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LABORATORY STUDIES OF IODINE BEHAVIOR
IN THE EBR-II MELT REFINING PROCESS

by

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ABSTRACT

Various laboratory studies have been conducted in an effort to predict the behavior of fission product iodine in the EBR-II melt refining process. Both highly irradiated EBR-II-type fuel and uranium-fissium alloys that had been spiked with iodine were used. When these materials were melt refined in lime-stabilized zirconia crucibles for one hour at 1400°C under an argon atmosphere, over 99% of the iodine was removed from the product ingot by volatilization. The volatilized iodine was collected primarily as CsI. These results confirmed earlier data obtained with unirradiated and low-activity-level fuel alloys, inasmuch as the iodine that had been volatilized during melt refining was not in the elemental form.

After the fuel had been melt refined and the furnace had been cooled to equilibrium with the ambient temperature, the argon atmosphere in the furnace contained less than 0.02% of the iodine activity in the original charge. Most of this activity was particulate in nature. A trap consisting of high-efficiency filters and an activated charcoal bed effectively removed the iodine activity from the argon atmosphere as it was pumped from the furnace.

In the EBR-II Fuel Cycle Facility, a Fiberfrax fume trap on top of the zirconia crucible will be used to collect the condensable materials that are volatilized during melt refining. Results of small-scale experiments indicate that the iodine activity collected by the Fiberfrax fume trap during melt refining will be released to the argon atmosphere of the process cell at a maximum rate of 0.2%/hr when the fume trap is removed from the furnace and placed in storage.

I. INTRODUCTION

The release of radioiodine during postirradiation heating of uranium and its alloys has been studied extensively. Most of the recent work, which has been concerned mainly with reactor safety problems, has involved a variety of fuels under different conditions of heating, atmosphere, and

burnup.⁽¹⁻⁶⁾ A smaller effort has been devoted to determining the chemical state of iodine released from metallic fuels heated in inert atmosphere.⁽⁷⁾ The purpose of the present work was to examine the behavior of fission product iodine in the EBR-II* melt refining process.

The initial fuel loading of EBR-II consists of about 50% enriched uranium alloyed with 5 w/o noble metal fission product elements that are referred to collectively as fissium.** The fuel pins, which are about $\frac{1}{8}$ in. in diameter, are clad with stainless steel and are thermally bonded to the cladding by a small amount of sodium in the annulus. After discharge from the reactor, the fuel pins are declad mechanically, chopped into convenient lengths (~2 in.), and processed by melt refining. The melt refining process involves melting the fuel pins in a lime-stabilized zirconia crucible and holding the molten alloy at 1400°C under an argon atmosphere for a period of 3 or 4 hr. During this procedure most of the fission products are removed from the fuel alloy through volatilization or through selective oxidation by the crucible. The purified metal ingot, formed by top-pouring into a mold, is used for the preparation of new fuel pins by injection casting. Unpoured metal and oxides remaining in the crucible in the form of a skull are subjected to an oxidation treatment so that the resulting oxide powder can be poured from the crucible. The uranium is recovered from this material by a separate process (Skull Reclamation Process) employing liquid metal solvents.

Since discharged EBR-II fuel at the time of processing may contain as much as one Curie of I^{131} activity per gram of fuel (~6000 Curies per melt refining charge), appropriate safeguards have been incorporated into the Fuel Cycle Facility to control the release of activity to the environment. To prevent excessive oxidation during the recovery, purification, and re-fabrication of the fuel, the Fuel Cycle Facility includes a shielded cell with an argon atmosphere. Provisions have been made to limit the concentrations of water and oxygen in the argon to 20 and 5 ppm, respectively. Although the nitrogen concentration in the argon may be as high as 5 v/o, excessive nitridation of the fuel can be avoided by handling procedures that minimize heating effects due to fission products.

The melt refining operation will be conducted in an induction furnace capable of handling about 10 kg of fuel alloy. The furnace is covered by a

*The second Experimental Breeder Reactor (EBR-II), located at the National Reactor Testing Station in Idaho, is a fast power breeder reactor designed to establish the feasibility of fast reactors for central-station power plants.

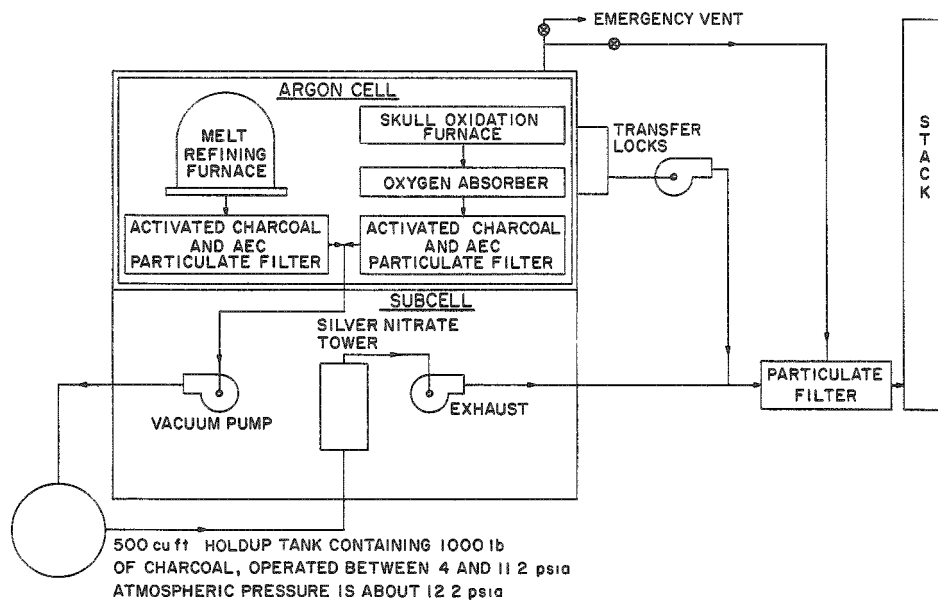
**The concentration of noble metals in the recycled fuel depends on fission yields and the amount removed in processing. In the first EBR-II core loading these metals are added to the fuel initially, in amounts corresponding approximately to their steady-state concentrations.

metal bell jar (volume of ~480 liters) which has a metal freeze seal. During melt refining, a porous molded Fiberfrax* fume trap with a wall thickness of $\frac{7}{8}$ in. will be inverted over the zirconia crucible to collect condensable fission products and volatilized sodium from the thermal bond. Most of the fission product iodine is expected to collect on this fume trap.

Upon the completion of melt refining, the argon atmosphere in the furnace will contain various fission product activities, primarily Xe^{133} , Kr^{85} , and a small amount of I^{131} . Most of the I^{131} will very likely be in particulate form. This gas will be passed through an activated charcoal bed and a high-efficiency glass media filter located in the process cell, and then through a vacuum pump located outside the cell to a holdup tank containing activated charcoal. When meteorological conditions are favorable, the gas in the holdup tank will be discharged through a heated $AgNO_3$ bed, a filter system to remove particulate activity, and a 200-ft stack. A flow-sheet for the discharge of gaseous wastes from the melt refining furnace is shown in Figure 1. A detailed discussion of the design and operation of the EBR-II Fuel Cycle Facility has been presented elsewhere.⁽⁸⁾

Figure 1

FLWSHEET FOR DISCHARGE OF GASEOUS WASTES
FROM THE EBR-II MELT REFINING FURNACE



Previous studies of the behavior of fission product iodine during melt refining were conducted with unirradiated uranium-fission alloys spiked with UI_3 and/or lightly irradiated uranium.⁽⁹⁾ When UI_3 was used,

*A product of the Carborundum Corporation. The reported composition of the amorphous fibers (w/o) is: Al_2O_3 (51.2), SiO_2 (47.4), B_2O_3 (0.7), and Na_2O (0.7).

it was added in amounts that approximated the fission product iodine concentration in highly irradiated fuel. These experiments showed that the volatilization of iodine from the molten alloy is strongly dependent on temperature, with negligible release at 1250°C and nearly complete removal at 1400°C during 2- to 4-hr heating periods.

It was observed that a major fraction of the volatilized iodine had escaped by diffusion through the crucible walls, rather than being released directly at the melt surface. Examination of the condensate showed that the iodine had formed moderately stable compounds with constituents of the melt and crucible. The effects of high burnup (other than those resulting solely from a relatively large iodine concentration) on the behavior of iodine during melt refining were not studied in these experiments. Additional studies were therefore deemed necessary under conditions that would represent more closely those expected during the reprocessing of fully irradiated (~2 total a/o burnup) EBR-II fuel.

In the present experimental work, additional information has been obtained on (1) the handling of furnace off-gases after melt refining, (2) the distribution of iodine activity in the ingot, skull, crucible, and condensate, and (3) the release of iodine to the argon atmosphere of the process cell when the Fiberfrax fume trap is removed from the melt refining furnace. Both highly irradiated uranium-fissium alloy, and either lightly irradiated or unirradiated alloy were used in the experiments. Some of the information on items (1) and (2) above was obtained in Experiments II, III, IV, and V, which were performed in conjunction with high-activity-level demonstrations of the melt refining process on a 400-g scale. These demonstrations have been reported in detail by Trice and Steunenber.⁽¹⁰⁾ Further studies dealing with item (2) comprised Experiments VI and VII, in which 7-g charges of highly irradiated uranium-fissium alloy were melt refined in apparatus designed to collect the condensable fission products that were volatilized. In Experiments VIII, IX, and X, approximately 20-g charges of unirradiated uranium-fissium alloy* were melt refined to provide confirmatory data on item (2). Lightly irradiated 20-g charges were melt refined with Fiberfrax fume traps in Experiments XI and XII to provide information on item (3).

*In Experiments IX and X, I^{131} activity was added to the charge to facilitate the analytical determinations.

II. EXPERIMENTS WITH HIGHLY IRRADIATED FUEL

A. Materials

The uranium-5 w/o fissium alloy used in these experiments was identical with that prepared for the first EBR-II core loading, except for a lower enrichment of the uranium (approximately 10 instead of 45.7 w/o U²³⁵). Injection casting was used to form 0.144-in.-diameter pins from the alloy.

The fuel was irradiated at unperturbed thermal fluxes of about 1.5 to 5×10^{13} nv in either the CP-5 research reactor or the Materials Testing Reactor (MTR) at central fuel temperatures varying from 240 to 550°C. During the irradiation the unclad, unrestrained pins were supported by loosely fitting spacers in a stainless steel capsule containing either sodium or sodium-potassium alloy as a heat transfer medium. After irradiation, the heat transfer medium was removed from the pins, and loosely adhering reaction products remaining on the surfaces of the pins were removed with emery paper or by tumbling the pins in a mixture of silicon carbide abrasives in a jar mill. Although the pins were typically warped, there was little evidence of severe surface cracking.

Certain constituents of the fuel are of importance because of their possible reaction with iodine at melt refining temperatures (1300-1400°C). The composition of the fuel prior to irradiation and the concentrations of the principal condensable fission products that are volatilized in the melt refining process are given in Table 1. Data on the total activity and the

Table 1

HIGHLY IRRADIATED FUEL ALLOYS USED IN MELT REFINING EXPERIMENTS

Constituent	Concentration Prior to Irradiation (w/o)					
	II	III	IV	V	VI	VII
Uranium	94.73 ^a				94.38 ^a	
Molybdenum	2.58				2.80	
Ruthenium	2.11				2.25	
Rhodium	0.26				0.27	
Palladium	0.19				0.20	
Zirconium	0.12				0.09	
Niobium	0.01				0.01	
Experiment						
Charge Wt (g)	392.5	362.5	364.2	382.2	7.196	6.662
Irradiation Data						
Burnup (% of total atoms)	0.22	0.74	0.87	1.75	1.18	1.18
Cooling Time (days)	28	14	35	25	25	35
Total Activity (C)	1970	3800	3600	5350	110	76
Approximate Content (ppm)						
Fission Product Cesium	250	850	990	2000	1350	1350
Fission Product Iodine	12	45	50	100	65	65

^aUranium enriched with 9.44 to 10.73 w/o U²³⁵.

individual fission product concentrations in the fuel were calculated by a method similar to one used by LaPlante.⁽¹¹⁾ Burnups were determined by comparing mass spectrographic analyses for U^{235} , U^{236} , and U^{238} in the fuel before and after irradiation. The composition stated by the supplier for the lime-stabilized zirconia crucibles used in the experiments was (in w/o): ZrO_2 (92.0), CaO (4.5), HfO_2 (1.5), SiO_2 (0.9), Al_2O_3 (0.6), TiO_2 (0.3), Fe_2O_3 (0.2).

B. Release of Iodine to Melt Refining Off-gases

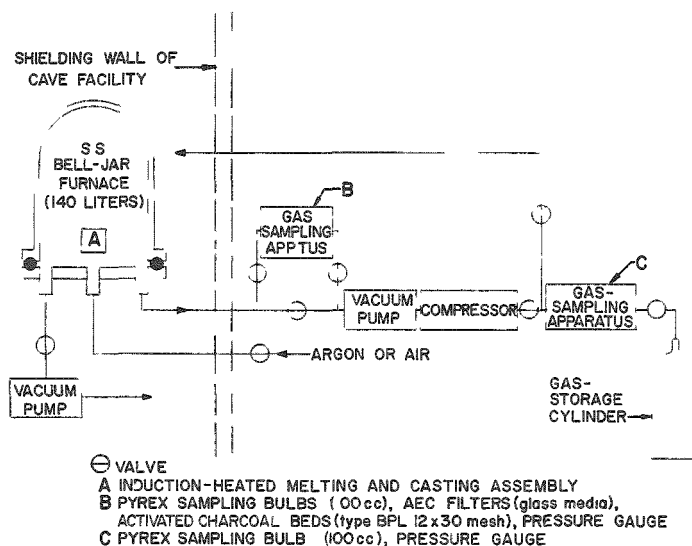
Information on the behavior of iodine activity in the furnace atmosphere after approximately 0.4-kg charges of highly irradiated fuel pins had been melt refined was obtained in four experiments. These experiments were carried out in conjunction with previously reported laboratory demonstrations of the EBR-II melt refining process.⁽¹⁰⁾

1. Experimental

The highly irradiated fuel was melt refined in a stainless steel bell jar-type furnace. The furnace, located in a multi-Curie cave with an air atmosphere, was equipped with a radioactive-gas-storage system. The arrangement of the furnace and storage system is shown schematically in Figure 2.

Figure 2

SYSTEM FOR TRANSFER AND SAMPLING OF RADIOACTIVE GAS IN MELT REFINING EXPERIMENTS WITH HIGHLY IRRADIATED FUEL



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The components of the melt refining furnace were arranged so that the irradiated fuel contained in the zirconia crucible could be heated to the selected temperature by an induction-heated tantalum susceptor, and,

if desired, cast into an ingot by top-pouring. The bell jar enclosure, which was sealed to a base plate by a neoprene gasket, was provided with sources of vacuum, argon, and air. The auxiliary gas-handling train for activities discharged to the furnace atmosphere during melt refining was functionally similar to that in the EBR-II Fuel Cycle Facility (see Figure 1). The train contained sampling ports to permit withdrawal of gas samples into previously evacuated 100-ml Pyrex bulbs, and facilities for passing the furnace off-gases through activated charcoal beds and/or AEC filters. By the use of a vacuum pump-compressor arrangement in the storage system it was possible to reduce the pressure in the system upstream from the vacuum pump from 1 atm to about 8 torr.

In the experiments concerning the behavior of iodine in furnace off-gases, the 0.4-kg charges were loaded into crucibles which had been given a preliminary outgassing treatment at 1400°C under a pressure of 25 μ . The loaded crucible was installed in the furnace, the bell jar was lowered into place, then the system was evacuated and held at a pressure of about 5 μ prior to adding argon at a pressure of about 0.8 atm. The charge was heated to a melt refining temperature of 1400°C (average heating rate, 20°C/min) and held at this temperature for periods of 1-3 hr. The purified metal was recovered by top-pouring into a mold.

The crucible containing the skull was cooled to an equilibrium temperature ranging from approximately 300 to 650°C, and the gases were pumped through the gas-storage train. The upper range of these temperatures approximated the maximum heating effect expected to result from fission product decay under actual Fuel Cycle Facility operating conditions. The gas was directed through either AEC-type filters* or an assembly consisting of these filters and activated charcoal. Included in the latter arrangement were an inlet filter, a seven-section bed of -12 +30 mesh activated charcoal (six 1.3-cm sections and a final 1.9-cm section), and a terminal filter. The pressure in the furnace was gradually reduced to approximately 10 torr and appropriate samples of gas downstream from the filter arrangement were withdrawn into evacuated Pyrex bulbs.

The above procedure was modified in Experiment IV. Unfiltered samples of the argon atmosphere in the furnace were taken when the melt refining operation was completed. Additional unfiltered gas samples were taken after successive replacements of this atmosphere with undried air or fresh argon. As in the above-described experiments, the ingot, skull, and crucible were left in the furnace during the gas-sampling operations.

The activities in the gas samples were analyzed with a 256-channel gamma spectrometer. In Experiments II and III, samples for the

*Glass-media filters reported to be efficient for removal of more than 99% of 0.3- μ particles at face velocities up to 200 ft/min.

determination of iodine activity in the AEC filters were obtained by leaching the filters with aqua regia containing a small amount of HF. Other samples from these experiments (vacuum pump oil and effluent gas), and all of the samples from Experiment V (filters, activated charcoal, and effluent gas) were counted directly. The distribution of iodine in various components of the gas-handling system in Experiments II and III was determined by relating the amount of I^{131} activity in the samples to that present in a control specimen. In Experiments IV and V the distribution data were obtained by relating the I^{131} activity in the samples to a calculated value for the total amount of I^{131} activity present.

2. Results

Because of experimental limitations, the EBR-II plant conditions were not completely duplicated in these studies. The major differences between the laboratory and plant operations were (1) the use of a ZrO_2 disc instead of a Fiberfrax fume trap to cover the melt refining crucible, (2) the reduced scale of the laboratory experiments (charge of 0.4 kg instead of 10 kg; furnace volume of 140 liters instead of 480 liters), and (3) the use of activated charcoal beds and/or AEC filters for only a single pumpdown of the furnace. In the plant the same charcoal beds and filters will be used repeatedly.

In Experiment IV, the effect of replacing the furnace atmosphere with air or fresh argon on the release of iodine activity from the melt refining furnace was determined after the melt refining operation had been completed and the furnace had cooled to an equilibrium temperature. The amounts of I^{131} activity in the original and replacement atmospheres are shown in Table 2. Less than 0.005% of the iodine present in the melt

Table 2

EFFECT OF ATMOSPHERE REPLACEMENT ON RETENTION OF IODINE-131 IN FURNACE GAS AFTER
MELT REFINING OF HIGHLY IRRADIATED FUEL AT 1400°C

	Experiment	IV	
	Furnace and Sampling Apparatus	See Figure 2	
	Melt Refining Conditions		
	Charge Wt (g)	364.2	
	Burnup (% of total atoms)	0.87	
	Cooling Time (days)	35	
	Total Activity (Ci)	3600	
	I^{131} Activity (Ci)	40	
	Duration of Refining (hr)	1	
	Melt Atmosphere	Argon	
	Skull Temp during Sampling (°C)	~300	
	Atmosphere ^a		
Sample No.	Type	Time of Exposure (hr)	Iodine Activity ^b (% of total in furnace x 10 ³)
1	Argon (Melt Refining Atmosphere)	21.9	4.5
2	Air	23.9	37
3	Air	2.8	24
4	Argon	119	0.8

^aFurnace was evacuated to ~10 torr between atmosphere changes. Prior to initial exposure of furnace contents to air (second sampling operation) the furnace atmosphere was replaced twice with argon to remove the radioactive xenon and krypton.

^bGas samples withdrawn from the furnace were unfiltered; accepted precision of analyses, ±40% (relative).

refining charge was found in the original argon atmosphere. However, the addition of undried air to the furnace increased the concentration of iodine in the atmosphere by a factor of eight, probably as a result of oxidation of deposited iodides by oxygen or moisture in the air.

The distribution of I^{131} in components of the off-gas system used in Experiments II, III, and V is shown in Table 3. The variations in results from the three experiments are believed to reflect differences in the treatment of the fuel prior to melt refining.

Table 3

TRANSPORT OF IODINE-131 DURING FURNACE PUMPDOWN AFTER
MELT REFINING OF HIGHLY IRRADIATED FUEL AT 1400°C

Furnace and Sampling Apparatus - see Figure 2

	Experiment No.		
	II	III	V ^a
<u>Melt Refining Conditions</u>			
Charge Wt (g)	392.3	362.5	382.2
Burnup (% of total atoms)	0.22	0.74	1.75
Cooling Time (days)	28	14	25
Total Activity (C)	1970	3800	5350
Air Exposure of Fuel (hr) ^b	19	68	0.5
Duration of Refining (hr)	3	1	1
Melt Atmosphere	argon	argon	argon
<u>Furnace Pumpdown</u>			
Charge Outgassing prior to Melt Refining			
Volume Collected (liters)	122	not collected	{ step eliminated
Charge Temp (°C)	to 850	to 800	
Pressure Reduction during Melt Refining			
Volume Collected (liters)	7	{ step eliminated	{ step eliminated
Charge Temp (°C)	1180		
Atmosphere Removal after Melt Refining			
I^{131} Activity in Furnace (C)	53	125	17
Flow Rate through Filter Assembly (ft/min, max)	1.2	1.2	200
Volume through Filter Assembly (liters)	91	105	195
Skull Temp (°C)	~300	~300	650
<u>Iodine Distribution, ^c % of Total in Furnace</u>			
Filter Assembly			
Primary AEC Filter	0.3	0.09	1.1×10^{-3}
Activated Charcoal Bed	not used	not used	0.4×10^{-3}
Secondary AEC Filter	2×10^{-2}	2×10^{-3}	4×10^{-7}
Vacuum Pump Oil	1×10^{-2}	2×10^{-3}	not analyzed
Effluent to Storage Tank	0.2	0.03	$<6 \times 10^{-6}$
Total Accountable in Off-gas System	0.53	0.12	1.5×10^{-3}

^aData from V. Trice⁽¹²⁾

^bThe total time includes the time during which the crucible was loaded, inserted in the furnace and pumped on prior to adding the final melt atmosphere; pressures over the fuel, at an estimated equilibrium temperature of 300°C, were varied from 760 to 5×10^{-3} torr.

^cAccepted precision of analyses: filter assembly components, $\pm 20\%$ (relative); other components, $\pm 40\%$ (relative).

After the loaded crucible had been placed in the furnace in Experiments II and III, the system was maintained at a pressure of 5μ for periods of 17 to 66 hr prior to melt refining. In spite of the low pressure, the leak rate of the furnace was apparently such that the fuel pins, which were at a temperature of about 300°C because of fission product decay heating, were sufficiently oxidized that difficulty was encountered in pouring the alloy after the melt refining step.⁽¹⁰⁾ It is suspected that this degree of oxidation would have caused the release of significant amounts of elemental iodine to the furnace atmosphere. In subsequent experiments the procedure was modified to minimize air exposure of the fuel pins. Experiments IV and V are therefore believed to be more typical of the plant operation, which will be conducted entirely in an argon atmosphere.

Of the total amount of iodine collected in Experiments II and III, from 56 to 75% appeared in the primary AEC filters, indicating that the activity in the furnace off-gases was largely particulate. The only activities other than I^{131} that were found in the filters and vacuum pump oil were Cs^{137} , Ba^{140} , and a trace of Ru^{106} . These experiments indicated that particulate filters alone in the pumping system did not provide efficient iodine removal from the melt refining off-gases.

In Experiment V a composite trap consisting of an AEC filter, a bed of activated charcoal, and a terminal AEC filter was used. Of the total iodine collected by this trap, about 73% appeared on the inlet (primary) filter, 27% in the charcoal bed, and 0.025% on the outlet (secondary) filter. All of the iodine retained by the charcoal was found in the first 1.3 cm of the 9.7-cm bed. A gamma scan of the filters showed that cesium and iodine were present in approximately equal atomic proportions. The amount of iodine downstream from the assembly was only 0.4% of the total amount accounted for in the pumping system.

C. Iodine Distribution during Melt Refining

Two types of experiments were performed in which approximately 7-g charges of highly irradiated fuel were melt refined. In the first, volatilized fission products were collected on a nickel condenser. In the second, the volatilized activity was exposed to a Fiberfrax bed. These experiments provided data on the chemical nature of the volatilized iodine and the distribution of iodine activity in various melt refining fractions (condensate, crucible, ingot plus skull).

1. Experimental

In these experiments the apparatus was placed inside the melt refining furnace described in the previous section. The assemblies that were used in the two experiments are shown in Figure 3. Assembly A was

used to determine the deposition of volatilized activity in various temperature zones along a nickel tube. Assembly B included a 3.3-cm-deep Fiberfrax bed for the collection of volatilized fission products; sodium was also vaporized to the fume trap during this experiment, since the amount of thermal-bond sodium adhering to the pins after decanning may comprise a large part of the condensable volatiles in a plant charge. The temperature profile of each assembly was determined prior to the experiment. The temperature gradient of the Fiberfrax (top surface, 450°C; bottom surface, 1000°C) was the same as that which had been observed in the Fiberfrax fume trap of the plant melt refining equipment.

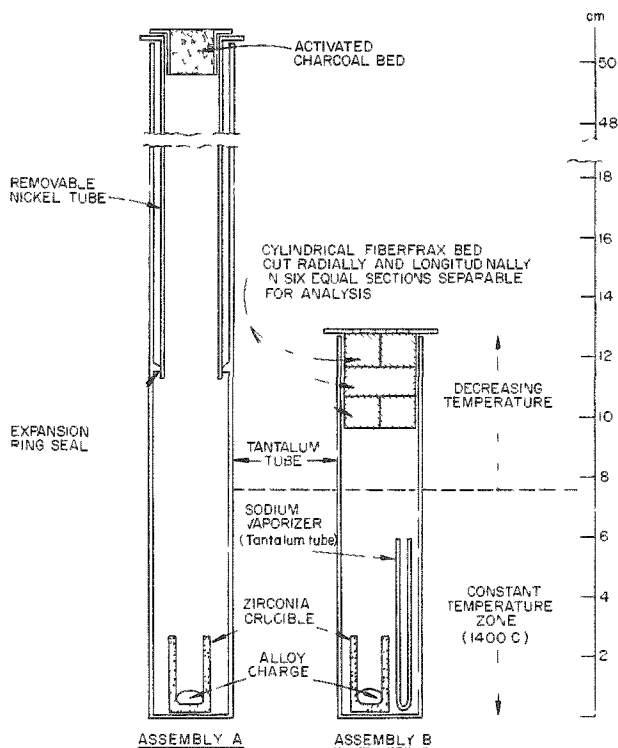


Figure 3

ASSEMBLIES FOR COLLECTION OF
VOLATILIZED MATERIAL FROM
HIGHLY IRRADIATED FUEL

	Assembly A	Assembly B
Min. Collector Temp	~200°C	450°C
Furnace	SS Bell Jar	SS Bell Jar

In each experiment the assembly containing the loaded crucible was placed in the furnace and the furnace was evacuated to 5μ while the assembly was outgassed at 200°C for 10 min. The furnace was then filled with argon at a pressure of 0.8 atm and the charge was heated to a melt refining temperature of 1400°C (average heating rate, 30°C/min) and held at that temperature for one hour. After the assembly had cooled, the argon atmosphere was replaced by air, and the assembly was dismantled for inspection and analysis.

To obtain samples for radiochemical analysis, the ingot and skull fractions were dissolved in aqua regia. The crucibles were ground and blended in an electric mortar, and samples for iodine analysis were obtained by leaching a portion of the ground crucible with aqua regia. Condensate samples were prepared by leaching the collector or the Fiberfrax with aqua regia containing a small amount of HF, or by alternate leaching

with this solution and a dilute solution of NaOH. The latter procedure, which was used to leach iodine activity from sections of the Fiberfrax trap, effectively decontaminated the material.

Standard radiochemical methods were used to separate and analyze the activities. Iodine, cerium, tellurium, and strontium were counted as beta activities; barium, cesium, zirconium, and ruthenium were counted as gamma activities. The distribution of activity in the various melt refining fractions was determined by relating the amount in the fraction to that in a similarly irradiated control specimen which was counted at approximately the same time.

2. Results

No attempt was made to determine a specific condensation temperature for the volatilized activity in these experiments. A different collector design might cause some shifting of the temperature region in which the activity is collected because of fractionation effects. However, the overall pattern of activity deposition is not expected to differ greatly from that found in the laboratory experiments.

The amounts of various elements in the condensate resulting from the melt refining of high-burnup uranium-fission alloy are given in Table 4. The elements listed in Table 4 account for more than half of the total fission product content of the fuel. The data show that cesium and

Table 4

ANALYSES OF MATERIAL VOLATILIZED DURING MELT REFINING OF HIGHLY IRRADIATED FUEL
FOR ONE HOUR AT 1400°C IN AN ARGON ATMOSPHERE

	<u>Experiment VI</u>		<u>Experiment VII</u>	
Crucible	Lime-stabilized zirconia		Lime-stabilized zirconia	
Charge	7.196 g of uranium-5.6 w/o fission irradiated to a total atom burnup of 1.18%		6.662 g of uranium-5.6 w/o fission irradiated to a total atom burnup of 1.18%, plus 0.43 g of sodium	
Collector	Assembly A, Figure 3 (tantalum and nickel tubes)		Assembly B, Figure 3 (Fiberfrax in tantalum tube)	
Analytical Methods				
Fission Products	Radiochemical ^a		Radiochemical	
Uranium	Fluorophotometric		-	
Material Collected	% of Charge	Gram-atoms x 10 ^{10b}	% of Charge	Gram-atoms x 10 ^{10b}
Cs	49	329700	89	556000
I	52	20100	32	11100
Zr	2×10^{-3}	34	d	-
Sr	7×10^{-3}	28	no analysis	-
Ba	7×10^{-3}	15	d	-
Ru	7×10^{-5}	12	d	-
Te	6×10^{-3}	4.5	d	-
Ce	2×10^{-4}	1	d	-
U	$<4 \times 10^{-3c}$	$<10700^c$	no analysis	-

^a Percentage values reported other than those for cesium and iodine may be high by a factor of two because of probable cross contamination during radiochemical separation; accepted precision of cesium and iodine analyses, $\pm 10\%$ (relative).

^b Gram-atom quantities of elements are based on percentages found in the volatilized fraction and calculated concentrations in the fuel charge.

^c Uranium concentration was near the limit of detection for the fluorophotometric technique employed.

^d Activities not detectable in the gamma spectrometric scan of the analytical samples.

iodine accounted for most of the condensed activity on the collector assemblies. The percentages of cesium and iodine collected as a function of collector temperature (Table 5) indicate that about 99% of the total amounts of these elements that were accounted for were found in temperature zones exceeding 450°C in Experiment VI (nickel tube collector). More than 70% of these activities was collected in zones exceeding 600°C in Experiment VII (Fiberfrax bed). In each of the temperature zones that were analyzed, the amount of cesium was in excess of the quantity necessary to account for the iodine as CsI.

Table 5

DISTRIBUTION OF VOLATILIZED CESIUM AND IODINE ACTIVITIES IN
VARIOUS COLLECTOR TEMPERATURE ZONES AFTER MELT
REFINING OF HIGHLY IRRADIATED FUEL

Experimental Conditions - see Table 4

Expt.	Collector	Collector Temp. °C	Iodine Collected		Cesium Collected	
			(% of charge)	(gram-atoms x 10 ¹⁰)	(% of charge)	(gram-atoms x 10 ¹⁰)
Assembly A (Figure 3)						
VI	Charcoal trap	~200	0.1	40	~0.1	700
	Ni tube	200-450	0.3	110	0.3	2000
	Ni tube	450-700	49.0	19000	37.0	25000
	Ni tube	700-900	2.1	800	10.0	7000
	Ta tube	900-1400	0.4	150	1.0	7000
Assembly B (Figure 3)						
VII	Fiberfrax bed section	450-600	8.0	3000	10.0	62000
	Fiberfrax bed section	600-800	15.0	5000	38.0	24000
	Fiberfrax bed section	800-1000	8.3	3000	40.1	25000
	Ta tube	1000-1400	0.3	100	0.6	4000

The major portion of the cesium and iodine found on the nickel collector in Experiment VI was condensed in the zone that had been at a temperature of 450 to 700°C. A dark-gray material had deposited in the same zone, forming a band about one inch wide on the collector. On the other hand, collection of these activities on Fiberfrax during Experiment VII showed a less definite pattern with a trend toward greater retention of the activities at higher temperatures.

The absence of a definite collection pattern in the Fiberfrax suggests that additional effects may influence the retention of iodine by Fiberfrax during or after melt refining. Iodine analyses of the Fiberfrax bed sections as a function of storage time in air indicated that a loss of iodine from the Fiberfrax occurs over a period of time. The data shown in Table 6 indicate that, of the iodine initially collected on the Fiberfrax, about 50% was lost in about 6 weeks. This loss might have resulted from the oxidation of iodine compounds by oxygen or atmospheric moisture. The greater retention shown by the bed section that had been heated to the highest

temperature during the experiment very likely resulted from entrapment of the iodine in glassy material formed by the reaction of sodium with Fiberfrax. Additional work concerning the release of iodine collected on a Fiberfrax trap during melt refining is discussed later under a separate heading.

Table 6

EFFECT OF TIME ON IODINE RETENTION IN FIBERFRAX
BED SECTIONS - EXPERIMENT VII

Experimental Conditions - see Table 4

Bed Section	Temperature during Experiment (°C)	Iodine Retention ^a (% of starting material)		Percent Released
		Initial Analysis (samples stored 1 day) ^b	Final Analysis (samples stored 42 days) ^b	
Top	450-600	8.0	2.0	75
Middle	600-800	15.0	5.0	67
Bottom	800-1000	8.3	7.3	12
		Total 31.3	14.3	

^aIodine leached from one-half sections of Fiberfrax beds after the indicated storage times; activity retention in each section determined by weighting amounts in analytical samples according to total weight of bed in temperature zone of interest.

^bSamples stored in air in separate containers prior to analysis.

Results on the distribution of iodine among various fractions produced during melt refining of the 7-g and previously discussed 400-g charges of highly irradiated fuel are presented in Table 7. In Experiments III, IV, and V the purified product (ingot) was recovered by top-pouring. In Experiment VI, the ingot and the adhering skull were recovered by inverting and tapping the melt refining crucible. The material in the ingot and skull was removed from the crucible in Experiment VII by oxidation at 700°C in an argon atmosphere containing 25 v/o oxygen, a procedure similar to that which will be followed in plant operation for the removal of skulls from crucibles.

Table 7

DISTRIBUTION OF IODINE ACTIVITY AFTER MELT REFINING OF HIGHLY IRRADIATED FUEL

Expt.	Uranium-Fissium Charge ^a		Collector for Volatilized Iodine	Melt Refining Fraction	Percent of Charged I ¹³¹ in Fraction ^b
	Total Atom Burnup (%)	Weight (g)			
III, IV, V	0.74 to 1.75	369.6 (av.)	None	Ingot ^c	0.3 ± 0.1
VI	1.18	7.196	Assembly A, Figure 3 (Ta and Ni tubes)	Ingot plus skull ^d Crucible Volatilized	1.3 1.5 52
VII	1.18	6.662	Assembly B, Figure 3 (Fiberfrax in Ta tube)	Oxidized ingot plus skull ^e Crucible Volatilized	0.25 (not analyzed) 32

^a Additional information on charge composition and irradiation is given in Table 1.

^b Average deviation shown for Experiments III, IV, and V; accepted precision of other analyses, ±10% (relative).

^c Ingot separated by pouring technique.

^d Unpoured fraction was physically separated from crucible.

^e Unpoured fraction separated from crucible by oxidation at 700°C in argon containing 25 v/o oxygen.

About 0.3% of the iodine was retained in the product ingot after the fuel was melt refined at 1400°C (Experiments III, IV, and V). In Experiment VI, most of the recovered iodine was present in the volatilized fraction with a small portion, about 1.5%, distributing to the crucible. In the same experiment, 1.3% of the iodine in the original charge was found in the unoxidized ingot and skull, whereas in Experiment VII, 0.25% was retained by the same fraction after complete oxidation of the ingot and skull to form a uranium oxide powder. This finding suggests that complete oxidation of the iodine-bearing skull produced during melt refining will result in partial release of the iodine from this fraction, and indicates that provisions are necessary for handling iodine activity in the off-gases from the skull oxidation equipment.

These experiments confirmed earlier results⁽⁹⁾ from work with synthetic charges which had indicated that melt refining at 1400°C removes nearly all of the iodine from the product ingot and that the iodine will be collected primarily as a compound, rather than as elemental iodine. In the earlier work, in which reaction with calcium in the crucible apparently resulted in the volatilization of CaI_2 , cesium was either absent or present only in low concentrations (<0.02 ppm). In the present studies there was no satisfactory way to analyze for inactive constituents. However, the absence of appreciable alkaline earth fission product activities in the volatilized deposits suggests the absence of calcium.

It appears that CsI is the predominant species collected when highly irradiated fuel is melt refined at 1400°C. No evidence was found for the formation of uranium iodides. Of the total amount of iodine recovered in experiments with the collector assemblies, 95% or more appeared in the volatilized fractions. The remainder was distributed among the crucible, skull, and ingot. The figure of 0.3% for the amount of iodine retained by the product ingot in Experiments III, IV, and V is considered to be a reliable indication of the amount that will remain in this fraction under plant conditions. However, experimental limitations were such that satisfactory material balances for iodine could not be obtained in these experiments. For those experiments employing collector assemblies, only 30 to 50% of the iodine initially present in the charge could be accounted for. The lack of satisfactory material balances was a matter of concern, since the fraction of iodine that was unaccountable could become a major problem if it were to appear unexpectedly at some point in the fuel cycle. Additional experiments with synthetic fuel were therefore performed in an attempt to confirm the results obtained with the highly irradiated alloy, but with the added objective of obtaining satisfactory material balances for iodine.

III. EXPERIMENTS WITH SYNTHETIC FUEL

A. Materials

Unirradiated and low-activity-level synthetic fuel was used in these experiments because of limitations imposed by the remote handling associated with highly irradiated fuel. Inactive or tracer-labeled iodides (UI_3 , KI, or CsI) and cesium were added to uranium-5 w/o fission alloy to simulate the presence of fission product iodine and cesium in highly irradiated fuel.* Although it was recognized that the chemical form and distribution of the elements in the charges would not exactly duplicate the conditions existing in high burnup materials, it was found that the fission product iodine in high-burnup alloy and the inactive iodine in the synthetic material behaved similarly in most of the melt refining experiments.

The uranium-fission alloy employed in the experiments had the following composition (w/o): natural U (95), Mo (2.46), Ru (1.96), Rh (0.28), Pd (0.19), Zr (0.10), and Nb (0.01). Except for the absence of enriched uranium, this composition corresponds to that of the alloy used for the first EBR-II core loading.

To prepare fuel samples containing iodine and cesium, holes were drilled in opposite ends of 0.34-in.-diameter, cylindrically shaped alloy sections. Cesium metal and the iodide were separately placed in these holes and covered with plugs machined from the same uranium-fission alloy. Unless otherwise indicated, the additives were sealed in the capsule by electron beam welding techniques. Information on the various types of additives employed in the experiments and the resulting cesium and iodine in the synthetic fuel samples is presented in Table 8. To facilitate capsule loading, the average ratios of cesium and iodine to uranium alloy were, respectively, about three and fourteen times greater than those for EBR-II fuel irradiated to two total a/o burnup and cooled 15 days.

Iodine was added as UI_3 in some of the experiments. The triiodide was used because of the stronger tendency of UI_4 to decompose at the elevated temperatures used in the experiments. The UI_3 was prepared by a method similar to one used by Gregory,⁽¹³⁾ which involved exposure of uranium heated to 520°C to gaseous iodine. Analysis of the product showed that it contained 65 ± 2 w/o iodine as compared with a theoretical 61.5 w/o iodine in UI_3 . For convenient analysis of volatilized products, tracer I^{131} (8.04-d half-life) and Cs¹³⁴ (2.3-yr half-life) were produced in the fuel used in selected experiments by irradiation of the natural uranium and cesium metal in unperturbed thermal fluxes ranging from about 10^{12} to 2×10^{12} nv for approximately 2 days. The metal was cooled approximately one month to permit decay of the 30-hr tellurium parent of I^{131} .

*The preliminary work with highly irradiated material showed that cesium and iodine accounted for nearly all of the condensable gamma activities volatilized during melt refining at 1400°C.

Table 8

SYNTHETIC FUEL USED IN MELT REFINING EXPERIMENTS

	Experiment				
	VIII	IX	X	XI	XII
Capsule ^a Wt (g)	19.555	19.490	19.859	19.731	19.631
Alloy Additives ^b	UI ₃ and Cs	KI labeled with I ¹³¹ and Cs	CsI labeled with I ¹³¹ and Cs	UI ₃ and Cs	UI ₃ and Cs
Charge Wt (g)	19.718	19.674	20.040	19.968	19.858
Irradiation	None	None	None	tracer level ^c	tracer level ^d
Cesium Content (ppm)	5730	6710	7600	9360	8810
Iodine Content (ppm)	1670	2030	1450	1650	1710

^aCapsules and covers for additives were fabricated from uranium-5 w/o fission alloy.

^bAdditives were hermetically sealed in capsules by welding covers on capsule, with the exception of the labeled compounds of cesium and iodine, which were confined in the capsule by press-fitted covers of the uranium-fission alloy.

^cAlloy plus additives irradiated in an unperturbed thermal neutron flux of 2×10^{12} nv for 48 hr and cooled 25 days prior to use.

^dAlloy plus additives irradiated in an unperturbed thermal neutron flux of about 10^{12} nv for 63 hr and cooled 35 days prior to use.

In other experiments, the iodine was added as CsI or KI labeled with I¹³¹. Potassium and cesium monoiodides were used because they were not likely to be subject to hydration during preparation of the compound by an aqueous method, and because both have high boiling points (CsI, 1280°C; KI, 1325°C). These activated compounds were prepared by inoculation of a saturated solution of the inactive compound with I¹³¹ in basic Na₂SO₃ solution. The labeled compound was fractionally precipitated by addition of isopropyl alcohol to the solution and the precipitated material was vacuum dried prior to use. Analyses of the product showed that the CsI contained 52 ± 2 w/o iodine (theoretical: 48.8 w/o). The KI contained 76 ± 2 w/o iodine (theoretical: 76.4 w/o).

B. Iodine Distribution and Material Balance during Melt Refining

1. Experimental

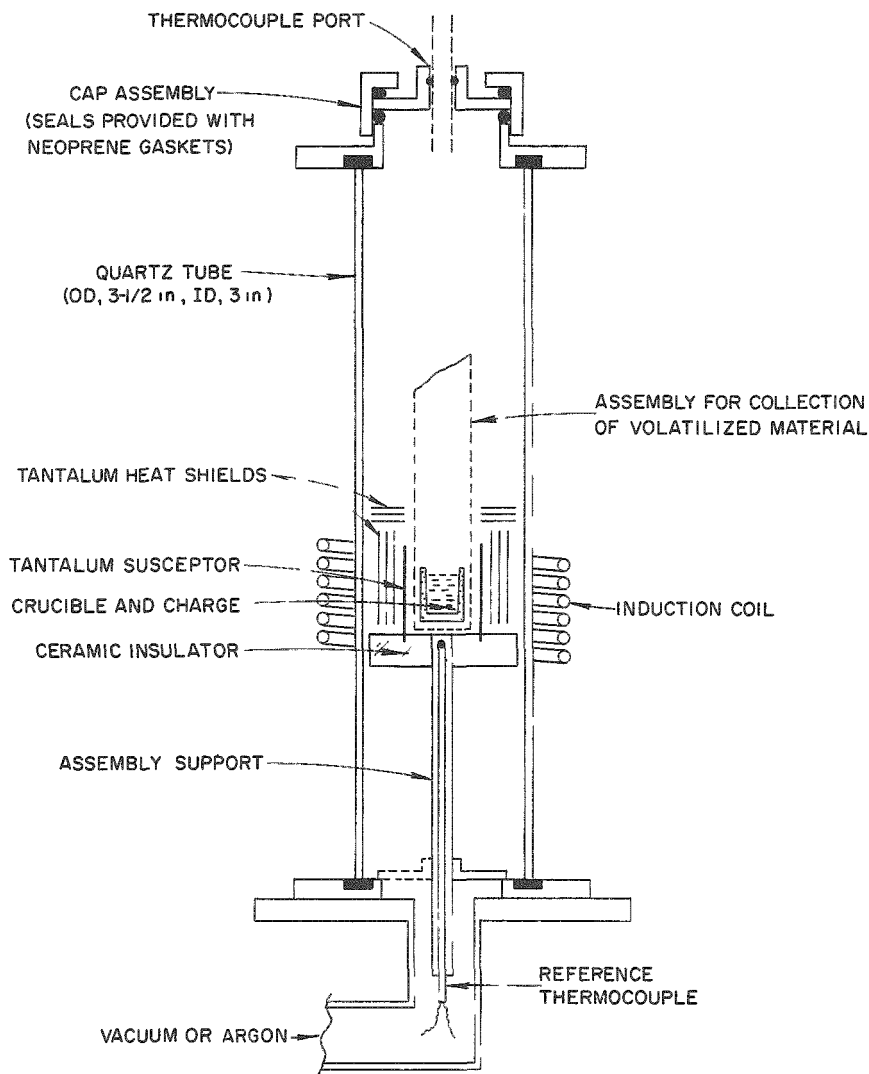
The experiments with synthetic, high-burnup alloy were conducted in a furnace that consisted of an induction-heated quartz tube. A vacuum ($< 2 \times 10^{-5}$ torr) could be maintained in the furnace by means of mechanical and oil diffusion pumps. Additional provisions were made to

blanket the melt with high-purity argon during the experiments. The units were installed in a ventilated hood and the furnace was surrounded with $\frac{1}{4}$ in. of steel shielding.

A sketch of the quartz tube furnace used for these melt refining experiments is shown in Figure 4. The vertically mounted quartz tube had an ID of 3 in. and a length of 27 in. The inner furnace parts were arranged so that the zirconia crucible (height, $1\frac{1}{16}$ -in.; OD, $\frac{9}{16}$ -in.) and a 20-g charge were uniformly heated by a tantalum induction susceptor.

Figure 4
INDUCTION-HEATED QUARTZ TUBE FURNACE
USED FOR MELT REFINING EXPERIMENTS
WITH SYNTHETIC FUEL

(Not to scale)

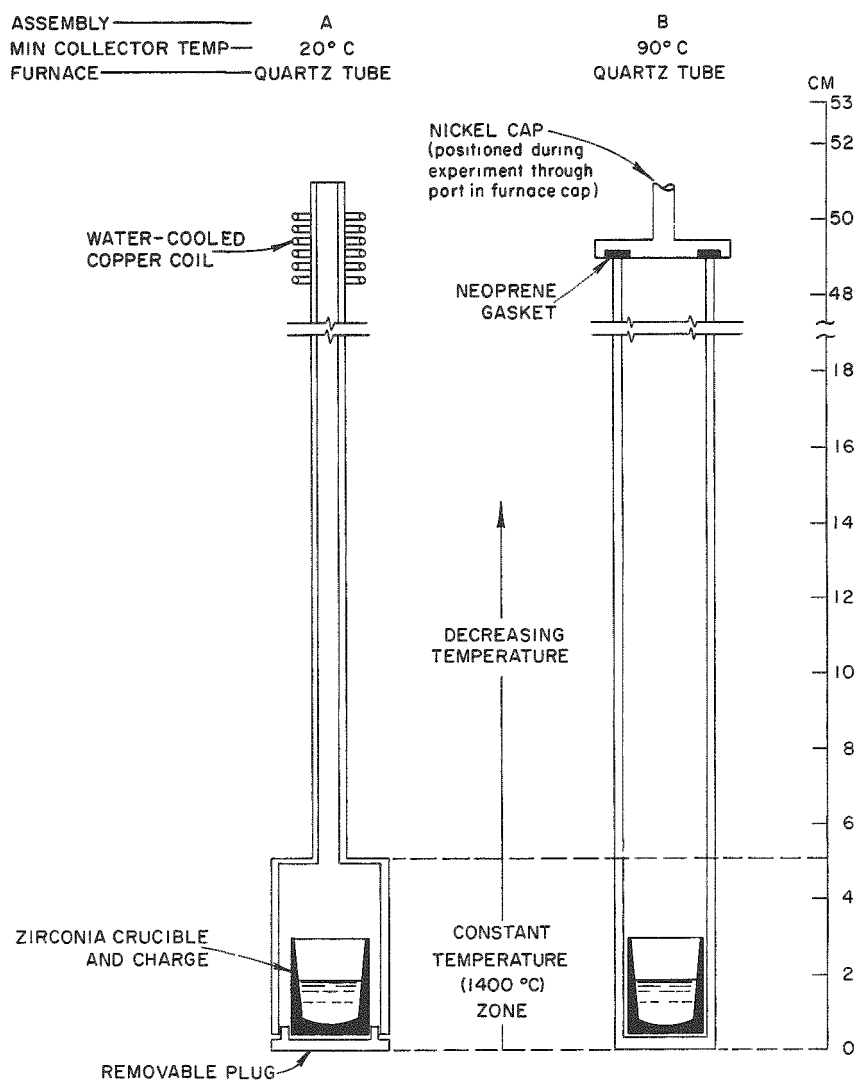


The temperature of the charge was measured with a Pt/Pt-10% Rh reference thermocouple which was located directly below the crucible. The reference thermocouple had been calibrated previously by means of another thermocouple located in the crucible. Although the temperature differential was of the order of 100°C when the charge was at the melt refining temperature (1400°C), the reproducibility of this differential in successive heats was within about 10°C . It is believed that the melt refining temperatures reported are correct to within $\pm 20^{\circ}\text{C}$.

Assemblies used for collection of volatilized material in the experiments with synthetic fuel are shown in Figure 5. Assembly A was

Figure 5

ASSEMBLIES FOR COLLECTION OF VOLATILIZED
MATERIAL FROM SYNTHETIC FUEL
(Assemblies fabricated from tantalum
except where indicated)



utilized in an initial attempt to collect all of the material that was volatilized from the melt. However, losses of volatile material to furnace areas outside the condenser indicated that modification of the collector assembly was needed. Therefore, in subsequent experiments a sealed collector, Assembly B, was employed. The use of the sealed collector permitted measurement of the condensed iodine activity as a function of collector temperature before the condensate was exposed to the air. The temperature profile of this assembly was determined prior to the refining experiment.

In each experiment the lime-stabilized zirconia crucible was first out-gassed at a minimum temperature of 1000°C and a pressure of 0.1 μ . The synthetic charge, of about 20 g, was placed in the crucible, which was then inserted in the collector assembly. After installation of the assembly in the furnace, argon purified by passage through a bed of uranium chips at 825°C was added to provide a pressure of 700 to 760 torr over the melt. The charge was heated to a melt refining temperature of 1400°C at an average heating rate of 18°C/min and was held at that temperature for one hour.* The furnace tube and its contents were then cooled overnight to room temperature.

Analytical samples were prepared by dissolving or leaching the various fractions in acid. The ingot and skull fractions were dissolved in aqua regia. Condensate samples were prepared by leaching the collector with aqua regia containing a small amount of HF. In material-balance experiments with iodine compounds labeled with I¹³¹, the activity was counted in a well-type scintillation counter without prior chemical separation. The crucibles that were employed in these experiments were counted intact after a light etching of the interior walls with aqua regia to remove adhering skull material. All samples were counted at approximately the same time to eliminate decay corrections. Other analytical methods for the inactive elements were: amperometric titration with AgNO₃ for iodine; flame photometry for cesium; fluorophotometry for uranium; emission spectrography for other elements. The relative precisions of the analyses were: inactive and active iodine, $\pm 5\%$; cesium, $\pm 5\%$; uranium, $\pm 10\%$; and others, factor of two.

2. Results

Examination of the condensate resulting from melting about 20 g of uranium-5% fission spiked with cesium and UI₃ for one hour at 1400°C yielded information on the type of material volatilized. Analyses of elements initially present in the charge and crucible that were found in the condensate are presented in Table 9. Intercomparison of the various element concentrations indicates that: (a) cesium and iodine accounted for nearly all of the

*Previous results with high-activity-level alloy had shown that one hour of melt refining on a small (7-g) scale is sufficient to remove 98% of the iodine from the ingot fraction.

Table 9

ANALYSES OF MATERIAL VOLATILIZED DURING
MELT REFINING OF SYNTHETIC FUEL

Experiment	VIII
Crucible	Lime-stabilized zirconia
Charge	19.718 g of uranium-5 w/o fission spiked with cesium metal and U_3
Melt Refining	One hour at 1400°C
Atmosphere	Argon
Collector	Assembly A, Figure 5
Analytical Methods	
Cesium	Flame photometry
Iodine	Amperometric titration
Uranium	Fluorophotometry
Others	Emission spectrography

Element ^a	Initial Concentration in Charge Assembly (mg)	Volatilized	
		(% of charge)	(gram-atoms $\times 10^6$)
Cs	113	27	22700
I	33	28	7300
Ca	576	3.5×10^{-2}	500
Na	1	5	220
Fe	22	1.5×10^{-1}	50
Al	43	2×10^{-2}	30
U	18577	2.6×10^{-3}	19
Ti	29	$\sim 2 \times 10^{-2}$	~ 12
Pd	37	$\sim 3 \times 10^{-2}$	~ 10
Zr	10970	$\sim 9 \times 10^{-5}$	~ 7
Nb	2	$\sim 3 \times 10^{-1}$	~ 7
Hf	21	$\sim 5 \times 10^{-3}$	~ 6
Mo	481	$\sim 4 \times 10^{-4}$	~ 2
Ru	383	$\sim 5 \times 10^{-4}$	~ 2
Rh	55	$\sim 4 \times 10^{-3}$	~ 2
Si	53	no analysis	-

^aIncludes elements present in the charge and 16.1-g crucible except for sodium, which was present as a contaminant of cesium metal used in charge preparation.

collected material; (b) calcium, if present as CaI_2 , would account for about 15% of the iodine collected; (c) a small amount of sodium was present in the charge as a cesium contaminant; and (d) only trace amounts of other elements present in the components of the melt refining apparatus were present. The results were consistent with similar data obtained earlier with

highly irradiated alloy (see Table 4) in that cesium and iodine were the predominant species in the condensate. Apparently, when both cesium and iodine are present in the concentrations expected in high-burnup fuel, reactions of iodine with the elements present in the zirconia crucible or with constituents of the uranium-5 w/o fissium alloy will not play a significant role in iodine volatilization. Of the iodine initially present in this experiment, 28% was found in the volatilized fraction and about 0.8% in the ingot-plus-skull fraction, giving an overall iodine material balance of approximately 30%.

In view of the low material balance obtained in the above-described experiment, two additional experiments were carried out, in which a closed tantalum tube was used as the collector (see Figure 5, Assembly B). The synthetic charges used in these experiments were prepared by spiking uranium-5 w/o fissium alloy with either KI or CsI, labeled with I^{131} . The iodine-distribution data after melt refining the charges for one hour at 1400°C are shown in Table 10.

Table 10

DISTRIBUTION OF IODINE AFTER MELT REFINING
OF SYNTHETIC FUEL

		Crucible	Lime-stabilized zirconia	
		Melt Refining	One hour at 1400°C	
		Atmosphere	Argon	
		Collector	Assembly B, Figure 5	
<u>Uranium-Fissium Charge</u>				
Expt	Treatment	Weight (g)	Melt Refining Fraction ^a	Percent of Charged I^{131} in Fraction
IX	Spiked with Cs and Ki labeled with I^{131}	19.674	Ingot plus skull	1×10^{-2}
			Crucible	0.1
			Volatilized	99
X	Spiked with Cs and CsI labeled with I^{131}	20.040	Ingot plus skull	0.6
			Crucible	3×10^{-2}
			Volatilized	106

^aCharges were solidified in the crucible at the end of the melt refining period; crucible surfaces were treated with acid to dissolve adhering skull products and were counted without further treatment.

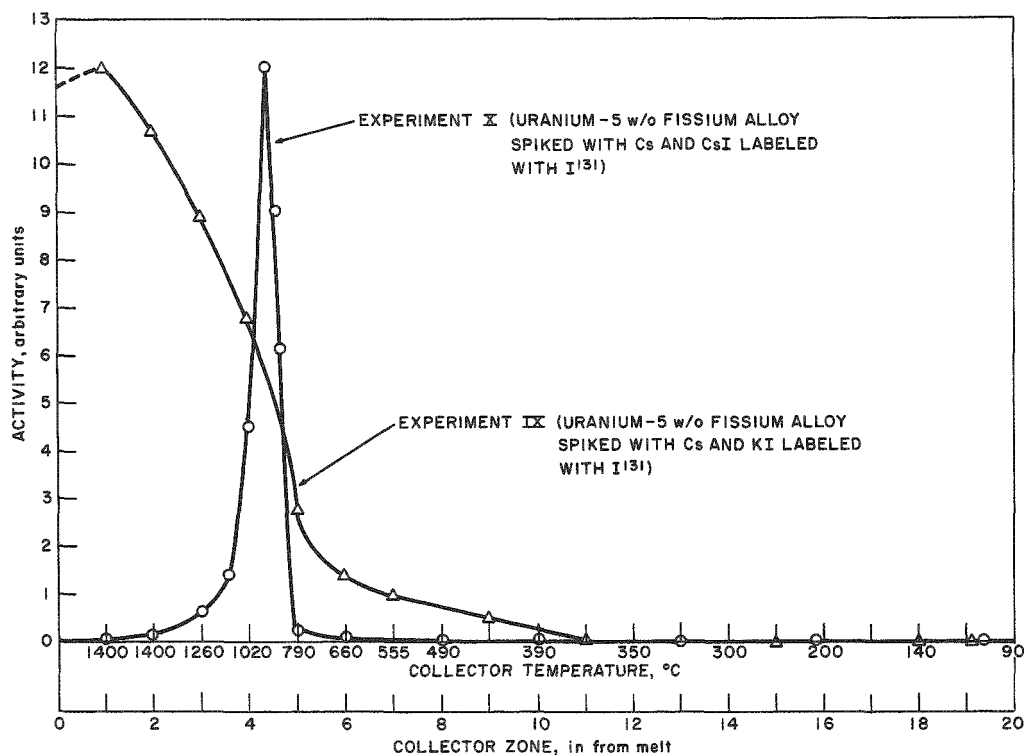
Within the limits of analytical precision, satisfactory activity balances were obtained for iodine. More than 99% of the charged radioiodine was volatilized and collected in the sealed collector. The ingot and skull

contained a maximum of 0.6% of the activity, and the crucible a maximum of 0.1%. The distribution of volatilized iodine along the collector tube in the two experiments is shown in Figure 6. Before the condensate was exposed to the air, the activity profile of the collector was measured by means of a scintillation counter with a $\frac{1}{8}$ -in.-wide collimator. Iodine added as KI (b.p., 1325°C) condensed in a higher-temperature region than that added as CsI (b.p., 1280°C) and was deposited over a wide temperature zone (from 350 to 1400°C). Most of the I^{131} added as CsI appeared in a band on the collector where the temperature had been between approximately 800 and 1000°C. The deposition pattern suggests that the activity volatilized mainly as KI in one case, and as CsI in the other. The effect of temperature on the distribution of iodine volatilized from a melt refining charge spiked with CsI is in reasonable agreement with that observed with high-burnup fuel. It is also consistent with the observation that fission product iodine volatilized to an inert atmosphere during melt refining at 1400°C is collected primarily as CsI.

Figure 6

DISTRIBUTION OF IODINE-131 IN A CLOSED COLLECTOR
TUBE AFTER MELT REFINING SYNTHETIC FUEL

(For experimental conditions, see Table 10)



The results from the experiments with the closed collectors suggest that a large fraction of the iodine in the previous work with synthetic and highly irradiated fuel had volatilized and escaped from the

apparatus. Previous difficulties in obtaining satisfactory material balances were therefore attributed to inadequate handling and collection techniques.

C. Release of Iodine from Fiberfrax

In the EBR-II melt refining furnace most of the iodine released during melt refining is expected to collect on the Fiberfrax fume trap. It was therefore necessary to estimate the amount of this activity that might be released to the argon atmosphere of the process cell when the fume trap is removed from the furnace and placed in storage. If the fume trap is kept on top of the crucible, fission product decay heat from the skull will produce a temperature gradient in the trap from about 700 to 350°C, the higher temperature being at the inner surface of the $\frac{7}{8}$ -in.-thick trap which sees the active skull. When lifted away from the crucible, the fume trap is expected to cool to a temperature of 150 to 200°C.

1. Experimental

Two experiments were performed to determine the rate of iodine release from Fiberfrax. The apparatus, shown schematically in Figure 7, consisted of (1) an induction-heated quartz tube furnace in which a synthetic fuel charge could be melt refined with a 1-in.-thick Fiberfrax plug serving as a fume trap,* (2) a separate resistance-heated quartz tube in which the Fiberfrax plug could be heated in a stream of argon after melt refining was completed, and (3) an assembly of AEC filters and charcoal traps to collect the iodine activity in the effluent argon stream. A diagram of the AEC filter-activated charcoal assembly is shown in Figure 8. Either two or three filter assemblies were used in each experiment, and they were alternated so that measurements of the activities could be made without interrupting the experiment.

In these experiments both the lime-stabilized zirconia crucibles and Fiberfrax covers were outgassed at a minimum temperature of 1000°C and a pressure of 0.1 μ prior to use.

The synthetic charge, prepared by separately spiking cesium metal and UI_3 to uranium-5 w/o fission alloy, was lightly irradiated to provide I^{131} and Cs^{134} activities for analytical purposes. The Cs^{134} was produced by neutron irradiation of metallic cesium in the charge.

This charge, along with about 0.2 g of sodium (to simulate the sodium from the thermal bond in the EBR-II fuel), was melt refined at 1400°C for one hour. After overnight cooling, the Fiberfrax plug was

*During this step the temperature gradient in the Fiberfrax (bottom surface, 1015°C; top surface, 540°C) approximated that observed in the top of the fume trap during tests of the plant-scale melt refining furnace.

withdrawn into the upper furnace of the apparatus, and Xe^{133} and Kr^{85} were removed by evacuating the system. The Fiberfrax was then isolated from the lower section of the apparatus by closing a gate valve and was positioned in the quartz tube furnace in such a way that the desired temperature gradient would be obtained.

Figure 7

APPARATUS FOR STUDY OF IODINE RELEASE
FROM A FIBERFRAX FUME TRAP

(Not to scale)

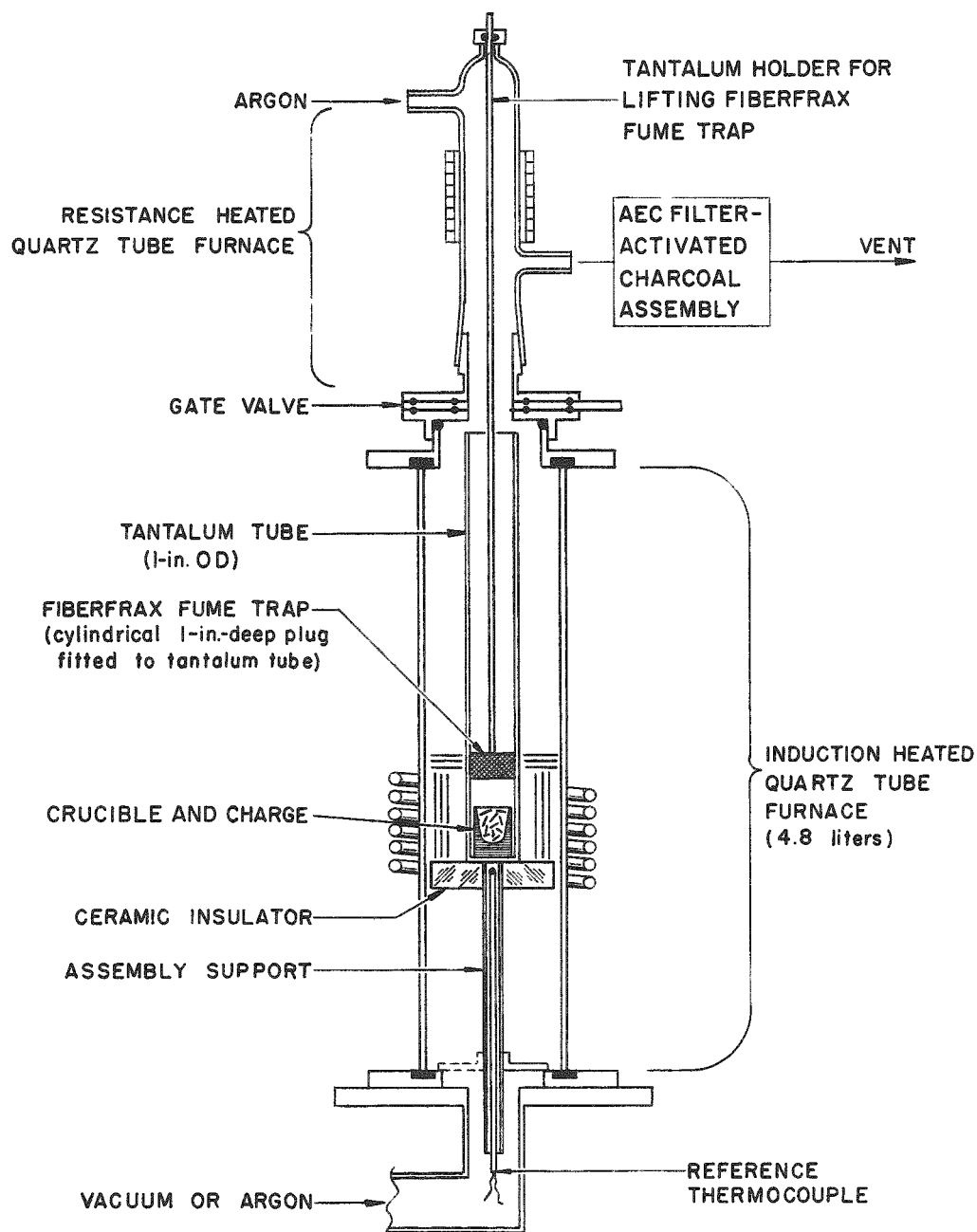


Figure 8

ACTIVATED CHARCOAL ARRANGEMENT FOR
COLLECTION OF ACTIVITY RELEASED
TO GAS STREAMS

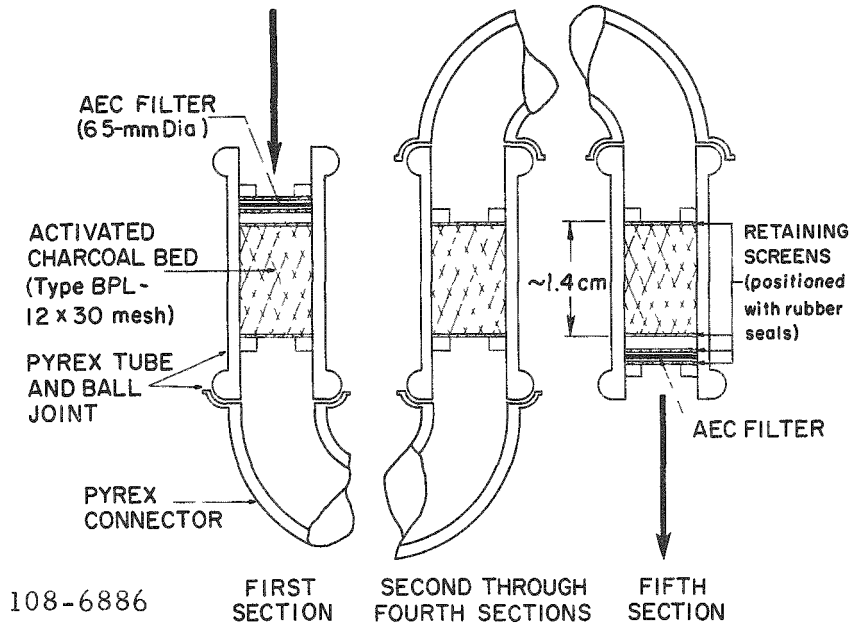
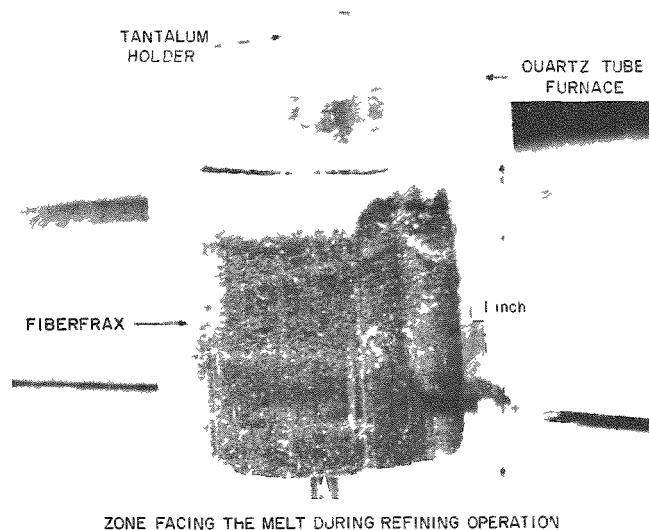


Figure 9 shows the appearance of the Fiberfrax trap after the melt refining operation. The blackening of the zone facing the melt is associated with a chemical reaction between the Fiberfrax and alkali metals

Figure 9

FIBERFRAX FUME TRAP USED DURING
MELT REFINING EXPERIMENT



108-6076-B

(sodium and cesium) that were volatilized during melt refining. Studies by LaPlante⁽¹⁴⁾ of the reaction of sodium with Fiberfrax at temperatures of about 500 to 750°C showed a similar blackening of the Fiberfrax, which corresponded to the extent of sodium penetration. Analysis of leachings from these treated samples indicated that the reaction resembled a basic fusion of silicate, in which the base metal is increased, converting the acidic silicate to a soluble basic form.

Argon containing either 2.2 or 175 ppm of oxygen and low levels of nitrogen and water vapor (<25 ppm and 5 ppm, respectively)* was passed over the surface of the Fiberfrax and through the AEC filter-activated charcoal assemblies. The flow rate was held constant at 6.6 ft/min over the sides of the Fiberfrax plug and about 34 ft/min through the filter assemblies. The flow of gas over the sides of the Fiberfrax plug corresponded roughly to the estimated natural flow rate in the Argon Cell atmosphere of the Fuel Cycle Facility. At frequent intervals one of the filter assemblies was removed from the system and the gamma activities were measured. While the assembly was being counted, it was replaced with another one so that the gas-transported activity was collected continuously, except for overnight periods when the bed was cooled to room temperature and maintained in a static argon atmosphere.

On completion of the experiment, the apparatus was dismantled, and samples for the determination of activities retained by the Fiberfrax and condensed on the walls of the resistance heated quartz tube furnace were obtained by alternately leaching these components with aqua regia containing a small amount of HF and a dilute solution of NaOH. All samples were counted with the use of a 256-channel gamma ray spectrometer.

2. Results

Table 11 is a summary of the analytical data that were obtained on heating the Fiberfrax traps used in melt refining Experiments XI and XII. In each experiment, the amount of I¹³¹ deposited on the quartz walls of the furnace was greater than the amount transported by the flowing atmosphere to the AEC filter-activated charcoal collector assemblies. Analyses of these fractions after more than 99% of the I¹³¹ had decayed showed that Cs¹³⁴ was the only additional gamma-active element present.

*The argon cell in the EBR-II Fuel Cycle Facility includes provisions for removal of oxygen and water, which will limit their levels to 5 ppm of water and 20 ppm oxygen. The equilibrium nitrogen content may attain 5 v/o. The concentration of nitrogen in the argon used in these experiments was not varied since the initial studies with highly irradiated alloy had indicated that the major condensable volatiles collected with iodine would be sodium and cesium, and neither of these would react directly with nitrogen under the experimental conditions.

Table 11

DISTRIBUTION OF IODINE-131 AFTER REHEATING FIBERFRAX FUME TRAPS
USED DURING MELT REFINING OF SYNTHETIC FUEL AT 1400°C

<u>Equipment</u>		See Figure 7						
<u>Melt Refining</u>								
<u>Charge^a</u>		Lightly irradiated uranium-5 w/o fission spiked with cesium and UI_3						
Charge Wt (g)		Expt XI, 19.968; Expt XII, 19.858						
Atmosphere		Argon						
Duration of Melt Refining (hr)		1						
<u>Fiberfrax Temp (°C)</u>								
Bottom area facing melt		1000 to 1015						
Top area		540						
<u>Fiberfrax Reheating</u>								
Temperature		Indicated below						
Argon Flow through Filter Assembly (ft/min)		34						
Argon Flow over Fiberfrax (ft/min)		6.6						
Impurities in Argon (ppm)		H_2O , 5; N_2 , <25; O_2 , indicated below						
Expt	Initial Iodine Activity (μC)	Fiberfrax Temp	Time (hr)	Oxygen Conc in Argon (ppm)	Iodine Distribution, % of Initial Activity			
					Collected by Filter Assembly	Condensed on System Walls	Retained by Fiberfrax	
XI	867.5	Constant heating; 680, 315°C ^b Varying ^c	34.2	2.2	5.5	13.6	79.7	
			23.2 ^d	2.2				1.2
XII	307.8	Constant heating; 170°C Constant heating; 170°C Varying ^c	30.2	2.2	2.8×10^{-3}	0.15	99.8	
			30.9	175				6.5×10^{-3}
			14	89 (av.)				2.6×10^{-3}

^aAbout 0.20 g of sodium metal was added to the irradiated charges of Experiments XI and XII to simulate the sodium present as a thermal bonding medium in the EBR-II fuel element.

^bTemperatures apply to bottom and top areas of fume trap, respectively.

^cCooled to room temperature during overnight holding periods and reheated to experimental temperature.

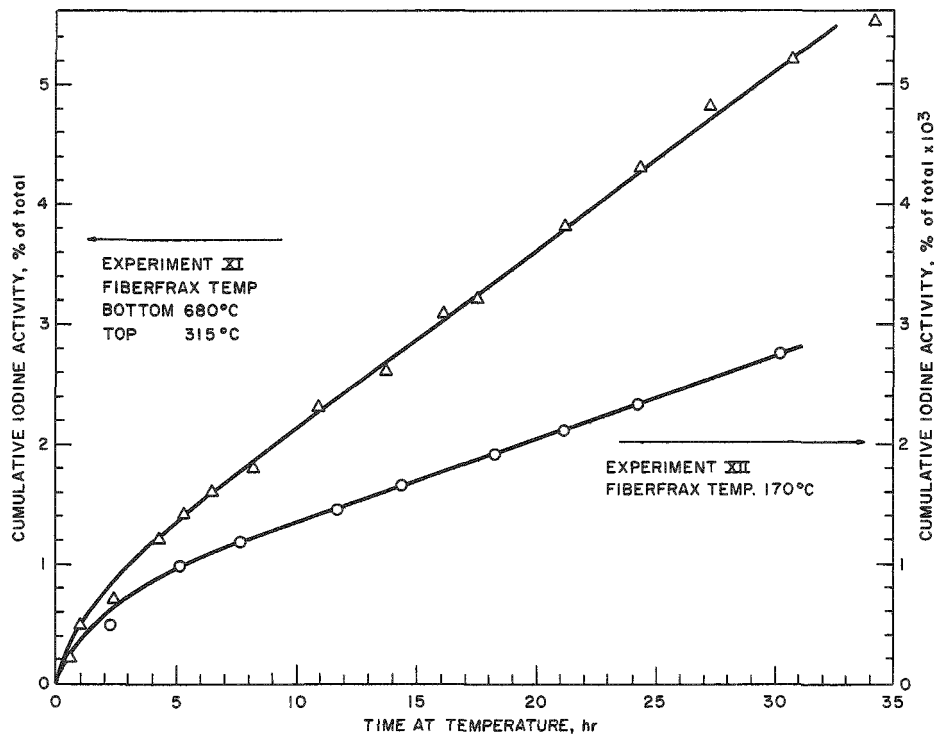
^dIncludes a short period (~5 hr) of constant heating during which the Fiberfrax was at a temperature of 110 to 150°C.

The rates of I^{131} collection by the filter assemblies for two conditions of Fiberfrax heating are shown in Figure 10. The cumulative percentage of activity is based on the amount of activity originally present in the Fiberfrax. Under both conditions of heating, the rate, after an initial period of more rapid release, appeared to be constant over a period of about 30 hr. The higher initial rate may have resulted from the more rapid release of activity which had deposited on the outer surfaces of the Fiberfrax during melt refining. The release rate of iodine was reduced by a factor of about 1000 by decreasing the Fiberfrax temperature from the 680 to 350°C-gradient temperature to 170°C.

Figure 10

EFFECT OF TEMPERATURE ON IODINE-131 RELEASE
TO ACTIVATED CHARCOAL ASSEMBLIES DURING
REHEATING OF FIBERFRAX FUME TRAPS

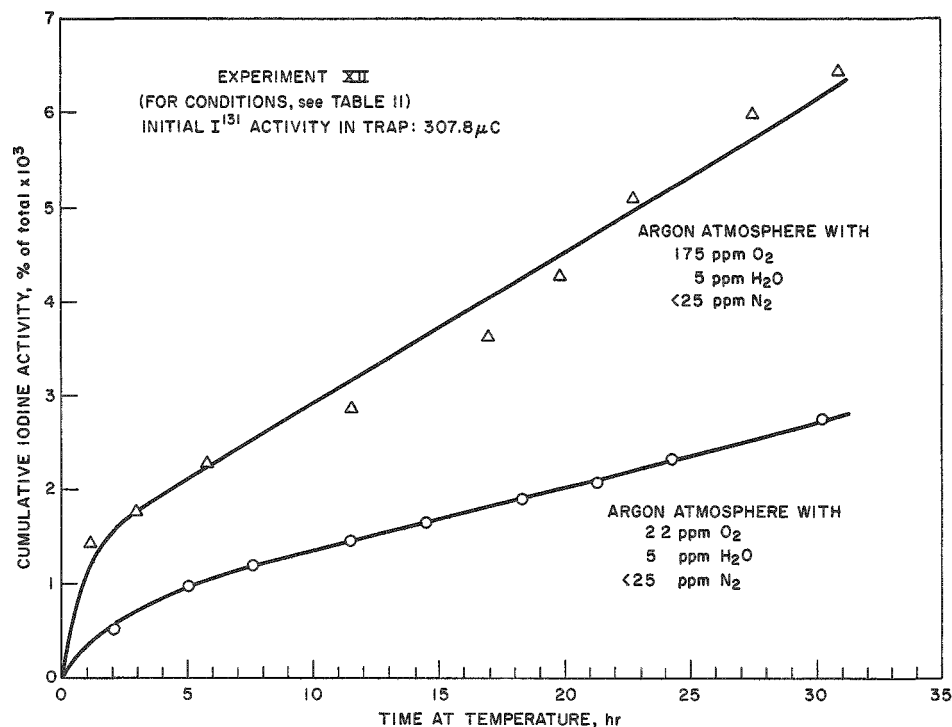
Expt	Conditions	Initial I ¹³¹	
		Activity in Trap (μ C)	Impurities in Argon (ppm)
XI	See Table 11	867.5	H ₂ O 5 N ₂ <25 O ₂ 2.2
XII	See Table 11	307.8	H ₂ O 5 N ₂ <25 O ₂ 2.2



The effect of raising the oxygen content of the argon atmosphere from 2.2 to 175 ppm on the release of iodine from Fiberfrax heated at 170°C is shown in Figure 11. With the higher concentration of oxygen in the argon stream (175 ppm), the release rate was again nearly constant with time (over a period of about 30 hr), but it was greater by a factor of 2.3.

Figure 11

EFFECT OF ATMOSPHERE CONTAMINATION ON IODINE-131
RELEASE TO ACTIVATED CHARCOAL ASSEMBLIES
DURING REHEATING OF FIBERFRAX
FUME TRAP AT 170°C



Distribution data for the iodine activity in the charcoal filter assemblies used in the two experiments are presented in Table 12. Of the total iodine collected in each assembly, more than 80% was found in the inlet AEC filter and first charcoal bed section (~1.3 cm). The remaining iodine activity was distributed about equally among the succeeding charcoal beds. The percentages of iodine found on the inlet AEC filters differed in the two experiments, with a retention of more than 50% of the total iodine collected in Experiment XI and less than 15% in Experiment XII. Since both the oxygen concentration in the carrier gas and the temperature of the Fiberfrax were varied in the two experiments it is not known which effect contributed more to this altered pattern. However, the higher retention by the AEC filter in Experiment XI is probably more nearly typical of the plant operation, for which the oxygen content of the argon atmosphere is not expected to be greater than about 20 ppm.

All components of the collector assemblies containing detectable amounts of I¹³¹ also contained Cs¹³⁴. The percentages of total cesium and iodine activity as a function of depth of granulated charcoal in the two assemblies used in Experiment XI are shown graphically in Figure 12. The constant ratio of iodine and cesium activities throughout all of the charcoal

bed sections is evidence that iodine was released from the Fiberfrax and transported by the argon carrier gas through the AEC filter was largely in the form of CsI. Analysis of a NaOH solution in a bubble trap downstream from the AEC filter-activated charcoal assemblies in this experiment showed less than $2 \times 10^{-4}\%$ of the total amount of iodine activity found in the assemblies ($58 \mu\text{C}$).

Table 12

IODINE DISTRIBUTION IN ACTIVATED CHARCOAL ASSEMBLIES
USED FOR STUDY OF IODINE RELEASE FROM FIBERFRAX

Experimental Conditions - See Table 11

Carbon Filter Assembly ^a	Experiment XI		Experiment XII		
	1	2	3	4	5
Depth of Charcoal Bed Sections (cm)	1.3 ± 0.1	1.3 ± 0.1	1.4 ± 0.1	1.4 ± 0.1	1.3 ± 0.1
Argon Flow through Filter Assembly (ft/min)	34	34	34	34	34
Total Activity Collected in Assembly (μC)	27.64	30.79	0.017	0.016	0.004
¹³¹ I Distribution (% of total collected)					
Section I					
Inlet AEC Filter	55	71	4	12	b
Activated Charcoal Bed	30	21	96	82	100
Section II					
Activated Charcoal Bed	5	2	b	b	b
Section III					
Activated Charcoal Bed	3	2	b	b	b
Section IV					
Activated Charcoal Bed	3	1	b	b	b
Section V					
Activated Charcoal Bed	3	1	b	b	b
Outlet AEC Filter	1	2	b	b	b

^aA sketch of the assembly appears in Figure 8, page 30.

^bIodine activity was below the detection limit for the gamma spectrometric measurements.

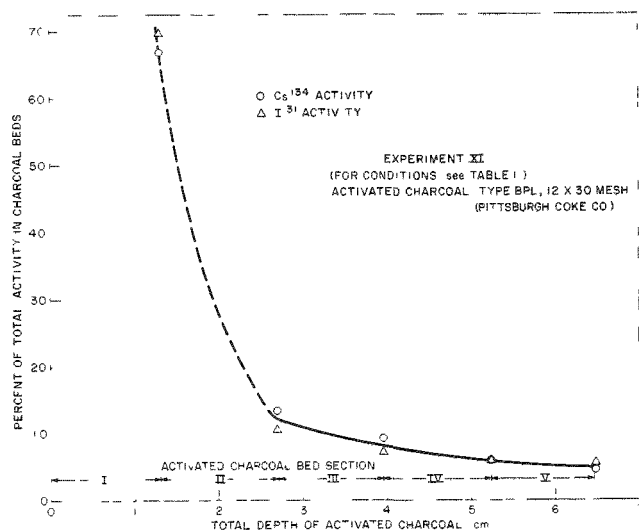


Figure 12
COMPARISON OF TOTAL IODINE AND CESIUM
ACTIVITY COLLECTED IN ACTIVATED
CHARCOAL BEDS USED FOR STUDY OF
IODINE RELEASE FROM FIBERFRAX

IV. DISCUSSION

It should be recognized that these laboratory results are not directly applicable to the plant-scale melt refining operations, since it was not feasible to duplicate all of the conditions in the EBR-II facility. For example, the plant operation will involve larger amounts of fuel, differences in the geometry of the melt refining charge and the equipment, and higher radiation levels. If these factors are taken into account, however, the laboratory results should be a reasonably reliable indication of the behavior of fission product iodine in the plant, and they should be useful in establishing necessary control measures and handling procedures.

A. Iodine Distribution during Melt Refining

The results from the melt refining demonstration runs with highly irradiated fuel (see data for Experiments III, IV, and V in Table 7) indicate that about 0.3% of the fission product iodine in irradiated EBR-II fuel will remain in the product ingot when the fuel is melt refined at 1400°C. Variations in burnup between 0.74 and 1.75 total a/o had no significant effect on the percentage of iodine retained by the product ingot. If it is assumed that iodine removal occurs by diffusion of the iodine through the molten alloy, the minimum diffusion path in the plant-scale equipment will be about twice that for the 0.4-kg laboratory demonstration runs.* On this basis, the longer liquation time in the plant (3 to 4 hr) might be expected to provide about the same degree of iodine removal as the one-hour periods used in the demonstration runs. However, approximately the same iodine removal was obtained in one-hour laboratory experiments in which charges varying from 7 to 400 g were melt refined. These results suggest that nearly all of the iodine removal occurs shortly after the fuel is melted, and that iodine removal may not be a determining factor in the required liquation time.

On the basis of information from experiments with both highly irradiated and synthetic fuel charges (see Tables 7 and 10), it is estimated that the melt refining skull and crucible will each retain approximately 1% of the iodine activity initially present in the charge. However, the situation in the plant equipment is somewhat different with regard to the crucible. In the laboratory studies the crucible was essentially isothermal at a temperature of 1400°C. In the plant, the lower portion of the crucible will be at this temperature, but areas near the top of the crucible wall will be at a considerably lower temperature (possibly as low as 600°C). A significant fraction of the volatilized iodine is therefore very likely to condense on this cooler zone. For this reason a higher percentage of the

*In the demonstration runs the diameter of the melt was about 3.5 cm, and the depth about 2.2 cm. In the plant operation the melts will be about 13 cm in diameter and 4.2 cm deep.

iodine is expected to be present in the crucible than that indicated in Table 10 for Experiments IX and X.

The experimental evidence from both highly irradiated and synthetic fuels indicates that the volatilized iodine activity is collected as CsI. It also shows that the cesium-to-iodine ratio in all the condensate fractions was much greater than unity.

There is insufficient information on the chemical state of fission product iodine in irradiated metallic fuels to justify a detailed interpretation of its behavior in these experiments. It is interesting, however, to compare these results qualitatively with those obtained by other workers. Castleman⁽⁷⁾ investigated the release of iodine from low-burnup ($\sim 10^{-2}$ total a/o) uranium-3.5 w/o molybdenum alloy that was heated for about one hour at 1205°C under a helium atmosphere. He concluded that the iodine was volatilized as a compound, presumably UI_2 . Although systematic data on the effect of burnup on the chemical state of iodine volatilized from uranium and its alloys in inert atmospheres are not available, this effect may be significant.

The solubilities of the rare gas fission products in uranium are low, with the result that they agglomerate into bubbles in the metallic matrix.⁽¹⁵⁾ Hilliard⁽⁵⁾ has examined the influence of burnup on the release of fission products from molten uranium under oxidizing conditions. With respect to certain volatile fission products (xenon, iodine, and cesium), he found variations for uranium samples that had been irradiated to burnups ranging from about 10^{-7} to 0.16 total a/o, the greater release occurring with the higher-burnup material. Although the fuel was heated under oxidizing conditions, the effect of bubble formation in the metal was believed to play an important role in the release of volatile fission products. The higher percentages of xenon, cesium and iodine release were explained on the basis that at high burnups and high irradiation temperatures (about 400°C) these activities would be contained primarily in bubbles or voids. The major escape process would then change from atomic diffusion to migration through expanded bubbles and cracks in the metal. Such bubbles and microcracks have been observed in uranium-fission alloys of the type used in the present experiments.⁽¹⁶⁾ In addition, previous work with uranium-fission alloys⁽¹⁷⁾ had indicated that irradiation level does influence the release characteristics of rare gas fission products when the fuel is melted in an inert atmosphere. Thus, in the present work, it appears likely that CsI was formed by reaction of the elements within the pores and microcracks in the metal. Under these conditions most of the iodine would be expected to volatilize as CsI during melt refining of the irradiated alloy, as was found in the experimental work. The deposition of fission product iodine from low-burnup uranium alloy fuel as a uranium iodide, as suggested by Castleman, is not in disagreement with this hypothesis, since the presence of bubbles, pores, or microcracks which would serve as sites for CsI formation would be less likely in fuel of lower burnup.

B. Release of Iodine to Melt Refining Off-gases

The melt refining operation is the principal source of high-activity gaseous wastes in the EBR-II Fuel Cycle Facility. At the end of this operation the furnace will contain gas-borne fission products, principally Xe^{133} , Kr^{85} , and I^{131} . As indicated earlier, these gases will be pumped to a holdup tank located outside the Fuel Cycle Facility before they are released to a stack. Controlled dilution with the stack gas will be used to reduce the concentration of rare gas activity to an acceptable level for discharge to the atmosphere. The iodine activity poses additional problems, however, because of the low tolerances on release to the atmosphere, and the fact that its chemical and physical state depends upon the particular process operation involved. To minimize shielding requirements for the off-gas handling equipment (piping, traps, vacuum pumps, hold-up tank), the I^{131} activity in off-gases from the melt refining furnace must be largely removed before the gas reaches the equipment in the subcell area (see Figure 1, page 7).

Considerable information on the trapping of iodine activity in gas streams has appeared in the literature.⁽¹⁸⁻²¹⁾ Much of this information pertains to the collection of elemental iodine, which is the predominant species released when irradiated metallic fuel is burned in air. However, the elemental iodine, when discharged to a volume such as a reactor containment vessel, does not remain primarily in the elemental form. British studies concerning the physical chemistry of fission product iodine and its removal from gas streams have shown that iodine released to an enclosure will adsorb rapidly on surfaces.⁽²⁰⁾ In addition, adsorption on gas-borne particles and reactions with constituents of the atmosphere will take place. Organic compounds have shown a particular tendency to react with fission product iodine in the gas phase. At Oak Ridge National Laboratory, Browning⁽²²⁾ has shown that the efficiencies of different devices for the removal of iodine from gas streams depend strongly on the size of the iodine-bearing particles in the gas. In general, differences in the results from various studies of iodine-trapping techniques probably can be attributed to variations in the physical state of the iodine under the particular conditions involved. However, there appears to be general agreement that activated charcoal is one of the most effective trapping materials for the removal of iodine activity from gas streams.

In the present study, the most reliable estimates of the amount of iodine activity present in the argon atmosphere of the furnace after melt refining were obtained from Experiments IV and V (see Tables 2 and 3). These results indicate that after highly irradiated fuel had been melt refined at 1400°C and the crucible assembly had been cooled to an equilibrium temperature,* less than 0.01% of the iodine in the original charge was

*When fully irradiated fuel is processed, that portion of the crucible containing adhering skull may not cool much below 650°C. Fission product heat will maintain temperature gradients in the Fiberfrax trap between about 150 and 700°C. In Experiments IV and V, the crucible and skull were at about 300 and 650°C, respectively, during the gas-sampling operations.

present in the furnace atmosphere. Pumping the furnace down to a pressure of about 10 torr during Experiment V had little effect on the release of iodine activity to the argon atmosphere.

In the plant operation it is expected that little iodine activity will be released to the furnace atmosphere, since all of the evidence has indicated that the iodine deposits on the cooler portions of the melt refining furnace, presumably in the form of CsI. Although exposure of this deposited activity to undried air (Experiment IV, Table 2) caused some increase in the amount of iodine in the furnace atmosphere, this effect is not expected to be significant in the melt refining furnace of the Fuel Cycle Facility where oxygen and moisture will be essentially absent. On the other hand, when Fiberfrax containing iodine and cesium that had been volatilized from the synthetic fuel was reheated in argon so as to have a temperature gradient from 680 to 315°C, the rate of iodine release was slow, but nearly constant with time over a period of about 36 hr (see Figure 10). These results indicate that successive furnace pumpdowns during the plant operation will not eliminate completely the activity in the furnace atmosphere, since some additional iodine will be released to the atmosphere in each cycle.

Examination of the AEC filter-activated charcoal assembly used during the investigation of melt refining off-gas handling procedures in Experiment V (see Table 3) showed a complicated picture. Since most of the activity was found on the AEC filters and since fission product cesium and iodine were present in approximately equal atomic proportions, with other gamma activities essentially absent, it appears that the iodine was transported primarily as CsI. In this event, the concentration of particulate CsI in the gas stream (based on the amount of iodine collected in the AEC filter-charcoal assembly and the total volume of gas involved) was of the order of 10^{-4} mg/liter. The reported efficiency of AEC filters indicates 99% removal of 0.3- μ particles at a concentration of 0.2 mg/liter and at face velocities up to 200 ft/min. Although the flow rates used in these experiments were in an efficient operating range for the filter, little is known concerning its collection efficiency at these very low levels of particulate concentration. The presence of iodine ($6 \times 10^{-6}\%$ of that in the charge) downstream from the filter-charcoal bed-filter assembly is evidence that the off-gases from the melt refining furnace contained some submicron iodine-bearing particulate material.

In the above-mentioned experiment the AEC filter-activated charcoal assembly was used in a furnace pumpdown over a period of about 1.8 hr. All of the detectable iodine retained by the charcoal was found in the first 1.3 cm of the 9.7-cm bed. In the plant operation it would be desirable to use a similar type of assembly for several hours. During the initial investigation of iodine release from Fiberfrax in a flowing argon atmosphere containing low levels of impurities (Experiment XI), similar distribution information was obtained on the activities present in two filter assemblies,

each of which was used about 29 hr. It was interesting to note that the efficiency of the bed was greatest in the first 2.5 cm of bed depth and thereafter decreased with bed depth to about 6.5 cm (see Figure 12). The percentages of total cesium and iodine activity collected as a function of bed depth were roughly the same. The decreased efficiency in the filter-charcoal bed assemblies that were used for the longer periods was therefore attributed to the carrying of iodine attached to carbon in a fine particulate state.

The overall results from these studies indicate that both filters and activated charcoal beds are necessary to collect iodine activity in the argon atmosphere that is removed from the melt refining furnace. The experimental evidence is inadequate to provide a prediction of the amount of iodine activity carried on submicron particles that will not be removed either by charcoal beds or by AEC filters, but it appears that this fraction will be small, compared with the total amount of iodine present in the furnace atmosphere.

V. CONCLUSIONS

The results of the laboratory studies described in this report have led to the following predictions concerning fission product iodine behavior during the melt refining of highly irradiated EBR-II fuel in the Fuel Cycle Facility:

(1) Under the conditions proposed for the reprocessing of EBR-II fuel (melt refining for 3 hr at 1400°C), more than 99% of the iodine will be removed from the product ingot by volatilization.

(2) Essentially all of the volatilized iodine will be deposited as CsI, rather than as elemental iodine.

(3) Most of the volatilized iodine will be collected in the Fiberfrax fume trap over the zirconia melt refining crucible, and a small amount (probably <1% of that present) will be retained by the skull material. A significant fraction of the iodine may be deposited on the crucible, depending on its temperature gradient during the melt refining process.

(4) After melt refining is completed and the furnace is cooled to equilibrium at the ambient temperature, a pumpdown of the furnace to 10 torr will effect a release estimated to be of the order of $10^{-2}\%$ of the total amount of iodine present to the furnace atmosphere.

(5) The release of iodine collected on a Fiberfrax fume trap will be small (<0.2% of the total iodine in the trap per hour) when the trap is heated at a temperature corresponding to the maximum heating effect that would result from fission products remaining in the crucible and skull.

(6) Iodine that is released to the furnace off-gas and to the Argon Cell of the Fuel Cycle Facility will be largely in a particulate form.

(7) A combination of high-efficiency filters and activated charcoal will remove nearly all of the iodine present in the furnace off-gases after melt refining.

This report covers most of the laboratory work that has been done on the behavior of iodine in the EBR-II melt refining process. A large amount of effort has also been devoted to this subject by others* who have been concerned with the design and operation of process equipment in the Fuel Cycle Facility. In addition, J. C. Hesson et al.⁽⁸⁾ have related the laboratory data to the handling and storage of solid and gaseous wastes containing iodine in the EBR-II facility. Their calculations indicate that

*L. F. Coleman and G. J. Bernstein of the Chemical Engineering Division have been particularly concerned with this problem.

the ground-level iodine concentration in the atmosphere near the plant facility should not exceed the maximum permissible concentration of 9×10^{-9} C/m³.* An exception could occur if direct venting of a fraction of the argon cell gas to the atmosphere should become necessary in an emergency. However, even under emergency venting conditions, the iodine level would not be greater than five times that permitted for discharge over a one-hour period in one week.

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*This maximum permissible concentration, established by the Atomic Energy Commission,(23) is based on 40 hr of human exposure in any period of 7 consecutive days.

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