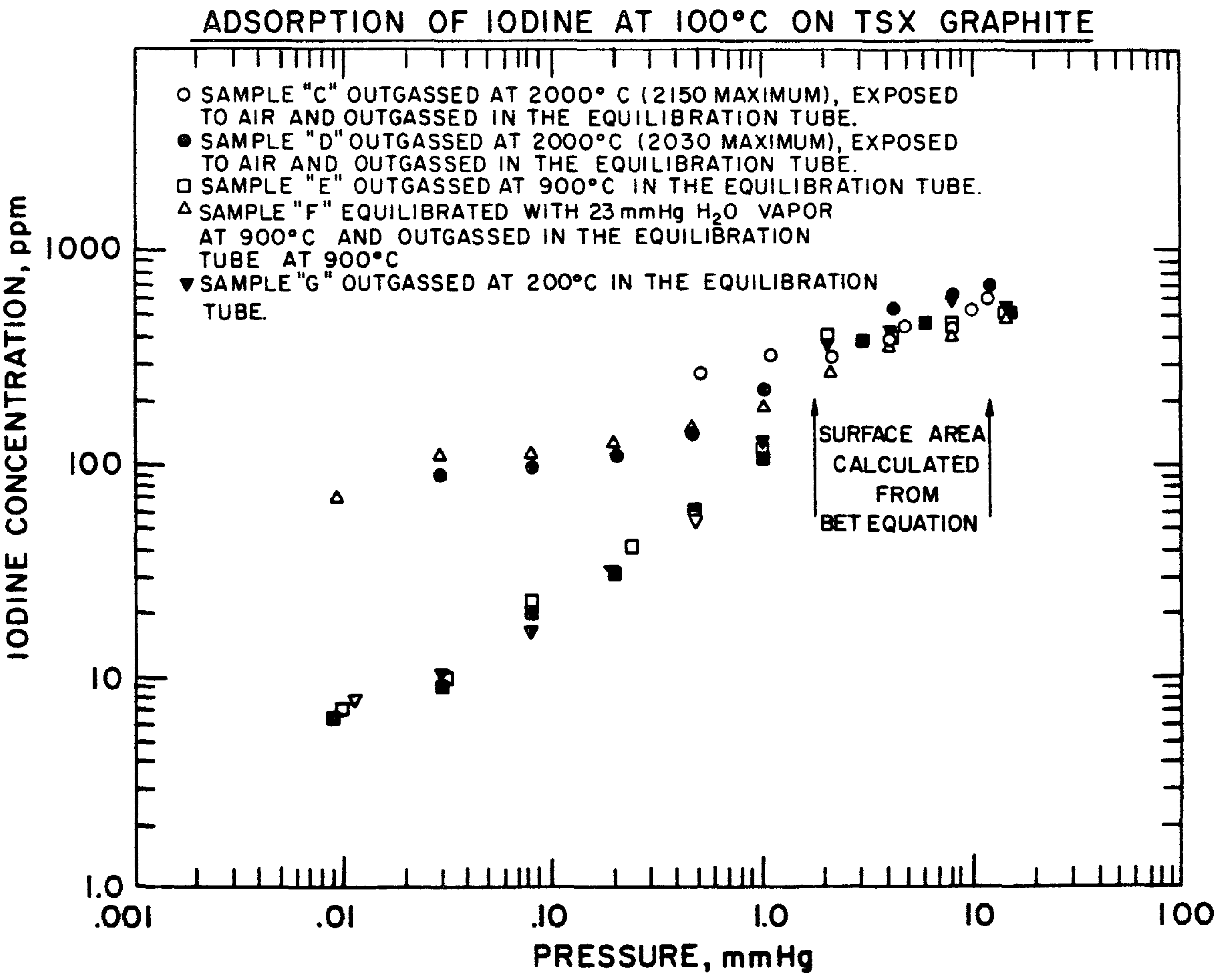

ADSORPTION OF IODINE AT 100°C ON TSX GRAPHITE
○ SAMPLE "C" OUTGASSED AT 2000° C (2150 MAXIMUM), EXPOSED TO AIR AND OUTGASSED IN THE EQUILIBRATION TUBE.
● SAMPLE "D" OUTGASSED AT 2000°C (2030 MAXIMUM), EXPOSED TO AIR AND OUTGASSED IN THE EQUILIBRATION TUBE.
□ SAMPLE "E" OUTGASSED AT 900°C IN THE EQUILIBRATION TUBE.
△ SAMPLE "F" EQUILIBRATED WITH 23 mmHg H_2O VAPOR AT 900°C AND OUTGASSED IN THE EQUILIBRATION TUBE AT 900°C
▼ SAMPLE "G" OUTGASSED AT 200°C IN THE EQUILIBRATION TUBE.
SURFACE AREA CALCULATED FROM BET EQUATION
IODINE CONCENTRATION, ppm
1000
100
10
1.0
.001
.01
.10
1.0
10
100
PRESSURE, mmHg

Figure 6

heat of adsorption from the measured data are not significant, owing to the flatness of the isotherms. Calculation of the isosteric heat of adsorption from isotherm data previously reported,(4) in the temperature range 200° to 450°C,* indicates that at low surface coverage the isosteric heat of adsorption was as high as 40 kilocalories per gram mole and decreased and approached the heat of vaporization (10.6 kilocalories per gram mole) at high surface coverage. Estimates of the heat of chemisorption of iodine on graphite, based on the strength of the carbon-iodine bond, indicate the heat of adsorption to be in the order of 44 kilocalories per gram mole when the iodine is chemisorbed as monoatomic iodine. Therefore, the value of 40 kilocalories per gram mole obtained in this study indicates the iodine to be chemisorbed at low surface coverages.

In the case of the 100°C isotherms there are no significant differences between the samples outgassed at 200° and 800°C. However, there is a considerable difference between these and samples outgassed at 2000°C and that treated with water vapor, though the surface areas of the samples are similar. The fact that the isotherms converge at 2 mm Hg and the fact that the surface areas calculated from the iodine adsorption are similar to the values obtained with nitrogen at -195°C over the same relative pressure range, indicate that at 100°C, above 2 mm Hg, iodine is held on the graphite by physical multimolecular adsorption.

In general, the difference between the high iodine adsorption on samples C, D, and F relative to sample E and G is due to the production of new chemisorption sites during the 2000°C outgassing and the treatment with water vapor. These sites are created by removal of surface carbon atoms, without altering appreciably the original surface area. These treatments apparently change the nature and number of the adsorption sites, as well as the distribution of energies among the sites.

Information which could be used to predict iodine adsorp-

---

*Graphite Specialties Company, R-4 graphite tion on graphite in a reactor core, either during normal operation or after accidental release of fission products, would be of value to those concerned with reactor safety. Such information can enable one to estimate the extent of iodine adsorption in the core, if its partial pressure were known. Because of the variable nature of the graphite surface and its sensitivity to various environmental conditions, this becomes, however, a very uncertain prediction. However, since a good estimate is better than none at all, it is suggested that the following relation be used to estimate iodine adsorption in a graphite reactor core:

$$Q = 3.2 \times 10^{-4} \frac{e^{20,000/RT}}{T^{1/4}} P^{1/2} ,$$

where Q is the quantity adsorbed in ppm, T is the absolute temperature, R is the gas constant, and P is the partial pressure of the iodine in mm Hg. The above is the low-pressure form of the Langmuir equation for adsorption of a diatomic gas which dissociates on a uniform adsorbing surface.(12) The constants in the equation are derived from the 800°C isotherm data obtained on the untreated TSX graphite (E), outgassed at 900°C. It should only be applied above the critical temperature of the iodine (553°C) and at pressures below 10^{-3} mm Hg.

REFERENCES

1. Castleman, A. W., Jr., "The Chemical and Physical Behavior of Released Fission Products," TID 7641, 3rd Conference on Nuclear Reactor Chemistry, October 1962.
2. Progress Report of Nuclear Engineering Department, BNL 799, Brookhaven National Laboratory, Jan. 1 - April 30, 1963.
3. Hölemann, P., Braun, A., Z. Physik Chem. 34, <u>5</u>, 381-95 (1936).
4. Salzano, F. J., "Summary of Fission Product Adsorption Work at BNL," Seventh AEC Air Cleaning Conference, held at BNL, Oct. 10-12, 1961, TID 7627 (March 1962).
5. Progress Report of Nuclear Engineering Department, BNL 696, Brookhaven National Laboratory, May 1 - August 31, 1961.
6. Hennig, G. R., J. Chem. Phys. 20, 1443 (1952).
7. Juza, R., Schmeckenbecker, A., Z. Anorg. u. Allgen Chem. 292, 46 (1957).
8. Herold, A., Bull Soc. Chem. France, 999, (1955).
9. Salzano, F. J., Prog. Rept. Nuclear Eng. Dept., BNL 659, p. 14, Sept. - Dec. 1960.
10. Young, D. M., Crowell, A. D., Physical Adsorption of Gases, Butterworths and Co., London, 1962.
11. Connor, P., Lewis, J. B., Thomas, W. J., The Adsorption of Iodine by Graphite, Proceedings of the Fifth Conference on Carbon 1962, Pergammon Press.
12. Trapnell, B. M. W., Chemisorption, London, Butterworths and Co., 1955.

DISCUSSION AND COMMENT

Session Chairman: Thank you, Mr. Gemmell. We realize that you are not prepared to enter into detailed discussion since you have not been associated with the fission product behavior study. We appreciate the fact that although you were primed to present the paper from the platform that you may not feel qualified to answer detailed questions.

Dr. Silverman: I am not certain this is going to be a fair question since you are filling in as a proxy, but the conclusions that Salzano drew that the iodines can absorb, and so on, are not new to us, but the data that he presented showing the measurement of surface area with nitrogen correlating so well with the measurement of surface area with iodine treatment has me puzzled, because we thought we had an excellent way to measure surface area using iodine adsorption, and yet when we tried to do this we found not monomolecular adsorption, but multiple molecular layers, and the correlation he showed us would contradict that conclusion. In fact I hope we were wrong and he is right!

Mr. Gemmell: Dr. Silverman's comments and question have been recorded. I regret very much that I am not sufficiently acquainted with the work to answer your problem. When I return to Brookhaven, I'll get in touch with Mr. Salzano and ask him to write a reply which will be included in the proceedings of the conference. In the meantime, we will contact Dr. Silverman by telephone and arrive at a mutually satisfactory answer. The authors of this paper have asked me to express their regrets for not being able to be here today.

Mr. Salzano: (Reply to Dr. Silverman's Question) The surface areas I measured were obtained from the 100°C isotherms. They were calculated from B.E.T. plots over the relative pressure range 0.04 to 0.30. If the temperature or relative pressure range were different than the above values the results might not agree with the nitrogen surface areas. I have not determined if this method works with other materials or at different temperatures.

Session Chairman: The last speaker during Session I is Mr. J. D. McCormack, of Hanford Atomic Products Operations, who has prepared a paper entitled, "Some Observations on Iodine Removal from Plant Steams with Charcoal."

SOME OBSERVATIONS ON IODINE REMOVAL FROM PLANT STREAMS WITH CHARCOAL

J. D. McCormack
General Electric Company
Hanford Atomic Products Operation
Richland, Washington

ABSTRACT

The performance of several large scale charcoal beds in radioiodine removal service is discussed. The efficiency of the beds was measured after service times of months to years, and appears to be related to the quality of the air being treated. Efficiencies of 99.9 per cent to nearly zero per cent were noted.

INTRODUCTION

Radioactive iodine must be effectively removed from air streams, which, through design or accident, may contain quantities of this isotope. Exhaust from fuel processing plants, reactor halls, and radiochemical laboratories must be treated to insure that iodine releases are minimal. The Federal Radiation Council recommended in 1961 that permissible concentrations for I^{131} in air be significantly lowered.(1) This ruling prompted even more restrictive limits to the quantity of I^{131} which could be safely released from large nuclear installations, and led to additional evaluations of existing and new iodine removal facilities.

Among the more common I^{131} removal systems are liquid scrubbers, silver reactors, and charcoal beds. While the scrubbers and silver reactors can be efficient iodine removers, charcoal beds are often favored because of their simplicity, compactness and efficiency.

Although very high I^{131} removal efficiencies may be demonstrated in the laboratory for fresh charcoal under a rather wide range of operating conditions, the proof of sustained efficiency must come through observations of the actual bed installation. Reduction in efficiency with time is a real possibility due to mechanical blinding of active centers with inert material, and to the eventual saturation of active centers by minute traces of unsuspected chemicals present, such as oil fumes and organic solvents. Another consideration which must be given attention is the potential that the iodine present in the stream may not be wholly molecular iodine. A charcoal showing 99.99 per cent removal of molecular iodine in controlled laboratory tests may conceivably be much less efficient on a plant stream. Less reactive species of I^{131} have been cited in the literature, but the physical and chemical nature of these forms have not been clearly revealed.(2,3)

Ten large scale charcoal beds have been operated at Hanford for periods ranging from a few months to several years. From 6000 to 100,000 cfm of air pass through these beds. Eight are part of the reactor confinement system, one is installed in a high level radiometallurgy laboratory, and one was more recently installed at a chemical separation plant (Redox) downstream from a high efficiency filter.

OBJECTIVE

It is the objective of this paper to present certain observations of the performance of these charcoal beds in service relative to I^{131} removal efficiency.

TESTING OF CHARCOAL SYSTEMS

Reactor Confinement Beds

The charcoal beds which treat the reactor building ventilation air are preceded by absolute filters. Their design was discussed in detail at the Seventh Air Cleaning Conference.(4) Perforated metal envelopes, containing test charcoal hung on the upstream face of the main 1-inch thick convoluted bed, were provided in the initial design to permit periodic checking of charcoal efficiency during service. The charcoal from these envelopes after a period in service is removed and repacked in 1-1/4-inch long by 7/16-inch-diameter beds. Filtered air containing I^{131} liberated by the evaporation of a carbon tetrachloride solution of iodine is drawn through the test coconut shell charcoal bed at a face velocity of 60 fpm. The test charcoal is followed with a similar cartridge of Pittsburgh BPL type activated carbon. This charcoal has been shown in previous tests to be a very efficient adsorber of molecular iodine. The I^{131} activity is determined by measurement of the 0.36 Mev gamma ray under conditions of constant counting efficiency. The iodine retention is then calculated as the ratio of the activity on the test cartridge to the sum of the activity on the test and the back-up cartridge. Table I shows the results of the laboratory retention measurement. The test charcoals had been exposed to the air stream for about one year. The "unexposed" charcoal standard, a sample of the original charcoal used in the installation, had been stored in a sealed glass jar.

TABLE I

IODINE RETENTION OF REACTOR CONFINEMENT CHARCOAL AFTER 1 YEAR OF EXPOSURE

Sample Location	% I^{131} Retained
B	99.8
C	99.7
D	99.8
DR	99.7
F	99.9
H	99.7
KE	99.6
KW	99.7
"unexposed"	100.0

The standard deviation of the tests, based upon the counting data, is about 0.07 per cent; hence, it can be seen that the deterioration of the charcoal is not highly significant.

Radiometallurgy Building Beds

The iodine removal charcoal beds used to treat 6000 cfm of hot cell exhaust air are quite similar to those just described and the testing was identical except that in this case one of the 2' × 2' modular beds was opened and the charcoal sample removed from the bed itself. Testing of this charcoal, which had been in service for over two years, showed a poor retention of molecular iodine. Because the grain size was larger than the previous charcoals which had been tested, and relatively large in relation to the 7/16-inch-diameter test cartridge, additional measurements were made with larger diameter test cartridges to check for wall effects. These results, and others, are shown in Table II, below.

TABLE II

RESULTS OF RADIOMETALLURGY BUILDING CHARCOAL TESTS

Test No.	Charcoal	% I^{131}* Retained	Comments
1	Exposed	58	As sampled.
2	Exposed	57	100 fpm; 7/8"-diameter.
3	Exposed	94	Abraded and washed.
4	Exposed	99.7	100 fpm; crushed to 14/20 mesh.
5	New	99.9	As sampled.

* Test bed was 7/16-inch-diameter × 1-1/4-inch long, with air flow of 60 fpm, unless otherwise noted under comments.

The sample of exposed charcoal definitely shows a low retention of the I^{131} vapors, as can be seen from test one, above. As noted, test two was made to check for wall effects. The results, similar to test one, show that wall effects were not important in the testing.

The loss of adsorptive capacity seems to be restricted to the surface of the charcoal grains, as shown by the increased retention on tests three and four. Indeed, the charcoal had a dull, dusty appearance. The presence of Sb^{125} activity could indicate some particle penetration of the high efficiency filters upstream of the charcoal. Either removal of the surface layer by mild abrasion and washing, or creation of new surfaces by crushing restores the efficiency of the charcoal to nearly that of new charcoal, shown in test five.

Separations Plant Bed

Earlier this year a charcoal bed was installed in the ventilation exhaust stream from the Redox plutonium separations plant. The location chosen was just downstream from the deep bed sand filter, through which pass all of the process building ventilating air and vessel vent air. Exhaust gases from the fuel dissolvers do not pass through the sand filter. Iodine appearing in the air entering the sand filter comes from tanks, columns, and process vessels at many points in the process and might be suspected of being associated with or in combination with other materials. An earlier study of charcoal capsules for measuring I^{131} in the total stack exhaust, which is made up of the sand filter stream and the treated dissolver off gases, showed that from 90 to 95 per cent of the iodine present would be trapped on charcoal during a 24-hour sampling period.(5) Although not as efficient as for wholly elemental iodine, the indicated efficiency was high enough to warrant the use of charcoal on the stream downstream from the sand filter.

The observed efficiency of the charcoal trap installed downstream of the sand filter has been very low. The sustained exposure to traces of organic vapors of hexone and degradation products appears to effectively block the I^{131} from adsorption sites although detailed causes are not known. As contrasted to the 95 to 99 per cent I^{131} efficiency for a 24-hour long sample drawn from the total exhaust through small charcoal capsules, the installed bed has a current efficiency of practically zero.

Some experiments were conducted to measure the loss of efficiency with time for a charcoal cartridge through which was drawn a long term sample of air taken upstream from the sand filter at Redox. An identical cartridge was operated in parallel on the same volume of air and replaced daily with a fresh charcoal cartridge. Results of these tests are shown in Figure 1. A face velocity of about 100 fpm was used.

These data show the progressive and rather complete loss of efficiency with time. The materials present in the stream explicitly responsible for this "poisoning" effect are not known at present.

Sampling of this stream does show that approximately one-half of the gaseous iodine is in a form not readily removed by caustic scrubbers, but is retained by fresh charcoal; that is, some form other than molecular iodine. This is in agreement with the finding of others.(6) The iodine which is retained by the charcoal seems firmly fixed and is not eluted through the bed by air and fluctuating concentrations of hexone vapors at room temperature. In addition, vacuum degassing of the charcoal at 100 to 200 C removed the hexone, but only a small amount of I^{131} -- say 10 per cent -- was removed. It seems, then, that the radioiodine is not chemically associated with the hexone vapors in the air stream. In our laboratory tests charcoal could be made inefficient when oil vapor was present. Hexone present did not materially reduce the initial efficiency. Long exposure studies were not conducted, however.

The efficiency of both new and exposed samples of the charcoal has been measured with molecular I^{131}. The efficiency of the exposed charcoal has also been measured in the Redox air stream with generated I^{131}. These results are shown in Table III.

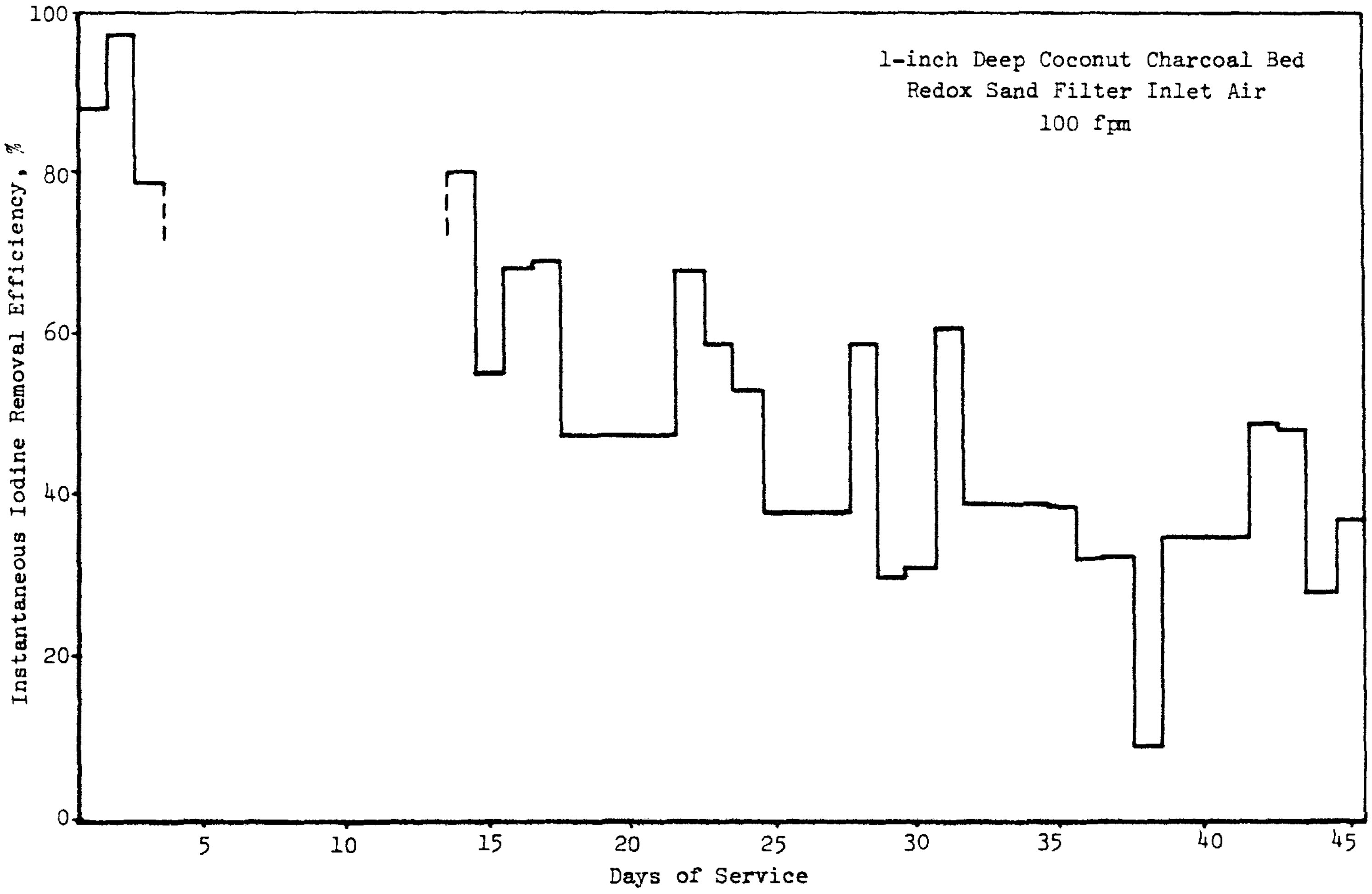
TABLE III

RESULTS OF REDOX BUILDING CHARCOAL TESTS

Test No.	Charcoal	% I^{131} Retention*	Comments
1	Unexposed	99.9	Filtered laboratory air.
2	Exposed	99.5	Exposed 15 days, eluted 23 days with air and 20 ppm hexone.
3	Exposed	86	Exposed 37 days, tested with generated I^{131} in process air.

* Charcoal beds were 7/16-inch diameter by 1-inch long with a linear flow of 100 fpm.

While the specific cause of the loss of efficiency has not yet been determined, the loss has been demonstrated to increase with time of exposure to the air stream.



<u>FIGURE 1</u>

<u>IODINE REMOVAL EFFICIENCY</u>

CONCLUSIONS

The efficiency of charcoal beds for iodine removal from air has been discussed as a function of length of service and complexity of the air composition. Beds in three types of installations were investigated. There seems to be a correlation between the retention of iodine removal efficiency and the quality of the air stream. Charcoal in the reactor building ventilation air, which can be thought of as clean air from a building which includes no chemical processing activities, showed no significant deterioration during one year exposure. Charcoal in service for over two years in a radiometallurgy lab showed loss of iodine retention, being only 58 per cent efficient under the test conditions. The air from the hot cell exhaust contains impurities generated from physical testing of irradiated fuel elements and from a small amount of chemical treatment of the specimens.

In the third application, in the process building ventilation air and vessel off-gas streams, charcoal lost its iodine removal efficiency during a period of a few weeks. This air stream contains organic and inorganic components arising from the routine processing of irradiated fuel elements.

The varying response of the charcoal behavior of these three filtered gas streams is some indication of the complex nature of iodine and the care that should be used in applying iodine adsorbing systems in real gas streams. In addition, the possible "poisoning" potential of trace components in the air being treated must be recognized. Because of this potential the performance of charcoal beds should be periodically monitored.

REFERENCES

(1) Federal Radiation Council. Protection Guidance for Federal Agencies; Memo for the President, Federal Register, September 26, 1961.

(2) C.W. Sill, J.K. Flygare, Jr. Iodine Monitoring at the National Reactor Testing Station. Health Physics, 2:261-268, February 1960.

(3) J.B. Morris, C.H. Romary. Tests on Absorbers for Iodine at Low Concentrations. AERE-R-4219. 1963.

(4) H.W. Heacock, C.E. Jones. The Hanford Reactor Confinement Program. Seventh AEC Air Cleaning Conference, Brookhaven, October 10-12, 1961. TID-7627, p. 284-308, March 1962.

(5) D. McConnon. Radioiodine Sampling with Activated Charcoal Cartridges. HW-77126. April 1963.

(6) G.K. Cederberg, D.K. MacQueen. Containment of Iodine-131 Released by the RALA Process. IDO-14566. October 1961.

DISCUSSION AND COMMENT

Although a caustic scrubber is not efficient for removal of iodine, remember that it has been treated in the plant with boost-over reactors. Silver reactors in the steam will remove some additional iodine. A charcoal bed behind the caustic scrubber will always pick up additional iodine, whereas a caustic scrubber behind a fresh charcoal bed will pick up essentially no additional iodine.

In the radio-metallurgical application upstream absolute filters preceded the charcoal. It was felt that in this series of results there was mechanical blockage of the carbon.

In the performance of a charcoal cleanup filter where primary coolant is released in steam into the containment, Savannah River has run numerous tests with activated carbon exposed to steam-air mixtures, as well as to steam. With new carbon it was found that the steam or steam-air mixtures, as long as they entrain water or a large fraction of it, is removed up-stream of the carbon filter, there is no adverse effect on the removal efficiency. Beds that are exposed to steam-air conditions until the carbon is essentially in equilibrium with the water vapor shows no adverse effects on iodine-removal efficiency. With exposure to normal rural air for as long as five months no adverse effects on the iodine-removal efficiency in steam-air mixtures. These results were reported in DP-778.

The UKAEA has been examining the performance of charcoal against iodine emissions from irradiated fuel under a variety of conditions and one of the species of iodine identified was methyl iodide. The performance of charcoal against methyl iodide appears to be somewhat complex but the salient point so far resolved is that up to a certain loading of methyl iodide, which is rather low, of the order of a few μg/g charcoal there is virtually complete retention; beyond this penetration increases and reaches high percentages.

There was no specific information regarding HAPO iodine concentrations in off-gas streams in respective loadings when decreasing efficiencies were observed; however, the iodine concentrate streams were low.

SESSION CHAIRMAN: These three papers we have heard are, of course, related to determining the extraction or release of fission products from fuel in the case of a reactor accident, characterizing the properties and behavior of these materials, and doing something about ameliorating the consequences of the accident. The motivation here, of course, is to assess the consequences of reactor accidents, and hopefully with the view to take steps that would allow one to relax siting criteria.

This raises an interesting question, I think; namely, to what extent have we been successful, through research and development, in doing something useful and constructive towards solving the reactor safety problem. We have an expert in the audience, Dr. Silverman of Harvard University. I wonder if he would care to say a few words about the impact this research has had on evaluating the consequences of reactor accidents, and to what extent it has been useful in relaxing siting criteria.

COMMENT BY DR. SILVERMAN:

First, let me say that we have enough confidence in what we think carbon can do, notwithstanding fires, and have recommended and have seen carried out multi-million dollar programs in reactor confinement at both Hanford and Savannah River, and you will hear about these in some detail. You probably heard at the Idaho Conference some of the orderly and positive planning.

I think those of you who are familiar with the reactor siting problem will get the notion, if we can be sure of the source for its strength and its chemical characteristics, that we ought to be able now, on the basis of our research and development, to design safeguards and feel a degree of confidence in their performance.

I might say, speaking entirely without regard to my regulatory status, that the Nuclear Ship Savannah has such safeguards aboard, and that these safeguards are being routinely tested and retested, because of the problems in entering ports throughout the world, and has shown the kind of performance that would permit one to make reliable estimates of the safety of its operation.

The results of our research and development are being put into effect. As you will see from some of the later discussion in regard to research and development, we still have some problems with charcoal that ignites. Activity may be lost, but there are ways to protect against that. Either substitute another adsorbent, or another technique.

All things considered, I think reactor safeguarding is coming closer and closer to the point when we can accept engineered safeguards, primary engineered safeguards, with a third degree of reliability, and I think what we are now arguing about essentially is whether or not the DF should be 10^0, 10^1, 10^2, et cetera. In other words, the release is zero. I am the only one who might raise some alarm as to how positive can you be that it is zero; we haven't got efficiencies of 100%, even though we are pretty close.

With that in mind I still think we have some objectives to achieve in engineered safeguards, but certainly we have come a long way.

What can we expect from the mechanical behavior of a system, because we test and retest? We have vibration and compaction taking place in charcoal beds, and I would take the attitude that if somebody can show me 99.5% efficiency after repeated retests, with both vibration and mechanical stress, then I would accept the 99.5%. I don't know how to give me an assurance that I will feel better. In other words should I say: "O.K. my safety factor is going to be 99.5% or reduce it to 99%." In other words I half believe that I should take 90%, because I think that somebody is going to become careless in routine surveillance, and so on.

If you have a system that is operating all the time that tests 99.5% before you enter a port, I think you have a pretty good feeling that it is going to be 99.5% all the time you are at dock-side, if we are talking about a nuclear-powered ship.

If we are talking about a power reactor in the center of Pittsburgh, or something of that nature, I think the frequency of your checking is going to give you the confidence in what numbers you can use.

So I don't think it is any different than taking out a coupon and checking it for irradiation characteristics, tensile strengths, and so on. It is the same basic philosophy. Our engineering safeguards for cleanup and protection of the public still, we hope, are never called on to act; but nevertheless, we have to have that area with some positive degree of assurance, in case all other things go wrong.

Sessions Chairman: Thank you. If there are no other comments this will conclude Session I.

SESSION II - TRANSPORT AND VENTILATION OF RADIOACTIVE AEROSOLS AND GASES

Morning - 22 October 1963

D. J. Keigher, RLO, Chairman

Session Chairman: Gentlemen, Session II concerns the transport and ventilation of radioactive aerosols and gases. The first paper has been prepared and will be delivered by Mr. T. W. Pickel of the Oak Ridge National Laboratory. The title of this interesting presentation has been announced as, "The Analog Computer as an Aid in Critical Ventilation System Evaluation."