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FISSION PRODUCT RELEASE FROM URANIUM HEATED IN AIR

R. K. HILLIARD

AUGUST 3, 1959

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FISSION PRODUCT RELEASE FROM URANIUM HEATED IN AIR

By

R. K. Hilliard

Chemical Effluents Technology
Chemical Research and Development Operation

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ABSTRACT

The release of fission products from small cylindrical specimens of normal uranium heated in an air stream was investigated in a laboratory study. The specimens were irradiated to 2.4×10^{14} nvt and allowed to cool one to three days before testing. Heating was accomplished out of pile in a resistance furnace with air flowing over the specimen. The off-gas stream was scrubbed free of radioactive material by suitable traps. Analyses were performed on the volatilized portion and on the dissolved residue to determine the fraction of fission products released. Analyses were made for I^{131}, Te^{132}, Xe^{133}, Sr^{89}, Cs, Ru^{103}, Ba^{140} and Zr^{95}. Twenty-nine tests were performed with air and one with a helium atmosphere. The furnace temperature was varied from 425 C to 1440 C while the time of heating varied from 2.5 to 232 minutes. The efficiencies of various filter media for retaining air-borne radioactive matter were investigated. An unsuccessful effort was made to separate the particulate from the elemental release. Data gathered in these tests were correlated to show the effects of temperature, time of heating and per cent of metal oxidized on the release coefficient for the fission products investigated.

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FISSION PRODUCT RELEASE FROM URANIUM HEATED IN AIR

INTRODUCTION

Many theorists have questioned the validity of the various estimates made on the possible damages which would result from an uncontrolled release of fission products from nuclear reactors. One uncertainty in the calculations is the lack of information concerning the amount and the rate of release of fission products and the physical characteristics of the radioactive matter released. The initial calculations reported by H. M. Parker and J. W. Healy at Geneva in 1955(1) assumed a 100 per cent release with the reader allowed to provide his own release factor. Present estimates assume a 25 per cent release from an accident such as meltdown, the release being fractionated as 100 per cent of the noble gases, 70 per cent of the halogens and 10 per cent of the remaining fission products.(2)

A literature survey made in 1957 revealed that very few experimental data were available to support these assumptions.(3) In the past two years some data have become available which indicate that fission products are retained by molten reactor cores to a greater extent than previously assumed.(4, 5, 6) A report evaluating the existing information and suggesting profitable avenues of study has been issued recently.(7)

A series of laboratory experiments was recently performed at Hanford to study the fission product release from natural uranium heated in air. The results of these experiments are reported in this document.

These experiments were designed to provide as much information as possible in a few tests and to determine whether laboratory data can be correlated to provide a basis for a realistic estimate of the nature of radioactive release from reactor incidents. A complete study of fission product release would investigate the effect of at least six variables: type of fuel, atmosphere in which heated, temperature, time of heating, fuel element geometry and irradiation level. In this limited study four of the variables were held constant and only the time of heating and temperature were allowed to vary. In selecting the parameters, conditions were chosen which were believed to give the highest release of fission products and therefore an upper limit to the release factor. Unclad uranium was chosen as the type of fuel element because of its simplicity and relatively low melting point. Air was used for the atmosphere because of the likelihood for greater release than in other atmospheres and high probability of air being present during most reactor accidents. Small cylinders irradiated to low levels were used to simplify experimental equipment and procedures.

The release of fission products in a steam atmosphere is currently being investigated. The experiments are similar in scope and procedure to the air atmosphere tests described in this report. Plans are also being made to investigate the effects of irradiation level and specimen size.

OBJECTIVES

The over-all objective of these experiments was to gather as much information as possible concerning the release of fission products from irradiated uranium heated in air, and to determine whether such data can be correlated to provide a basis for prediction of the nature of fission product release during a reactor incident if conditions within the reactor are known.

Study of every individual fission product isotope would be laborious and probably unwarranted. Therefore eight fission product elements were selected for analysis. They were iodine, tellurium, xenon, strontium, cesium, ruthenium, barium and zirconium. The specific objectives of the experiments were to determine for the eight elements just listed:

1. The effect of temperature on the fraction released.
2. The effect of time at temperature on the fraction released.
3. The effect of air velocity on the fraction released.
4. The tendency to condense and deposit on tube wall surfaces and traps.

5. The radioactivity associated with particulate emission and, if possible, measure particle sizes.
6. The efficiencies of several filter media for retaining the air-borne radionuclides.
7. A comparison of release in air and in helium atmosphere.
8. Whether release is related to uranium metal oxidation.
9. Whether data gathered by isothermal tests can be integrated to predict release during dynamic temperature conditions.

SUMMARY OF RESULTS

Though the information gathered by these experiments by no means furnishes a complete understanding of the fission product release problem, some definite trends and correlations were observed. For the conditions of these experiments the following observations and conclusions were found:

1. Xenon, iodine and tellurium were, as expected, the most volatile fission product elements. The maximum release from the specimen was 90% for iodine and 80% for xenon and tellurium at the highest temperatures employed. The rate of release was proportional to the rate of uranium oxidation. Continued heating after all the uranium was converted to oxide did not release significant additional amounts of these elements.
2. Cesium and ruthenium ranked next in order of volatility, with a maximum of 6% cesium and 15% of the ruthenium released. The rate of release of these two elements was slightly time dependent, and ruthenium was released at a higher rate after all the uranium was oxidized.
3. Strontium, barium and zirconium behaved similarly and all three were quite non-volatile. In an air atmosphere the maximum release observed was 0.1% of the strontium, 0.16% of the barium and 0.07% of the zirconium. Time of heating did not significantly affect the total release of these elements, but higher temperatures gave a higher release.

4. The air flow rate was found to have a minor effect on the release of all fission products tested. However, the volatilized portion was retained to a much greater extent within the furnace tube at low flow rates than at higher velocities.
5. A CWS "Absolute" filter placed at the furnace tube outlet retained about 55% of the iodine and strontium, 75% of the barium, 93% of the cesium and 97% of the tellurium and ruthenium.
6. Fission product release during the single test using a helium atmosphere was considerably different than in the air experiments. With other conditions held constant, a helium atmosphere gave considerably lower release of iodine, about the same release of cesium and barium, and about four times greater release of strontium than did air.
7. The tendency of the volatilized portion of the fission products to deposit on tube walls varied considerably. About 7% of the iodine, 20% of the tellurium, 30% of the cesium, 40-45% of the barium and zirconium, 50% of the strontium and 85% of the ruthenium deposited on the walls of the furnace tube.
8. The release of iodine, tellurium and xenon during dynamic temperature conditions agreed within experimental error with that predicted by graphical integration of isothermal data. Use of the correlation between per cent of uranium oxidized and fraction released can also be used to predict the release of these elements if the per cent of oxidation is known or can be estimated accurately.
9. The radioactivity associated with particulate emission was not directly determined. Discrete particles were not observed by means of optical microscope or radioautography. Any particles released were invariably contaminated with large amounts of iodine and tellurium. Efforts to separate the iodine and tellurium from particles were unsuccessful. Even 99.5% removal of the iodine and 95% removal of the tellurium left a filter contaminated to such an extent that a gamma scan showed only iodine and tellurium.

EXPERIMENTAL PROCEDURE

Bare natural uranium cylinders measuring 1/4 inch diameter by 3/4 inch long and weighing 11.5 grams were polished and irradiated to about 2.4×10^{14} nvt. They were allowed to cool 22 to 70 hours before testing. The burning procedure was to preheat the furnace to the desired temperature and insert the specimen in the cool upstream portion of the furnace tube. A zirconia combustion boat was used to contain the specimen during heating. Filtered and dried air was then fed through the furnace tube at 2300 cc/min (STP), equivalent to 500 cm/min velocity at standard conditions of pressure and temperature. The furnace, which was mounted on wheels, was then rolled over the specimen and maintained at isothermal temperature for the duration of the test. The off-gas appeared to cool rapidly before reaching the various filters and traps used to remove the radioactive material. After the desired heating period, the furnace was rolled off the specimen along the downstream end of the furnace tube. By this procedure the specimen attained test temperature and cooled rapidly. A flow diagram of the heating equipment is shown in Figure 1.

After the specimen had cooled, the furnace tube was removed and allowed to cool. The specimen residue and the zirconia boat were then transferred to a dissolver flask and the residual uranium metal and oxide dissolved in concentrated nitric acid. A sketch of the dissolving equipment is shown in Figure 2. After the residue was dissolved, the acid solution was purged of fission gases by sparging with helium. Analyses of the cold and caustic traps in the dissolving apparatus showed that, with the exception of xenon, less than one per cent of the radioisotopes left the dissolver flask.

The furnace tube, connecting lines, caustic traps and cold trap were decontaminated by a minimum of three series of rinses with water, HNO_3 and caustic. Washing was continued until the residual activity in the equipment registered less than five per cent of the original value by GM counter.

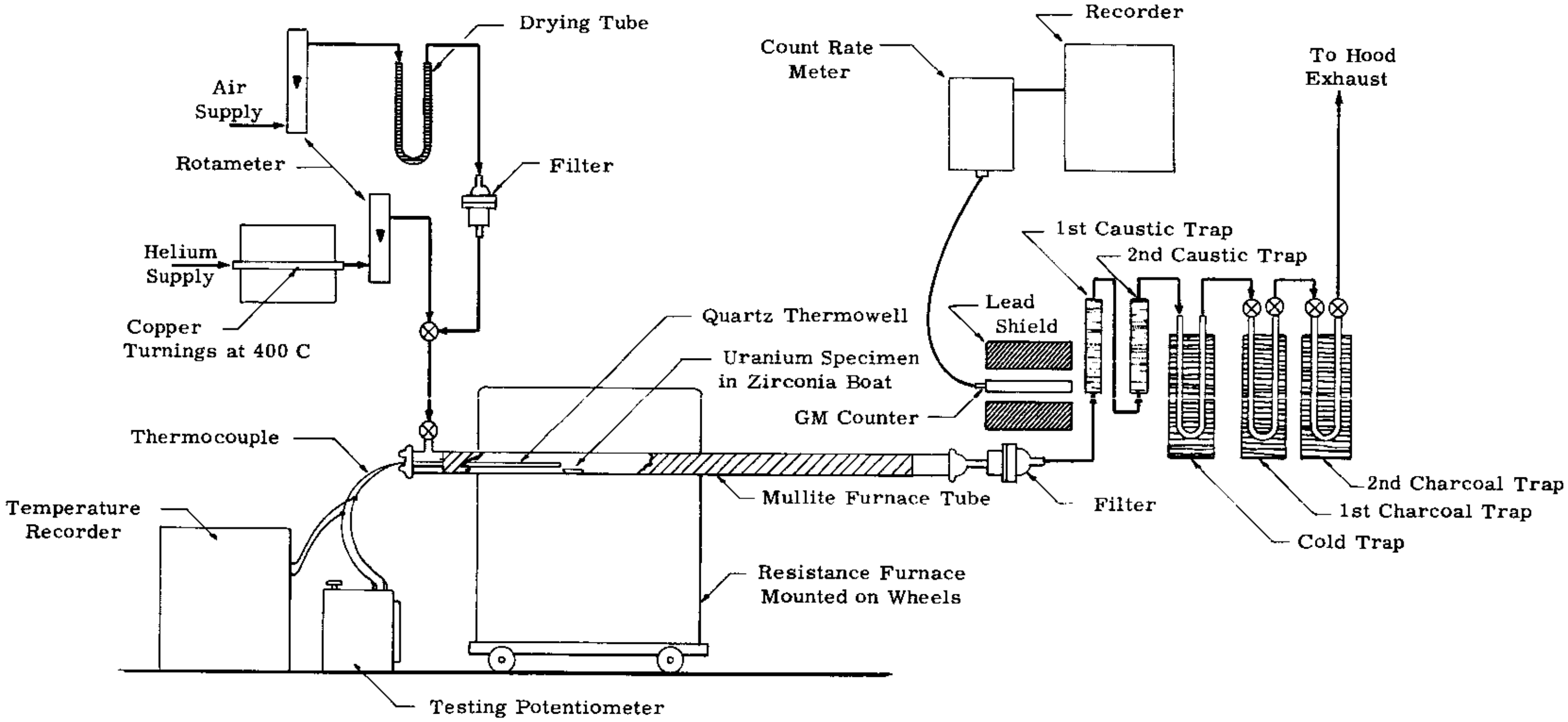

FIGURE 1

Flow Diagram of Fission Product Release Apparatus

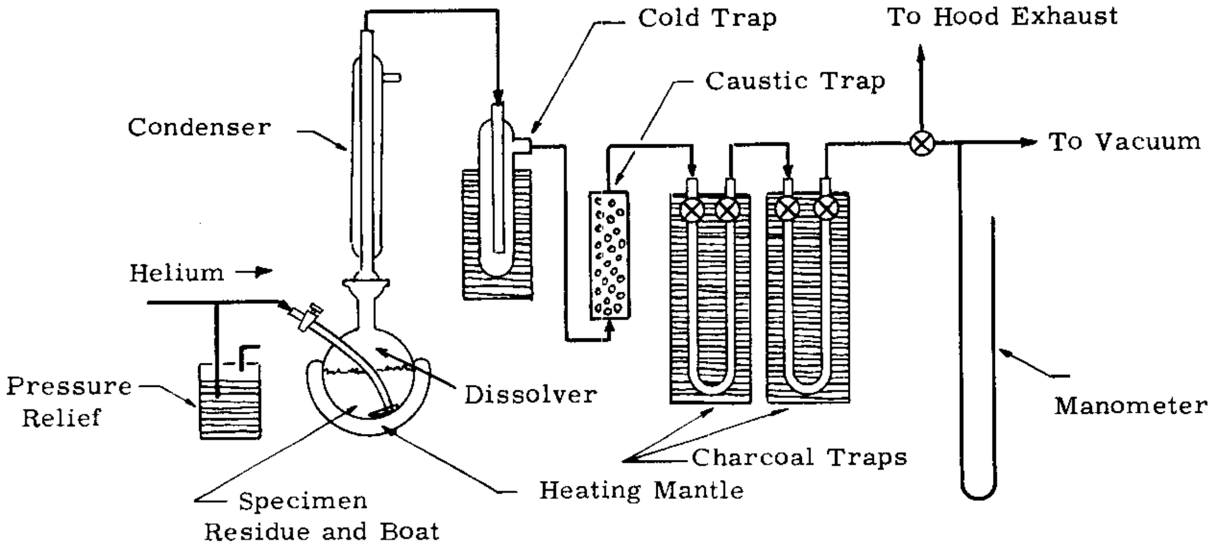

FIGURE 2

Dissolving Apparatus

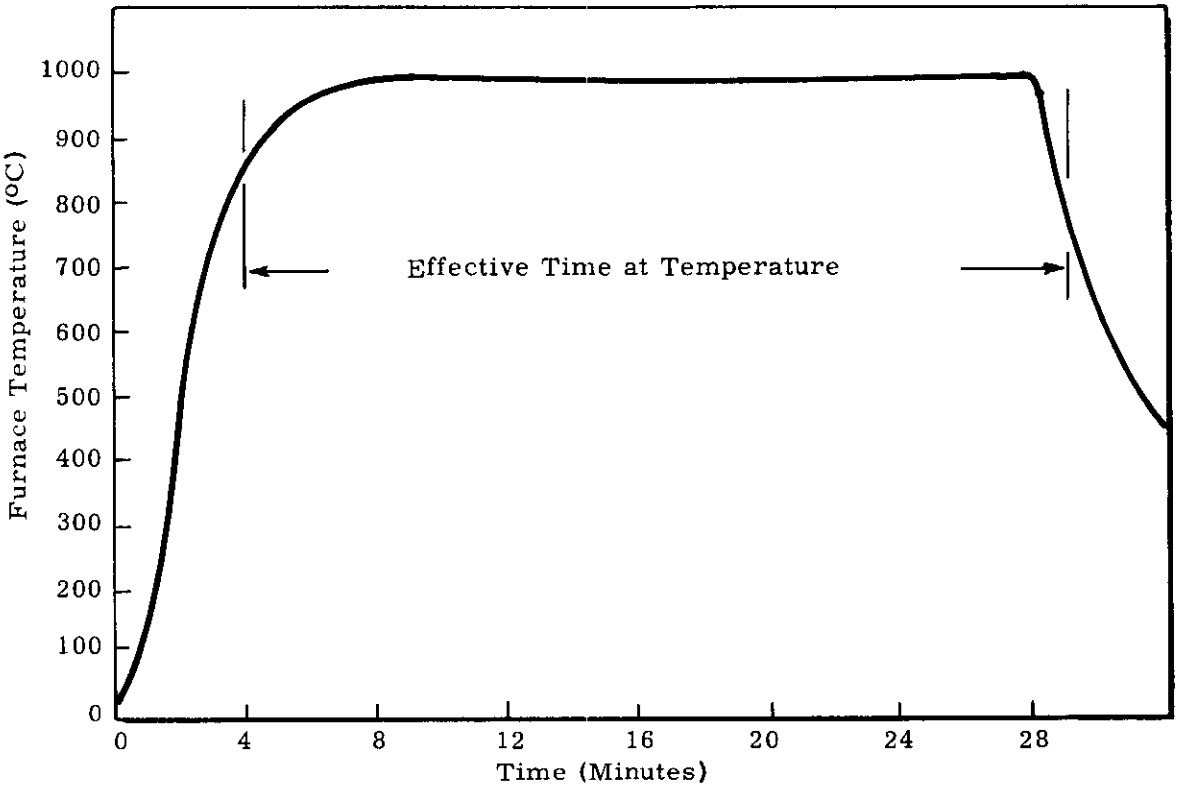

FIGURE 3

Typical Time vs. Temperature Curve

The furnace tube washings were always analyzed individually. In several runs each caustic and cold trap was analyzed separately, but to save analytical effort they were usually combined for analysis. When a filter was used in the test, special treatment was given it in an effort to detect particles. Techniques used were direct gamma scanning, radioautograph study after removal of most of the condensed radioactive vapors and observation under optical microscope.

During the heating period the radioactivity in the first caustic trap was monitored by a mica window counter and the buildup recorded. In two tests a scintillation counter and 256 channel analyzer were used. Only iodine, tellurium and xenon peaks were observed and the ratio of the peaks did not change during the run, so this system was discontinued in favor of the simpler counting system.

The furnace was of the silicon carbide resistance type, capable of a maximum continuous temperature of 1450 C. The Mullite furnace tube was 1-1/6 inch ID by 48 inches long, to which pyrex end adapters had been flame sealed. The caustic traps were pyrex filled with 30 grams of NaOH pellets each. The cold trap was simply a pyrex U-tube in a dry ice-isopropanol bath. The charcoal traps were stainless steel U-tubes loaded with 12.5 grams of activated coconut charcoal each immersed in a dry ice-isopropanol slurry. The charcoal was analyzed for xenon and other gamma emitters by gamma scanning with a multi-channel analyzer.

The furnace temperature was measured by a Pt—Pt-13% Rh thermocouple located in a quartz well, the tip of which touched the zirconia boat. Experience with burning unirradiated uranium(8) where the specimen temperature was measured by inserting a thermocouple in a hole drilled in one end of the specimen showed that the specimen temperature was always higher than the furnace temperature due to self-heating by the exothermic oxidation reaction. The difference between the two measurements varied from about 20 C at 400 C furnace temperature to as much as 500 C during thermal excursions at 620 C furnace temperature. Over 620 C the temperature difference was not as great but was more continuous. Because of the difficulty in measuring and controlling the temperature of the specimen, only the furnace temperature was recorded in the present work and all correlations were made with this parameter.

During cooling of the specimen some flakes of uranium oxide usually snapped off the surface and fell outside the boat. Since these large pieces were obviously not volatilized or air-borne, an arbitrary procedure was established in removing them from the furnace tube. The tube was tilted and the pieces of oxide tapped into a beaker. Then the tube was rinsed in a vertical position with about 100 cc of distilled water, collecting the rinse in the beaker. This rinse was filtered through Whatman No. 41 paper and added to the furnace tube washings. The oxide particles were added to the residue.

RESULTS

The total amount of each isotope present in the specimen before heating was calculated by adding the analyses of the residue, furnace tube washings, caustic traps, cold trap and charcoal trap and assuming that the sum of these analyses represented the original content. The fraction released was then simply the sum of the volatilized analyses divided by the total. All analyses were corrected for decay to the time of the heating period. Losses were believed to be less than five per cent of the volatilized portion and less than one per cent of the residue.

The amount of radioactivity handled is indicated by Table I, which lists the average total isotopic content of all specimens tested. Two specimens were irradiated at a time. One was tested about 22 hours after irradiation, the other after about 68 hours cooling. Some of the fluctuation shown in the analyses is due to the separate irradiation exposures. The analyses are believed to be reproducible to within ± 20 per cent except for cesium, which was present in very small concentrations in the volatilized portion.

TABLE I

AVERAGE FISSION PRODUCT CONTENT

(11.5 gram Normal Uranium Specimen
Irradiated to 2.4 x 10^{14} nvt)

Specimen	Total Isotopic Content by Analysis*							
Age (hr)	I^{131}	Te^{132}	Xe^{133}	Sr^{89}	Cs	Ru^{103}	Ba^{140}	Zr^{95}
22	8.26 ±22%	70.1 ±21%	15.8 ±28%	7.46 ±35%	0.04 ±87%	1.71 ±15%	2.87 ±16%	2.5 ±12%
68	7.90 ±19%	47.8 ±13%	24.2 ±30%	6.49 ±29%	0.05 ±91%	1.19 ±57%	2.55 ±14%	2.5 ±12%

* Sr^{89} and total Cs results are expressed in μc by beta counting. All other isotopes expressed in c/m x 10^{-6} by gamma counting on 256-channel analyzer, in 1-dram vial, in well, no absorber. All analyses corrected for decay to time of heating.

A summary of the experimental conditions is given in Table II. All tests were at essentially isothermal conditions except runs A-19, A-30 and A-31, which were programmed for 10 C/min temperature increase. It was not possible to attain true isothermal conditions throughout the test because of thermal inertia in heating and cooling the specimen. A typical time versus temperature curve is shown in Figure 3 (page 10). The arbitrary method of determining the effective time of heating is shown by the figure.

A summary of the experimental results is given in Table III. Results are expressed as per cent of the isotope released from the specimen.

Effect of Time of Heating on Release of Fission Products

The effect of the time of heating cannot be fully appreciated without concurrently considering the oxidation reaction. In many of the tests, heating continued sufficiently long for all of the uranium metal to oxidize. The specimen then existed as uranium oxide, probably U_3O_8. An earlier investigation(8) of the oxidation of unirradiated uranium was of great value in interpreting the results of the present experiments. For example, at a furnace

TABLE II

SUMMARY OF EXPERIMENTAL CONDITIONS

Run No.	Furnace Temp. (°C)	Time (min)	Air Velocity (cm/min)	Remarks
A-1	1200	10	500	*
A-2	1210	10	500	*
A-3	1215	50	500	*
A-6	1215	25	500	"Quartz Wool" Filter used.
A-7	1215	44	500	Porous silica filter used.
A-8	1215	51	500	
A-9	1215	86	500	
A-10	1215	2.5	500	
A-11	1215	85	500	
A-12	1215	48	500	Fall-out trays used.
A-13	1440	24	500	
A-14	990	24	500	
A-15	620	24	500	
A-16	1215	26	500	Separate train of traps during cooling.
A-17	1215	25	25	Air flow 1/20th normal.
A-18	1215	24	500	CWS "Absolute" filter used.
A-19	30-1325	150	500	Furnace programmed for 10 C/min rise.
A-20	1440	11	500	
A-21	620	99	500	
A-22	1220	10.5	500	
A-23	1215	120	500	
A-24	990	50	500	
A-25	425	232	500	
A-26	1215	84	500	40 min. in Air, then 44 min. in Helium.
A-27	535	115	500	
A-30	70-1030	80	500	Furnace programmed for 10 C/min rise.
A-31	70-1170	110	500	Furnace programmed for 10 C/min rise.
H-1	1215	25	500	Helium atmosphere.

* In the first three runs, the specimen was brought up to temperature and cooled in helium atmosphere. In all other runs air flowed over the specimen during the entire run.

TABLE III

SUMMARY OF EXPERIMENTAL RESULTS

Run No.	Furnace Temp. (°C)	Time (min)	Per Cent Released from Specimen							
			I^{131}	Te^{132}	Xe^{133}	Sr^{89}	Cs	Ru^{103}	Ba^{140}	Zr^{95}
A-20	1440	11	67	47	65	0.07	0.5	2.3	0.14	
A-13	1440	24	90	76	80	0.07	1.0	2.8	0.15	
A-10	1215	2.5	4.6	9.1	(a)	0.001	0.1	(a)	0.03	
A-1	1200	10	40	35	(a)	0.03	0.6	0.08	(a)	
A-2	1210	10	7.3	4.4	(a)	0.04	0.2	0.04	(a)	
A-22	1220	10.5	61	34	45	0.03	0.4	1.0	0.05	
A-18	1215	24	80	73	20	0.03	0.4	0.50	0.07	
A-6	1215	25	69	52	(a)	0.04	1.1	0.73	(a)	
A-16	1215	26	56	57	55	0.04	1.4	0.72	0.11	
A-7	1215	44	84	81	55	(a)	0.6	1.6	0.13	
A-12	1215	48	69	66	43	0.03	0.8	1.0	0.16	0.07
A-3	1215	50	80	69	(a)	0.02	0.9	(a)	(a)	
A-8	1215	51	77	75	58	0.10	0.8	2.0	0.07	
A-11	1215	85	71	84	(a)	0.01	0.6	4.3	0.05	0.01
A-9	1215	86	72	73	(a)	0.02	1.5	4.6	0.03	
A-23	1215	120	82	77	65	0.01	0.8	8.6	0.01	
A-14	990	24	8.6	8.9	18	0.03	0.2	1.0	0.04	
A-24	990	50	18	18	36	0.01	(a)	1.4	0.01	
A-15	620	24	2.2	0.54	10	0.004	0.6	0.38	0.004	
A-21	620	100	47	0.50	62	0.05	6.0	7.2	0.02	
A-27	535	115	38	0.67	64	0.03	0.7	16.	(a)	
A-25	425	232	16	0.15	22	0.02	1.4	1.6	0.008	
A-17	1215	25	45	32	8.2	0.02	0.2	0.48	0.05	
A-26	1215	84(b)	79	69	60	0.02	2.7	1.8	0.05	
A-19	30-1325	150	78	70	75	0.02	0.9	12.	0.03	
A-30	70-1030	80	25	9.3	36	0.02	2.6	2.2	0.02	
A-31	70-1170	110	30	40	66	0.006	0.2	2.8	0.03	
H-1	1215	25	41	4.2	10	0.18	1.2	0.09	0.08	

(a) Not analyzed.
(b) 40 minutes in air then 44 minutes in helium.

temperature of 1215 C it was known that the specimen was completely oxidized in 48 ± 4 minutes. Table III reveals that at 1215 C iodine, tellurium and xenon continued to be released with time up to 100 per cent oxidation. Further heating did not release significantly additional amounts of these elements. Strontium, barium, and zirconium release was independent of time. The release of cesium appeared to be slightly dependent upon time of heating, but the results are scattered. Ruthenium behaved peculiarly, with a small time dependency up to 100 per cent oxidation, when a much faster release began.

The effect of time on the release of iodine tellurium and xenon is shown graphically by Figures 4, 5 and 6, respectively. To illustrate the relationship between fission product release and extent of oxidation, the oxidation curve is also plotted on these graphs. Sufficient data were not gathered to present curves at other furnace temperatures, but Table III indicates that for the three volatile elements the time of heating is important.

It is surprising that quantitative release of xenon was not found to occur even with prolonged heating at 1215 C furnace temperature -- approximately 100 C above the melting point of uranium. Iodine and tellurium remaining in the residue may be chemically bound, but no apparent explanation can be found for the retention of the inert element xenon.

Effect of Temperature on Release of Fission Products

All other conditions remaining constant, temperature had a profound effect on the fraction of fission products released. Figure 7, plotted from the data in Table III, is a graph of the temperature versus the per cent of iodine, tellurium and xenon released. In this figure, a 24-minute heating period was used for all experimental points. The area near 1130 C, the melting point of uranium, is uncertain, but probably an inflection point occurs near this temperature for all three elements. To display the correlation with per cent of oxidation the oxidation curve is also shown.

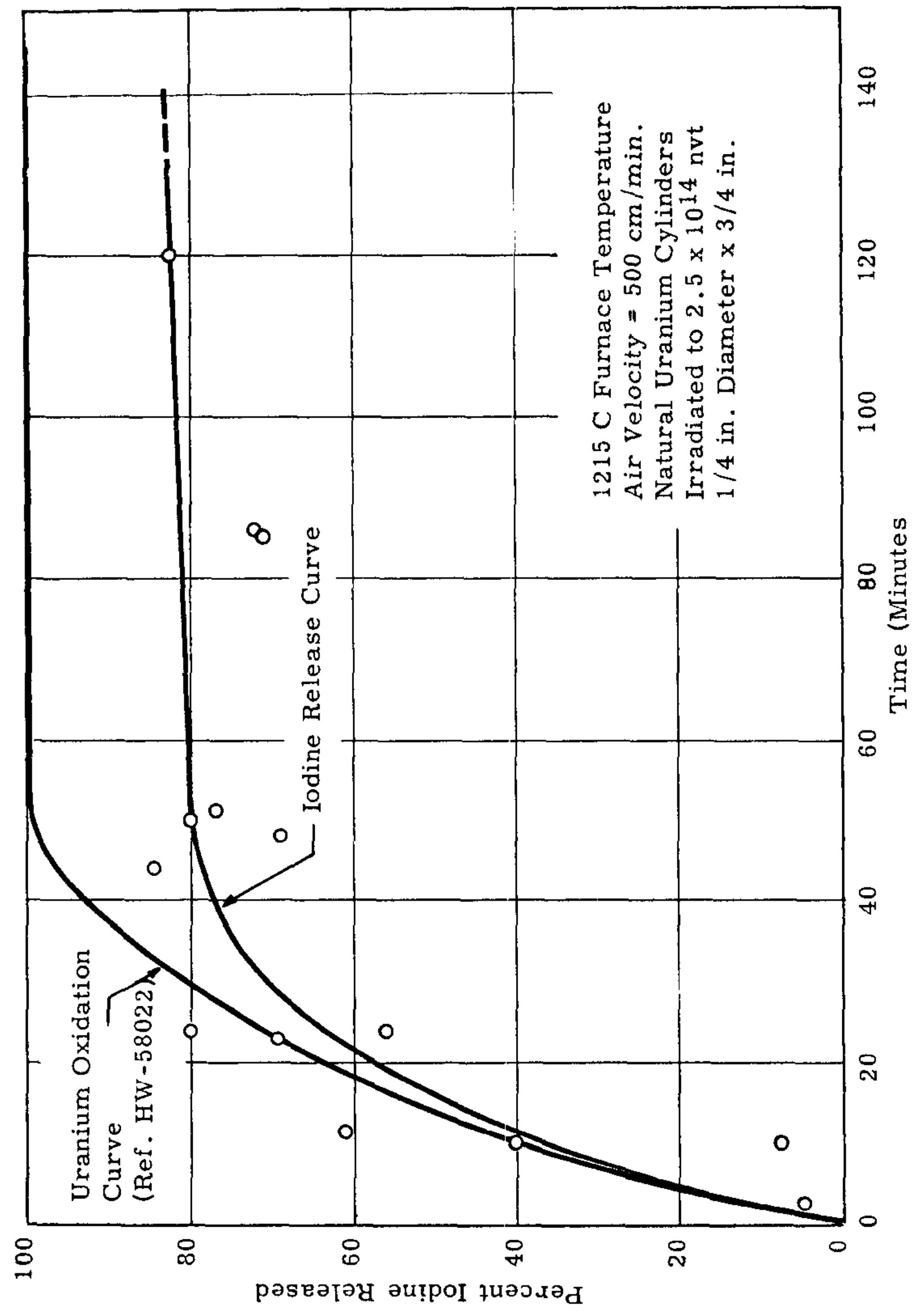

FIGURE 4

Effect of Time on Release of Iodine

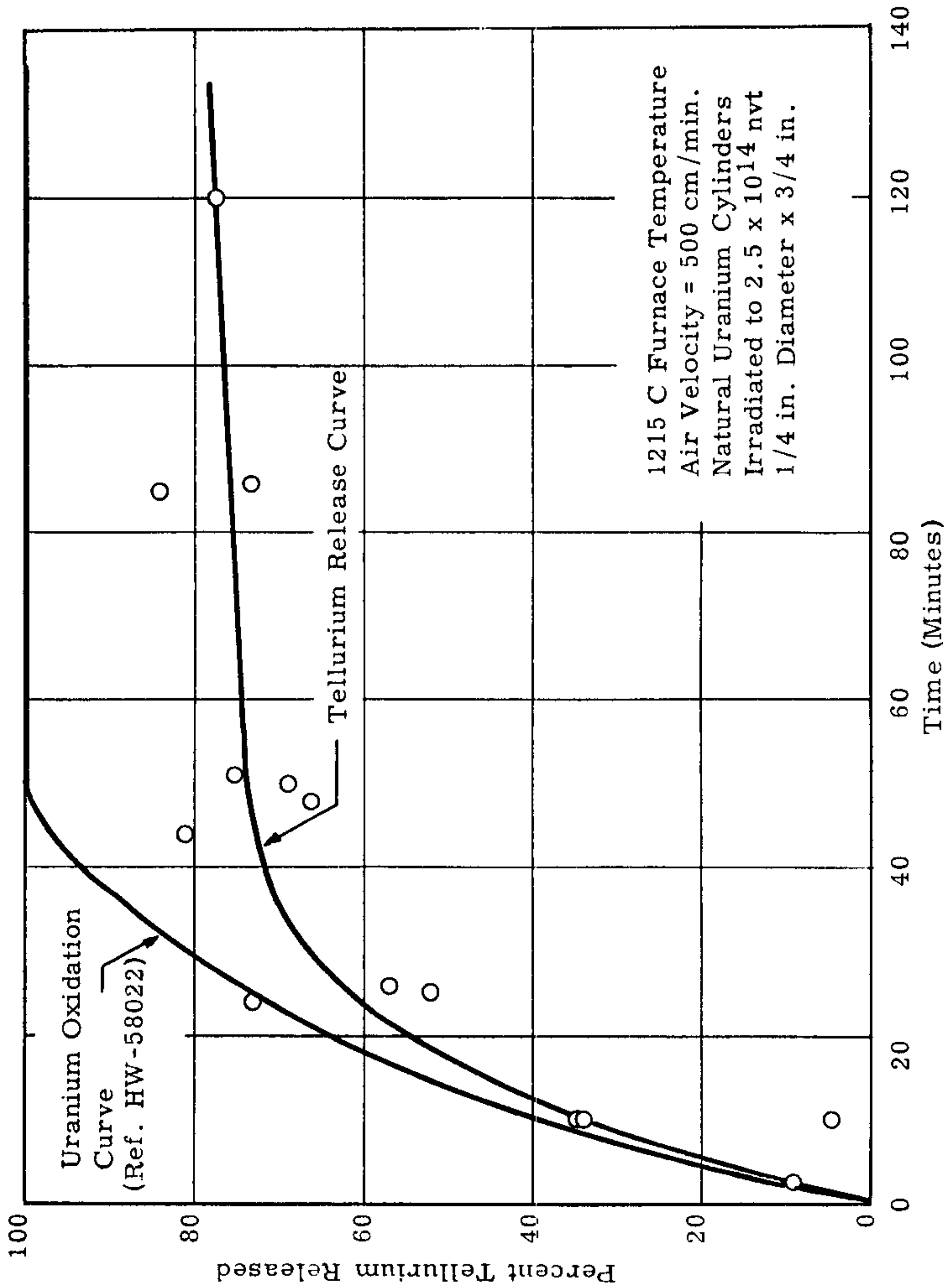

FIGURE 5

Effect of Time on Release of Tellurium

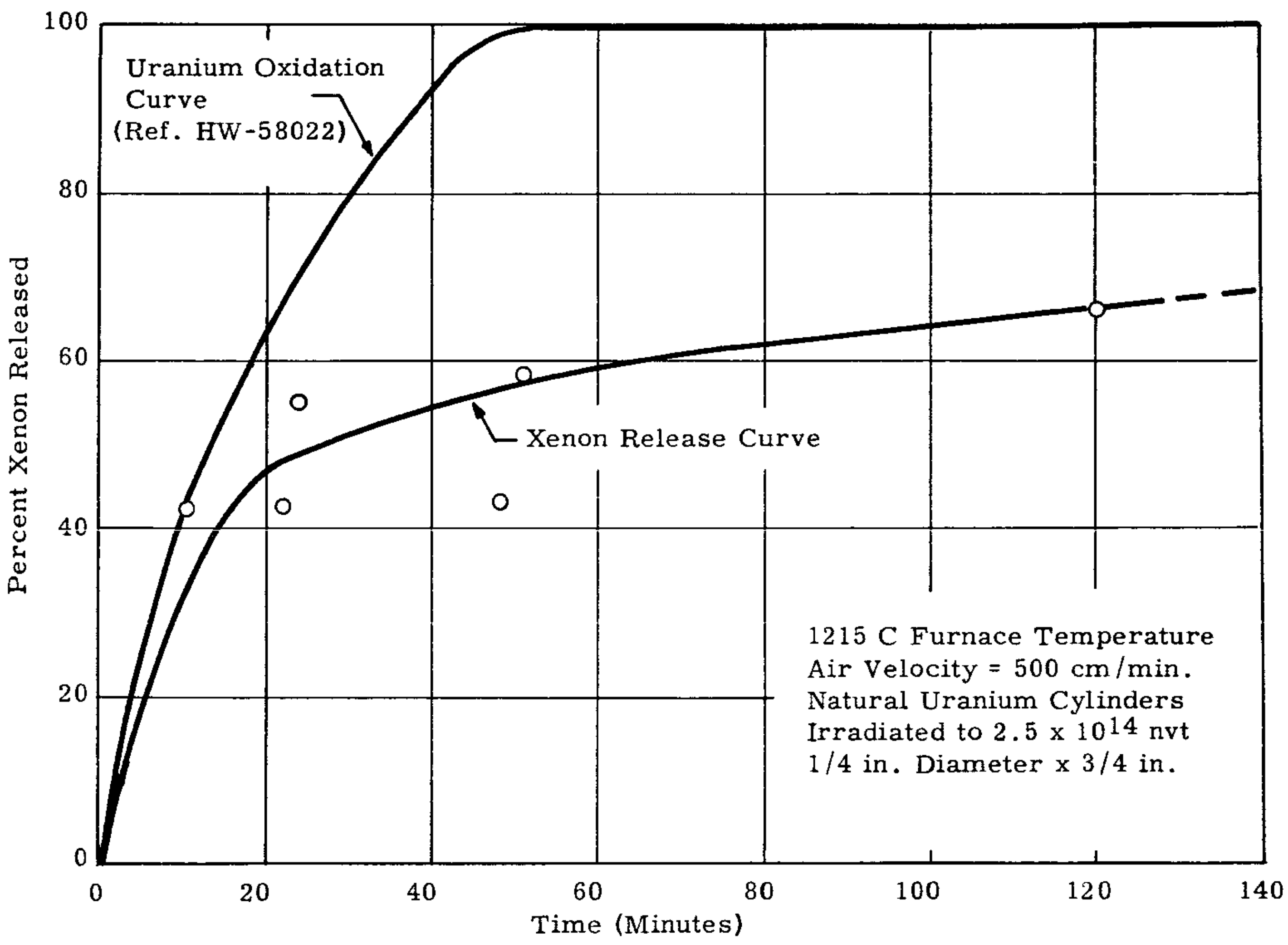

FIGURE 6

Effect of Time on Release of Xenon

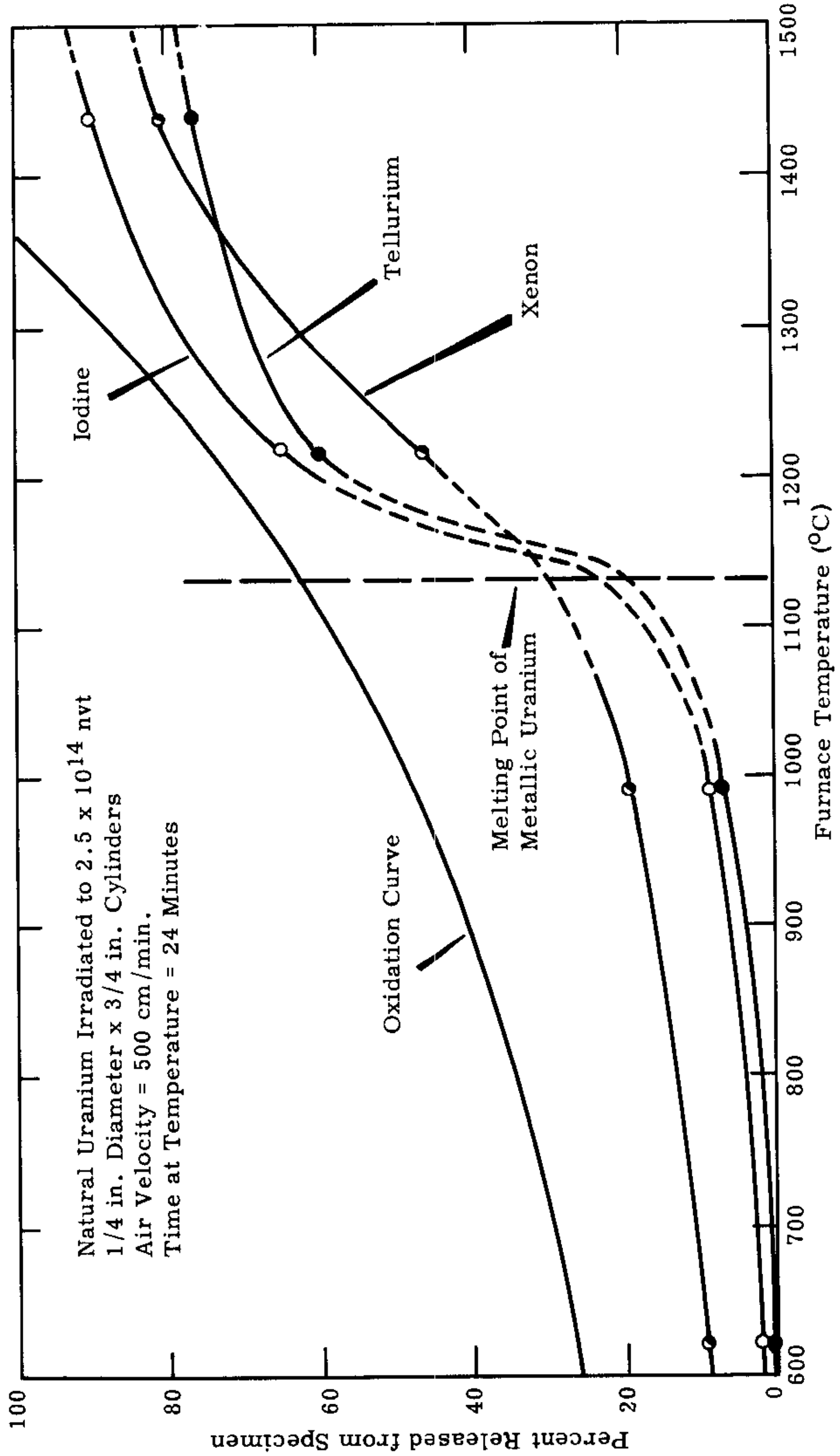

FIGURE 7

Effect of Temperature on Release of Iodine, Tellurium and Xenon

The effect of temperature on the release of the "non-volatile" elements, Sr, Cs, Ru and Ba, is less discernible, but a definite trend was obtained, as shown by Table III.

Deposition Pattern of Released Isotopes

The tendency of each of the isotopes investigated to deposit on tube walls and in the various traps was measured. Table IV shows the average per cent of the air-borne material to be deposited in each of the several places analyzed. Insertion of a filter at the outlet of the furnace tube changed this deposition pattern considerably as shown by Table V. Both tables are for tests at 1215 C furnace temperature. At lower temperatures the fission products were deposited to a greater extent on the furnace tube walls. Lower air velocity also caused more deposition within the furnace tube.

TABLE IV

DEPOSITION PATTERN
WITHOUT FILTER IN OFF-GAS SYSTEM

	Per Cent of Volatilized Material Deposited							
Location	I^{131}	Te^{132}	Xe^{133}	Sr^{89}	Cs	Ru^{103}	Ba^{140}	Zr^{95}
Furnace Tube	6.9	19.2	*	53	32	85	45	40
1st Caustic Trap	90.0	58.8	*	13	49	14	48	55
2nd Caustic Trap	0.9	19.6	*	14	12	0.4	5	5
Cold Trap	0.05	0.5	*	20	7	0.2	2	*
1st Charcoal Trap	1.95	1.5	99.95	*	*	0.35	*	*
2nd Charcoal Trap	0.2	0.4	0.05	*	*	0.05	*	*

* Not analyzed

TABLE V

DEPOSITION PATTERN WITH CWS FILTER IN OFF-GAS SYSTEM

	Per Cent of Volatilized Material Deposited							
Location	I^{131}	Te^{132}	Xe^{133}	Sr^{89}	Cs	Ru^{103}	Ba^{140}	Zr^{95}
Furnace Tube	6.9	19.2	*	53	32	85	45	*
Filter	52.2	78.5	*	25	36.3	14.5	40.4	*
1st Caustic Trap	39.6	1.7	*	6.3	22.8	0.5	12.8	*
2nd Caustic Trap	0.4	0.6	*	6.7	5.6	t	1.3	*
Cold Trap	0.02	0.01	*	9.0	3.3	t	0.5	*
1st Charcoal Trap	0.8	0.03	99.95	*	*	t	*	*
2nd Charcoal Trap	0.1	0.01	0.05	*	*	t	*	*

* Not analyzed
t = trace

Filter Efficiencies

The efficiency of various filter media in removing radioactive material from an air stream passing over burning uranium is of interest in design of confinement facilities. Three types of media were tested under similar experimental conditions. The CWS "Absolute" filter was a Cambridge type CM-115 supported by a Millipore filter holder. The porous silica was a fritted glass laboratory filter disk of medium porosity. The "Quartz Wool" was a plug weighing 132 mg and approximately 3/4 inch diameter by 3/4 inch thick. The temperature of the air stream at the filters was not measured but is estimated to have varied between 150 and 300 C during the run. This estimate was based on experience accumulated during the work with unirradiated uranium oxidation. Table VI lists the efficiencies of these three filter media tested in runs at 1215 C and 24 minutes of heating.

TABLE VI

FILTER EFFICIENCIES
FOR REMOVAL OF AIR-BORNE FISSION PRODUCTS

Type of Filter	Per Cent of Air-borne Material Retained by Filter I^{131}	Te^{132}	Sr^{89}	Cs	Ru^{103}	Ba^{140}
CWS "Absolute"	56.0	97.2	53.4	92.8	96.9	73.2
Porous Silica	0.8	99.8	52.9	80.8	99.1	37.5
"Quartz Wool"	78.2	95.6	69.1	35.6	98.8	*

* Not analyzed

Effect of Air Velocity on Release of Fission Products

The velocity of the air stream over the heated uranium specimen proved to be of minor influence on the total release of fission products. All runs except A-17 used an air flow of 2300 cc/min, measured at standard pressure and temperature. This is equivalent to 500 cm/min velocity through the 1-1/16 inch ID furnace tube. In run A-17, the flow rate was 115 cc/min, or 1/20th the normal rate. Table III shows the reduced fission product release. It is known from the oxidation study on unirradiated metal(8) that the oxidation rate is slightly dependent upon air flow rate. The reduced oxidation in Run A-17 is probably responsible for the slightly slower release of fission products.

Although the total release of fission products was not greatly affected by a low air velocity, the deposition pattern was shifted so that much more of the volatilized material was retained within the furnace tube. Table VII shows this effect. The significance of this observation is that for a reactor incident involving low air velocities most of the volatilized fission products would be retained by reactor tubes and ducts. Considerably more work is required to satisfactorily appraise the effect of gas velocity on deposition patterns.

TABLE VII

EFFECT OF AIR VELOCITY ON DEPOSITION PATTERN

(Specimen heated 25 minutes at 1215 C)

Air Velocity (cm/min)	Per Cent of Volatilized Material Deposited in Furnace Tube					
	I^{131}	Te^{132}	Sr^{89}	Cs	Ru^{103}	Ba^{140}
25	70	99	93	73	99.4	92
500	6.9	19	53	32	85	45

Release of Fission Products in a Helium Atmosphere

Pyrochemical separations technology has provided considerable information regarding the release of fission products from fuels heated in an inert atmosphere.(3) For comparative purposes, a single run was made using helium for the atmosphere during heating to 1215 C for 25 minutes. Table VIII lists the results compared to those obtained in air under otherwise similar conditions. Compared to air, a helium atmosphere gave considerably lower release of tellurium, ruthenium and xenon. Iodine release was slightly lower. Cesium and barium release was about the same as in air. The fraction of strontium released was about four times greater than in air.

The low release of tellurium and ruthenium in an inert atmosphere was expected, since the vapor pressures of these elements are considerably lower than their oxides. On the other hand, elemental strontium is much more volatile than its oxide so that an air atmosphere would be expected to give a lower release of strontium, which was the observed case.

TABLE VIII

COMPARISON OF FISSION PRODUCT RELEASE IN AIR AND HELIUM ATMOSPHERES

(Specimen heated 25 minutes at 1215 C)

Atmosphere	Per Cent Released from Specimen						
	I^{131}	Te^{132}	Xe^{133}	Sr^{89}	Cs	Ru^{103}	Ba^{140}
Air	65	60	50	0.04	1.0	0.65	0.09
Helium	41	4.2	10	0.18	1.2	0.09	0.08

Buildup of Radioactivity in Caustic Trap

The bulk of the radioactivity released from the heated uranium specimens was iodine, tellurium and xenon. Most of the iodine and tellurium was caught on the first caustic trap so that this made a convenient place to monitor the activity buildup during the run. A GM counter was mounted within lead shielding and the activity of the bottom portion of the trap registered by a count rate meter and recorder. Figure 8 is a typical curve showing how the activity increased smoothly with time during isothermal heating. At the end of the run, as the furnace was moved off the specimen and along the downstream end of the furnace tube, some of the condensed vapors were invariably revolatilized and deposited in the caustic trap. This effect is shown by the hump in the curve in Figure 8. The possibility that some of this terminal buildup might be caused by additional release from the specimen during cooling was not investigated. Figure 8 shows the curve obtained during a run in which heating continued for about 35 minutes after all the uranium had been converted to oxide. It clearly shows that no major amount of gross gamma activity was released after complete oxidation had occurred.

In runs where the furnace temperature was programmed for a 10 C/min increase, the activity build-up curves showed two points of inflection at about 700 C and 800 C and then a steeply rising slope at higher temperatures. Figure 9 illustrates a curve obtained from such an experiment. The points of inflection probably correspond with thermal excursions caused by self-heating of the specimen by the exothermic oxidation reaction. Activity build-up curves in isothermal runs at furnace temperatures in the range where thermocycling is expected also showed similar points of inflection. Work done at Hanford(8) with unirradiated uranium oxidation and recently at Argonne National Laboratory(9) showed that large temperature peaks occur under certain conditions. The furnace temperature is insensitive to these specimen excursions and thus the furnace temperature recorder did not show these peaks.

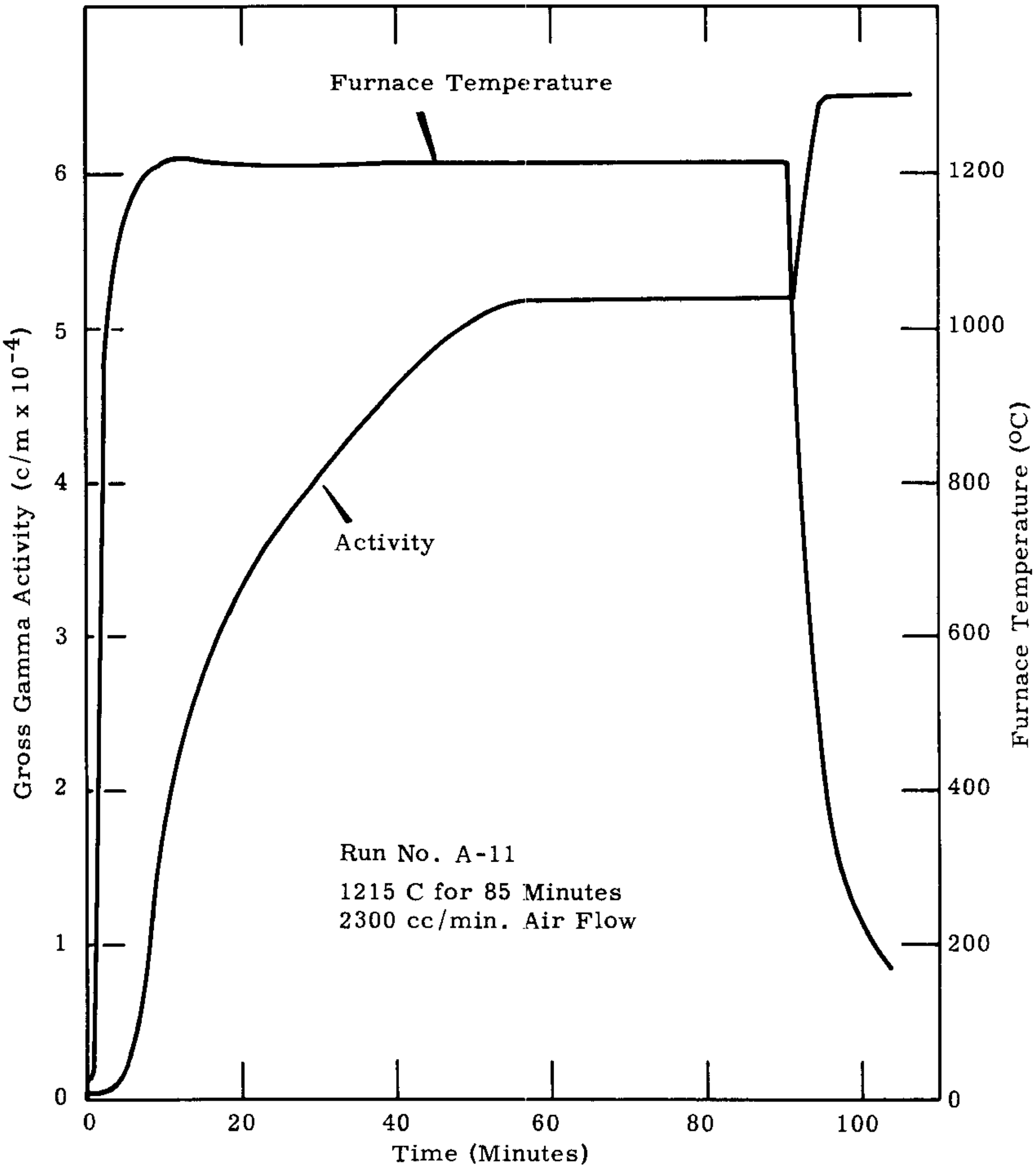

FIGURE 8

Buildup of Radioactivity in Caustic Trap
for a Typical Isothermal Test

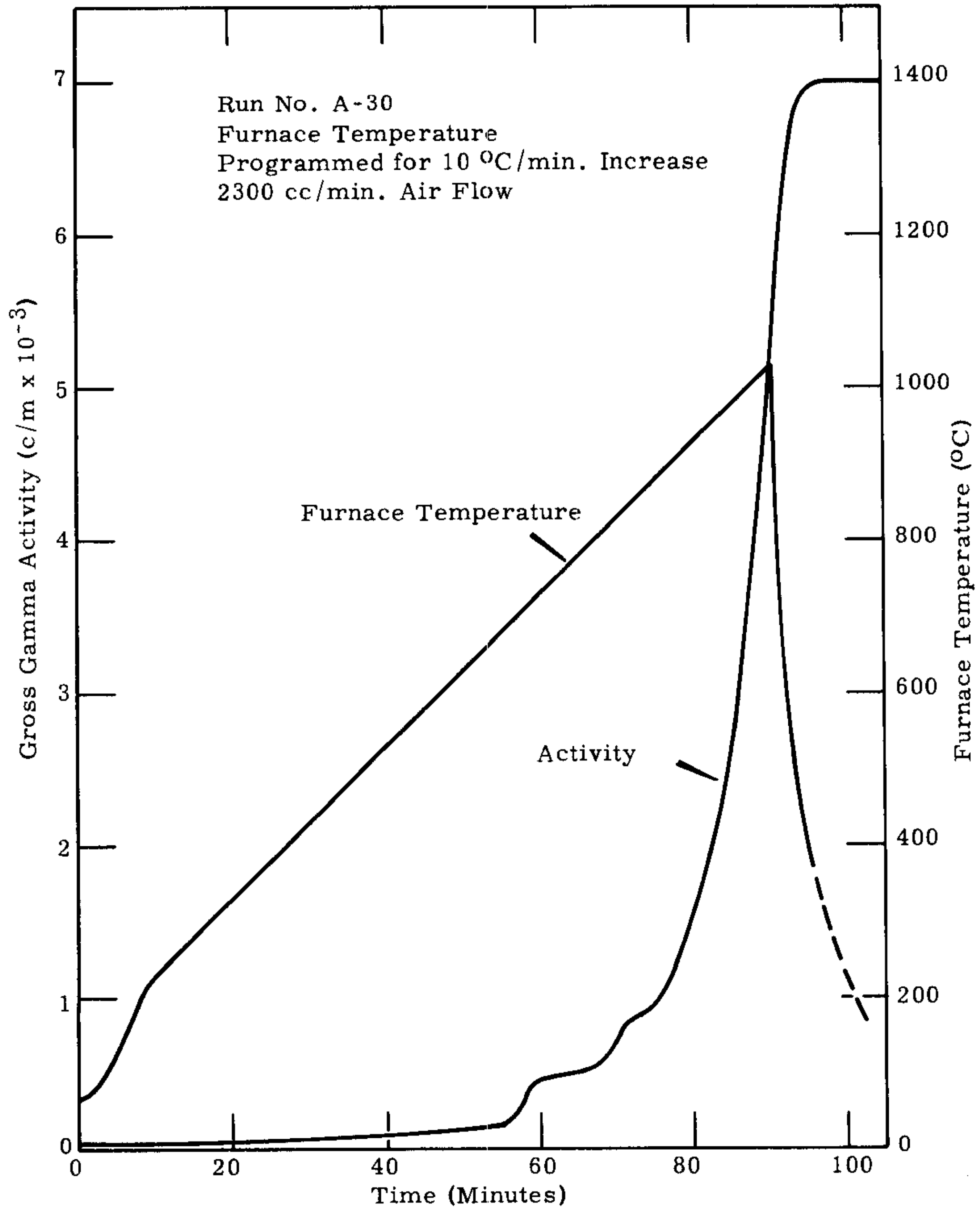

FIGURE 9

Buildup of Radioactivity in Caustic Trap
for a Typical Dynamic Temperature Test

Multi-channel gamma scans of the caustic trap during heating showed only iodine, tellurium and xenon peaks, with the same ratio throughout the tests.

Particulate Emission

Several attempts were made to measure the radioactivity associated with particles in the off-gas. All attempts to observe and identify individual particles were unsuccessful. In Run A-12 two "fall-out" trays were placed in the downstream end of the furnace tube. Visual examination of these trays at 500 X did not reveal any particles caught. Filters located at the outlet end of the furnace tube caught large amounts of iodine and tellurium. After 99.5 per cent of the iodine and 95 per cent of the tellurium had been removed by rinsing with weak caustic solution, the residual iodine and tellurium still masked any gamma activity from particles containing other fission product isotopes. Subsequent radioautographs of the filter medium were uniformly darkened. The "quartz wool" filter was heated at 800 C for about 10 minutes with helium flowing through it. About 95 per cent of the iodine and tellurium was driven off, but a gamma scan of the residual activity showed only iodine and tellurium peaks. The conclusion to be made from these tests is that particles emitted from irradiated uranium heated in air at high temperatures are extremely small, probably sub-micron in size.

Correlation of Oxidation with Fission Product Release

Table VIII shows that all fission products studied except strontium were released at a higher rate in air atmosphere than in helium. The reaction between uranium and oxygen would be expected to change the release mechanisms of the fission products. Whereas in an inert atmosphere release is limited chiefly by diffusion to the surface of the metal and evaporation in the same chemical form, an oxidizing atmosphere provides several effects which accelerate release of most fission products. Diffusion and evaporation are expedited, especially in small specimens, by lessening the thickness of metal through which the radionuclide must diffuse to the metal-gas interface. Certain elements, such as tellurium and ruthenium react with oxygen at the surface to form their oxides, which are much more volatile than the elements. The exothermic uranium-oxygen reaction provides localized heating which under some conditions can raise the temperature of the entire specimen several hundred degrees centigrade above the surroundings. All these effects tend to release fission products at the same rate as uranium oxidation progresses. If oxidation rate is the controlling step in release of fission products, a correlation of per cent of uranium oxidized versus per cent of fission product released should be observed.

The per cent of uranium oxidized was measured directly in only two runs. However, reference (8) allowed a close extimate to be made. Table IX lists the estimated per cent of uranium oxidized for all runs where correlation was possible. From this table Figures 10, 11 and 12 were plotted, showing the correlation for iodine, tellurium and xenon, respectively. The release of other isotopes was somewhat independent of oxidation.

A great deal of imagination was used in constructing Figures 10, 11 and 12. The few data available, the experimental error in the fission product release figures, and the fact that the per cent of uranium oxidized was estimated all contributed to scattering of points in the graphs. It appears that not only the per cent oxidized but the temperature at which oxidation occurred is important in obtaining a correlation and thus temperature was plotted as a parameter.

Thermocycling at lower furnace temperatures caused difficulty in correlating the results. For example, the iodine releases at 535 C and 620 C furnace temperatures were higher than at 990 C for the same per cent oxidized. This is explainable when it is remembered that, after "induction periods" at these lower temperatures, the specimen temperature

TABLE IX

RELATIONSHIP BETWEEN FISSION PRODUCT RELEASE AND PER CENT OF URANIUM OXIDIZED

Run Number	Uranium Oxidized (%) (a)	Furnace Temp. (°C)	Per Cent Released from Specimen						
			I^{131}	Te^{132}	Xe^{133}	Sr^{89}	Cs	Ru^{103}	Ba^{140}
A-20	65	1440	67	47	65	0.07	0.5	2.3	0.14
A-13	100	1440	90	76	80	0.07	1.1	2.8	0.15
A-19	100	1325(b)	78	70	75	0.02	0.9	12.	0.03
A-10	15	1215	4.6	9.1	(d)	0.001	0.1	(d)	0.03
A-1, A-2, A-22	40	1215	36	34	32	0.03	0.4	1.0	0.05
A-6, A-16, A-18	65	1215	57	55	45	0.04	1.0	0.7	0.08
A-7	94	1215	84	81	55	(d)	0.6	1.6	0.13
A-3, A-8, A-12	100	1215	80	75	57	0.03	0.8	1.0	0.16
A-9, A-11, A-23	100	1215	82	76	65	0.02	1.0	3.4	0.03
A-31	80(c)	1170(b)	30	40	66	(d)	(d)	(d)	(d)
A-30	56(c)	1030(b)	25	9.3	36	(d)	(d)	(d)	(d)
A-14	47	990	8.6	8.9	18	0.03	0.2	1.0	0.04
A-24	65	990	18	18	36	0.01	(d)	1.4	0.01
A-15	22	620	2.2	0.54	10	0.004	0.6	0.38	0.004
A-21	70	620	47	0.50	62	0.05	6.0	7.2	0.02
A-27	73	535	38	0.67	64	0.03	0.7	16.	(d)

(a) Per cent of metal oxidized estimated from reference 8.

(b) Maximum temperature attained.

(c) Per cent of metal oxidized determined by pickling and weighing residue.

(d) Not analyzed.

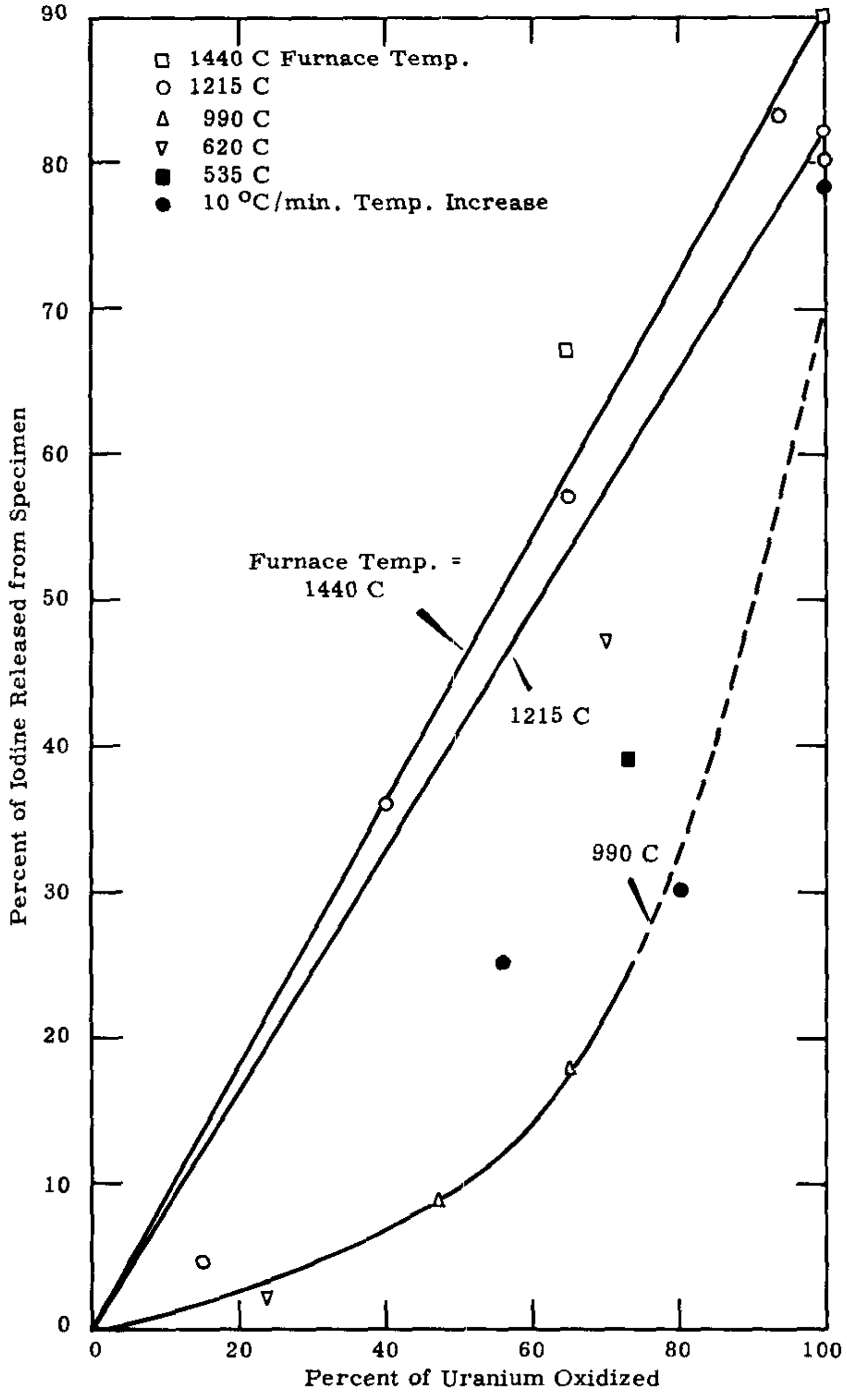

FIGURE 10

Release of Iodine as a Function of Uranium Oxidation

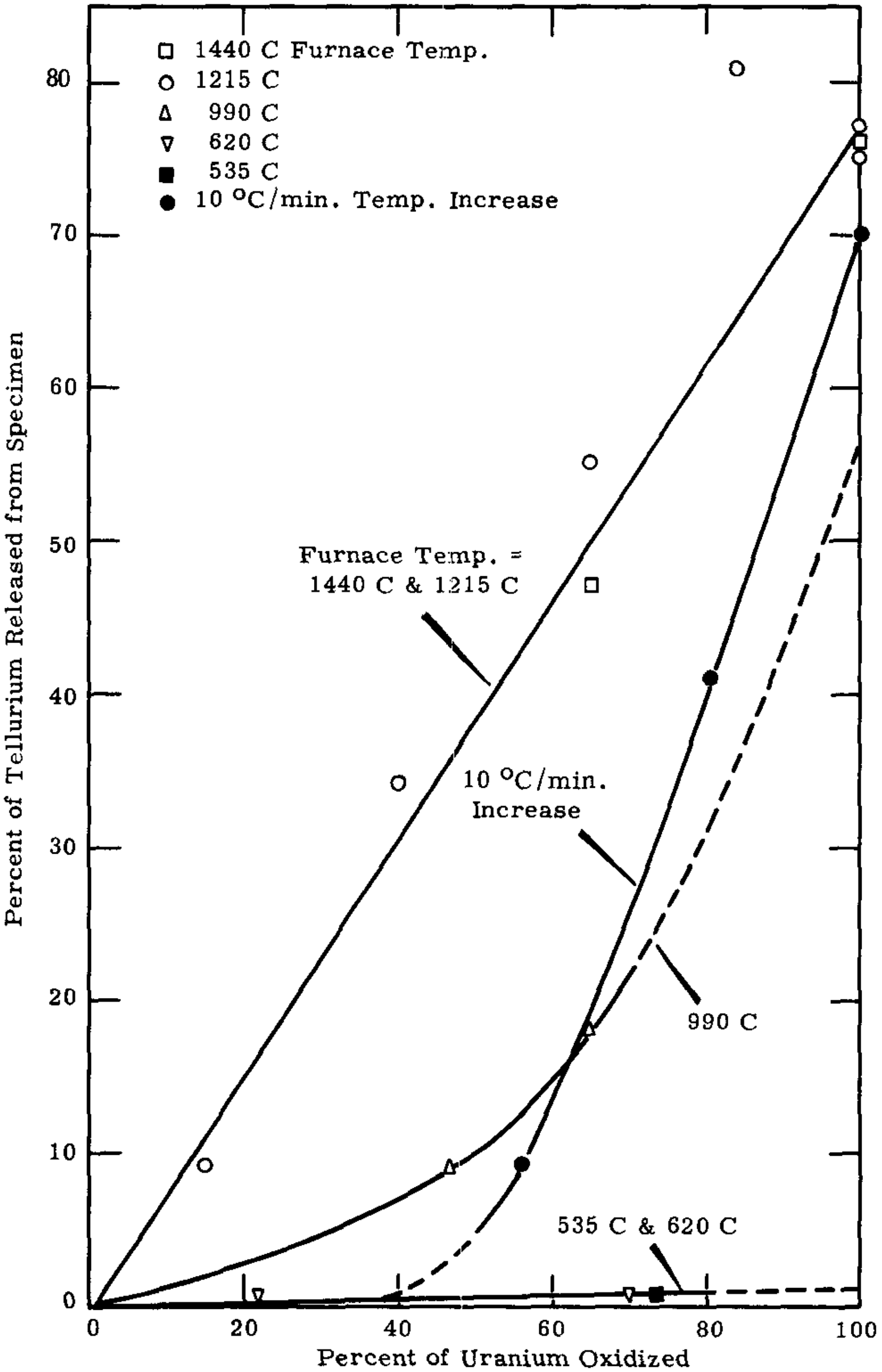

FIGURE 11

Release of Tellurium as a Function of Uranium Oxidation

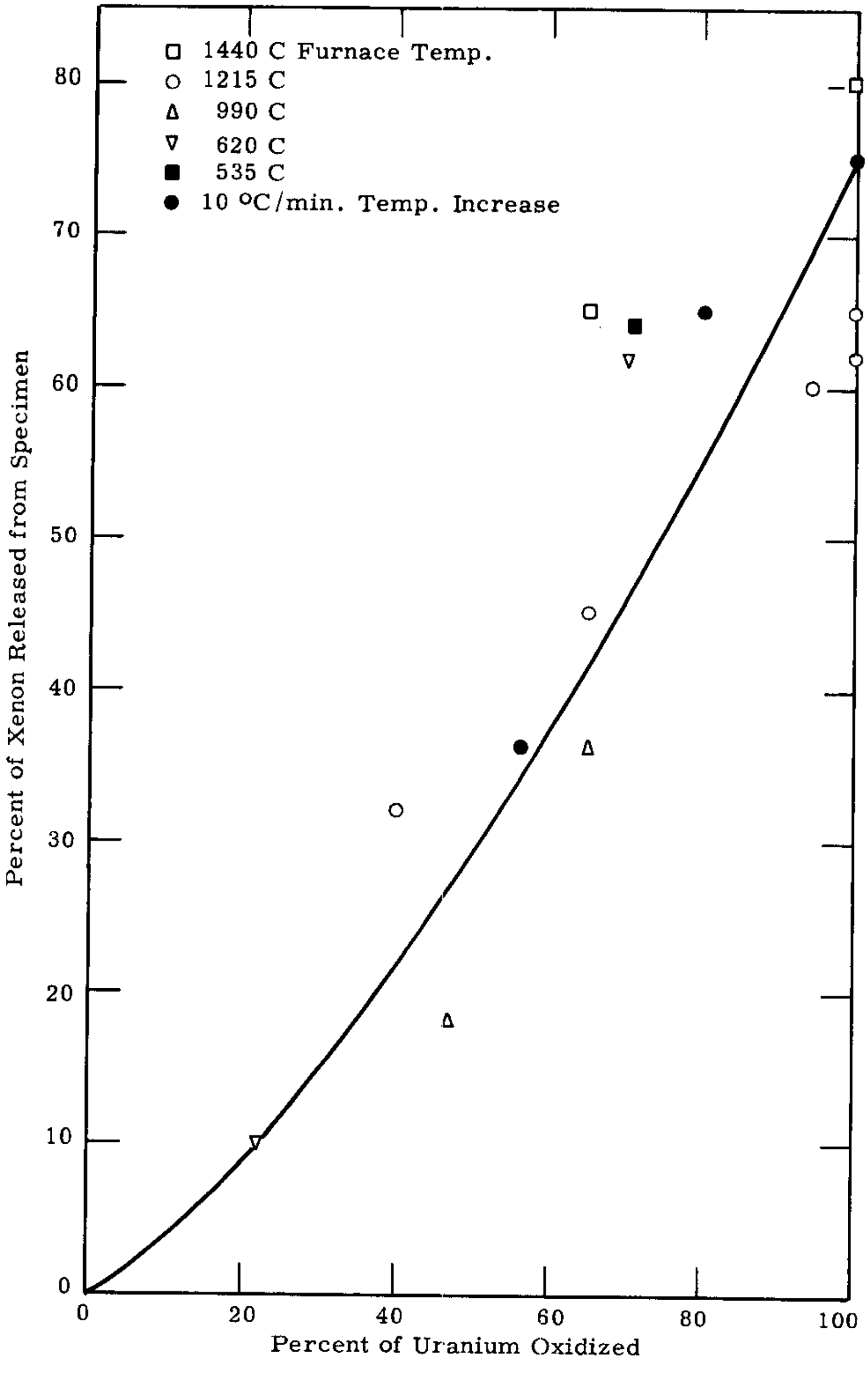

FIGURE 12

Release of Xenon as a Function of Uranium Oxidation reaches as high as 1130 C. With furnace temperatures above 650 C, thermal excursions were much lower with the size specimens used in these tests.(8)

The low release of tellurium compared to iodine at 620 C can only be explained by the fact that TeO_2 sublimes at 450 C, higher than the 184 C boiling point of iodine. Because of the greater temperature dependence of tellurium volatilization, a separate curve was constructed in Figure 11 for the dynamic temperature tests at 10 C/min furnace temperature increase. This curve takes into account the negligible release of tellurium at moderate temperatures where oxidation is appreciable.

A complete understanding of the uranium oxidation reaction would be of great value in understanding the release of volatile fission products from uranium heated in air.

PREDICTION OF FISSION PRODUCT RELEASE

The chief purpose of this laboratory investigation was to obtain information suitable for making estimates of the release of fission products from uranium reactor fuels heated, by fission product decay or other means, in an air atmosphere. Doubt exists in the minds of many persons that a laboratory investigation can be used to predict the effects of such incidents. Admittedly the many variables involved and the odd behavior of the uranium-air reaction present difficulties in correlation and interpretation of laboratory data. However, large-scale field release tests also present problems in complexity, expense and time consumed. Also, the same number of variables exist if any possible reactor accident is to be considered.

Most of the tests in this laboratory investigation were performed at isothermal temperature conditions, whereas many reactor accidents would entail slow heating of the fuel. To determine whether the isothermal data gathered by these tests could be used to predict the release during a dynamic temperature condition, three experiments were made where the furnace was programmed for a 10 C/min temperature rise. Two methods were used to predict the release of iodine, tellurium and xenon. The first used a graphical integration of the release, utilizing Figure 7. The second method used the estimated extent of oxidation and Figures 10, 11 and 12. Both methods gave reasonably good estimates of the actual release as shown by Table X. It is encouraging to find that even an incomplete investigation such as this shows promise of enabling an accurate estimate to be made for fission product release during any possible reactor accident where fuel is overheated.

TABLE X

ESTIMATION OF FISSION PRODUCT RELEASE DURING DYNAMIC TEMPERATURE CONDITIONS

Run A-30, temperature increased 10 C/min from 70-1030 C
56% of the uranium oxidized

Temperature Increment (°C)	Time (min)	Effective Temperature (°C)	Estimated Release (%)(a)		
			I^{131}	Te^{132}	Xe^{133}
70 - 310	8	220	0	0	0
310 - 550	24	460	2	0.1	3
550 - 790	24	700	3	0.8	12
790 - 1030	24	940	8	8.0	18
70 - 1030	80		13	8.9	33
Estimated from Amount of Oxidation(b)			20	10	42
Actual Release by Analysis(c)			25	9.3	36

(a) Refer to Figure 7.
(b) Refer to Figures 10, 11 and 12.
(c) Refer to Table III.

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