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PRODUCT RELEASE FROM IRRADIATED URANIUM.

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FROM: G. W. Parker, G. E. Creek, W. J. Martin and C. J. Barton

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SUMMARY

Comparative studies of the rate of reaction of highly irradiated uranium with air, CO_2 and steam have been conducted in an investigation of the fission product release potential in a loss-of-coolant type accident postulated for the plutonium producing reactors. Highly irradiated uranium is found to be more reactive, probably because of the defects in the oxide coating formed by the inclusion of fission products. Complete oxidation or melting is found to release rare gases, iodine and tellurium semi-quantitatively in most atmospheres. Other fission products: ruthenium, cesium, and strontium are released to a lesser extent and apparently in proportion to the amount of self-heating induced. In order of their relative tendency to release fission products the atmospheric conditions investigated could be rated in order: $\text{air} > \text{CO}_2 > \text{steam}$.

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HAZARDS OF FISSION PRODUCT RELEASE FROM IRRADIATED URANIUM.

ABSTRACT

Continuing fuel element catastrophe investigations have included: a study of GE-ANPD fuel which has been reported; a study of UO_2 fuels suitable for power reactor use which is in progress; and a recently completed study of the oxidation of uranium in various atmospheres and the attendant fission product release from irradiated uranium. The results of some experiments in which uranium was incompletely oxidized in air were briefly summarized in a previous report. These results are given here in detail along with additional oxidation data obtained in CO_2 , steam and air and with fission product release figures obtained when irradiated uranium was oxidized by these gases.

Oxidation rates of irradiated uranium (0.2 at. % burn-up) and unirradiated uranium in air, CO_2 , and steam were compared at 800, 1000 and 1200°C. Irradiated uranium oxidized more rapidly than unirradiated uranium, both above and below the melting point. This indicates that oxidation rates measured with unirradiated uranium can not be applied directly to predict the oxidation behavior of highly irradiated uranium present in operating reactors.

Fission product releases were measured when uranium, irradiated to only trace level, was partially oxidized in air and steam. Fission products released on oxidizing highly irradiated uranium in air, CO_2 and steam were also measured; and some experiments were performed to determine the fission products released in helium on melting uranium which had been irradiated at both levels. Several fission products including strontium, cesium and the rare gases were found to be released at 1200°C to a greater extent from uranium which had been irradiated at high levels than were found by another investigator using uranium irradiated at trace levels.

The rare gases were essentially completely released on oxidizing irradiated uranium in air at 1000 to 1200°C, even with short burning times and low amounts of oxidation. After 20 minutes in air at 1000°C, uranium was about 50% oxidized and the iodine release approached 65%, cesium 2%, and strontium 0.05% (as determined by radiometric analyses). At 1200°C, uranium was 75% oxidized in 20 minutes. Under these conditions about 70% of the iodine, 70% of the tellurium, 18% of the cesium, 2% of the ruthenium, and 2% of the strontium were released. High ruthenium release values were obtained from completely oxidized samples, as compared to the low values observed in partial oxidation experiments. This indicates that ruthenium is released mainly near the end of the oxidation process.

Fractional releases of iodine and tellurium were comparable to those obtained in air when irradiated uranium was oxidized in CO₂ at 1000 and 1200°C. Ruthenium and cesium release values obtained in CO₂ were approximately 1/10 of the values in air at these temperatures. The release values obtained in steam were much lower than those obtained in CO₂ and air, except that at 1200°C tellurium was released to about the same extent in all three oxidizing atmospheres. A comparison of fission product release data obtained in different atmospheres is given.

Fission product ratios calculated from the release data obtained in air at 1200°C were in very good agreement with reported fission product ratios calculated from measurements of fall-out following the Windscale incident.

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THE HAZARDS OF FISSION PRODUCT RELEASE FROM IRRADIATED URANIUM.

INTRODUCTION

Since the historic incident of the Windscale No. 1 Pile⁽¹⁾ in October, 1957, the value of previous estimates of the consequences of such an accident has been the subject of review. In the initial estimates of the effects of a major reactor accident,^(2,3) a very conservative approach invariably led to the proposal of excessively high release values. In this most significant of all incidents of fission product release, the observed semi-quantitative volatilization of iodine and the less important contributions from tellurium, cesium, ruthenium and strontium can be closely correlated with the majority of the experimental work now completed.

Normal metallic uranium as a reactor fuel is primarily of importance in the cases of plutonium-producing reactors which have volatile or gaseous coolants such as air, water or CO₂ gas. Consequently, the high temperature interaction of uranium with these materials as well as others in the reactor environment (e.g., graphite) is of vital importance in considering possible failure of containment of fission products. For this reason, the oxidation of metallic uranium at high temperatures as a process which contributes to fission product release has been systematically investigated as a mechanism for creating a reactor accident hazard.

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1. "Accident at Windscale No. 1 Pile on 10 October 1957." Her Majesty's Stationery Office, London, November 1957.
 2. H. M. Parker and J. W. Healy, "Environmental Effects of a Major Reactor Disaster", Geneva Conference Paper, No. 482, 1955.
 3. "Theoretical Possibilities and Consequences of Major Accidents in Large Nuclear Power Plants", WASH-740, U.S.A.E.C., Washington 1957.

In the present work, as in the previous tracer level work by Hilliard,⁽⁴⁾ small cylindrical uranium specimens were used to carry out the many oxidations in the various media. The point of major difference between the present and the former work is in the higher irradiation level to which some of the metal specimens were subjected. Significant burn-up effects have been noted previously⁽⁵⁾ and were expected in this case. The burn-up level investigated was approximately 0.2 total atom percent in all cases although there were slight differences between samples, all of which were machined in a hot cell from a uranium fuel rod. The experiments were conducted in two groups, the differences being mainly in the percent of oxidation accomplished and the method of following the progress of oxidation. This is important in that in the first type of experiment where incomplete oxidation was the rule, specimens were heated for a measured length of time, varying from 5 to 50 minutes, resulting in oxidation of 25 to 85% of the metal. The metal residue remaining was quantitatively determined by chemical titration in each case.

In the second type of experiment, the uranium specimens were completely oxidized while the change in sample weight was automatically recorded on a thermobalance. Some unexpected effects of the experimental differences were observed in the fission product release results.

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4. R. K. Hilliard, "Fission Product Release from Uranium Heated in Air", HW-60689, August 1959.
 5. G. W. Parker, G. E. Creek, and W. J. Martin, "Experiments on the Release of Fission Products from Molten Reactor Fuels", ORNL-2616, July 1959.

OBJECTIVES OF THE STUDY.

1. To Compare Oxidation Rates of Irradiated Uranium With Unirradiated Uranium in Air, CO_2 , and Steam.

In studying the oxidation rates of uranium, one effect was emphasized, that is, a clear correlation of the oxidation rate of irradiated metal as compared to unirradiated uranium under the same conditions.

2. To Determine the Effect of Atmospheric Environment During Oxidation On Fission Product Release Values.

3. To Determine the Effect of Oxidation Temperature on Fission Product Volatilization.

Oxidations were performed at 800° , 1000° , 1200°C , and some at 1400°C .

4. To Observe Particles and Particle Sizes.

In all experiments, "absolute" filters were installed in the gas stream to collect solid materials that were dispersed during the oxidation. The nature and amount of radioactivity associated with such particles was ascertained.

5. To Determine the Extent of Vaporization of Uranium Oxide (UO_3) at Various Temperatures.

An investigation was conducted to determine the temperature increase in the metal due to the heat of reaction at high temperatures.

6. To Determine the Effect of Aluminum Cladding on Oxidation Rate and Fission Product Release.

The incidental effect of incorporation of metallic aluminum in the molten uranium, such as might occur in a reactor channel, was briefly investigated.

7. To Compare the Extent and Rate of Fission Product Volatilization With the Fraction of Irradiated Uranium Oxidized.

8. To Correlate Results of Laboratory Fission Product Release Experiments With Those Determined for the Windscale Incident.

The published fall-out data on the Windscale release suggested the possibility of applying experimental results to an analysis of the observed fission product release.

3.0 SUMMARY OF RESULTS

3.1 Trace Level Irradiated Uranium Oxidation in Air.

As in most experimental work involving highly irradiated fuel, it was useful to conduct an initial series of experiments at trace level. These were performed with uranium of the same metallurgical type as that in the highly irradiated metal. In all cases a significantly slower oxidation rate on the trace level material, as compared to that of the highly irradiated uranium, was observed. Several fission products also showed significantly lower release rates. The strontium, cesium and rare gas values were perhaps the most affected. Those experiments in which the samples were incompletely oxidized were performed in an open ceramic boat enclosed in a horizontal silica tube while the complete oxidations were performed in a porous alumina extraction thimble enclosed in a vertical Mullite furnace tube. Some geometric or other effects may have influenced results.

3.2 Highly Irradiated Uranium With Incomplete Oxidation in Air.

In these experiments, also conducted in the horizontal silica tube and open-boat, the rare gases were essentially completely released even at the shortest heating times and lowest amount of oxidation. After 20 minutes at 1000°C., uranium was about 50% oxidized and the iodine release approached 65%, cesium ~2%, and strontium ~0.05%. At 1200°C., uranium was 75% oxidized in 20 minutes; iodine was

about 70% released; tellurium 70%; cesium 18%; ruthenium 2% and strontium ~2%. Release values for strontium and cesium are higher by a factor of 10 or more than in Hilliard's⁽⁴⁾ tracer level experiments in air. The reason for the discrepancy between our results and Hilliard's is not known at the present time.

3.3 Highly Irradiated Uranium with Complete Oxidation in Air.

Some striking differences were observed between the results of these experiments and those above with incomplete oxidation. For example the ruthenium released increased rapidly at 1200°C to 70-80% (approximately the same as for the tellurium) indicating that ruthenium is released mainly near the end of the oxidation process.

3.4 Highly Irradiated Uranium-Oxidation in CO₂.

In CO₂ at 1000-1200°C., iodine and tellurium were released at a rate comparable to that in air, 60-80%. The ruthenium release was suppressed as was cesium by a factor of about 10 as compared to the release of these activities in air at the same temperature. The admission of even a small amount of air, however, served to increase the ruthenium release to a value comparable to that obtained in air.

3.5 Trace Irradiated Uranium-Oxidation in Steam - Air Mixture.

In a mixture of steam and air in the ratio of 12:1, the essential pattern of the release values was the same as at 1200°C. in air but the rate of fission product release as well as the rate of oxidation was considerably lower. At 1000°C. the releases were lower by an order of magnitude. The steam flow rate was equivalent to 3600 cc/min.

3.6 Highly Irradiated Uranium - Oxidation in Steam-Helium Mixture.

At a gas flow rate of only 300 cc/min. steam and 300 cc/min. helium, all release values were strongly suppressed as compared to air release values at the same

4. R. K. Hilliard, op. cit.

temperature except tellurium at 1200°C which was equivalent to that in air or CO₂ at this temperature. At 1000°C iodine was lower by a factor of 15 and at 1200°C by a factor of 7. Cesium and ruthenium were essentially not released at all.

3.7 Comparison of the Windscale Release Incident with a Predicted Fission Product Spectrum.

The observed fission product fall-out ratios following the Windscale accident have been used in preparing an approximate analysis of the percentages released. These results in turn have been compared with those obtained from experimental measurements made at a gas temperature of 1200°C. The calculated releases when normalized to our result of 70% iodine release corresponding to 75% uranium oxidation gave excellent agreement with the experimental values for tellurium, cesium, ruthenium and strontium.

4.0 Discussion of the Behavior of Individual Fission Products.

1. The rare gases, xenon and krypton, were apparently essentially completely released from 0.2 at. % burn-up uranium when melted or when completely oxidized in all atmospheric systems tested except steam. In the steam oxidation experiments, the dense, adherent oxide coating efficiently trapped the gas and prevented complete oxidation of the uranium. While it has been clearly demonstrated that a small fraction of the xenon and krypton is released on slow cooling of melted uranium, it is believed that on heating and cooling rapidly a more significant amount of gas may be retained which could be expelled by remelting the uranium, and cooling it through solidification and the transition temperatures.

2. Iodine was released semi-quantitatively from molten uranium to about the same extent under most conditions and atmospheres tested. It was predominantly in the form of free iodine. In some instances at trace concentration, iodine was

released even more completely than the rare gases. In oxidizing atmospheres below the melting temperature the percent released was about equivalent to the percent uranium oxidized.

3. Cesium was observed to vaporize more readily than any other fission product except the halogens, tellurium and the rare gases, since it has the lowest boiling point and is readily dissociated from oxygen at high temperatures. Such behavior is evident in the results of one experiment (4-21-1) in Table X in which, for reasons not clearly understood, the specimen reached an abnormally high temperature ($>1800^{\circ}\text{C}.$) At lower temperatures, however, as in air at 1200° , only 10-20% of the cesium was vaporized and it seems certain that this depended to some extent on self-heating of the specimen to a much higher temperature than that of the air. In CO_2 , He, and steam when self heating was negligible, little vaporization (1-2%) of cesium was observed.

Cesium was released predominantly at higher temperatures. Increasing the gas temperature from 1000°C to 1200°C resulted in a 10 fold increase in cesium released in air.

4. Ruthenium showed the most divergent behavior of all the fission products. When only a fraction of the uranium was oxidized in air, little of the ruthenium was vaporized even at 1200°C . As oxidation of the uranium approached completion, the release increased rapidly to almost 100 percent. Even in a CO_2 oxidation experiment in which a little air was inadvertently pulled into the furnace tube (Run H-84) a very high ruthenium release was observed. In a steam atmosphere, with incomplete oxidation, significant amounts of ruthenium were not released. A large part of the ruthenium released was apparently in the form of very small particles (perhaps as RuO_2). In one experiment in which a high helium velocity was employed (Run H-84) after oxidation was completed, ruthenium particles penetrated

several thicknesses of "absolute" filter papers.

5. Tellurium like ruthenium was observed to be only partially released by oxidation of a fraction of the uranium specimen. Other metallic systems when melted rapidly have shown little or no release of these two elements since they normally alloy readily with uranium. As oxidation proceeded to completion however, at temperatures above 800°C , tellurium was volatilized in most experiments at about the same rate as iodine. The one exception observed was in steam at 1000°C where only 2% of the tellurium was released while 34% of the uranium was oxidized. A high proportion of the tellurium was found on the filters as was the case with ruthenium.

6. Strontium can most readily vaporize as the element, i.e., in oxygen deficient systems. In a helium atmosphere at 1200°C some vaporization (1-2%) occurred. Experimentally, an inconsistency in our strontium results was found in the thermobalance data in which a deep alumina crucible was used as the uranium container and a Mullite furnace tube was employed. It is believed that both of the pieces of apparatus chemically adsorbed some strontium as well as cesium and prevented its complete recovery. The quartz tube-horizontal furnace system consistently indicated a 2-3% release at 1200°C , while results obtained in the thermobalance apparatus indicated ~ 0.02 percent. The latter results may be modified by analysis of the furnace tube and alumina crucible in later experiments.

7. Other long-lived fission products, at $1200 \sim 1400^{\circ}\text{C}$ normally show no significant releases. In the "run-away" oxidation in Run 4-21-1 both cerium (32%) and plutonium (3.5%) were released. This type of behavior is not considered a reasonable occurrence however, and this one anomalous experiment is not sufficient to establish these elements in the volatile class.

5.0 Apparatus and Experimental Procedures

Two experimental arrangements were used or modified for all release experiments. For experiments with air or CO_2 the apparatus was slightly less complicated than that used with steam as the oxidizing agent. For the trace level experiments, uranium metal of the β -stabilized type was machined, but not polished, in order to duplicate the rough finish of the highly irradiated specimens. To prepare for a series of experiments, several clean, degreased uranium cylinders, $1/4" \times 11/16"$, were sealed in silica ampoules, given an irradiation of about 3×10^{17} nvt and then cooled several days to a week or more. The ampoule was broken in a hot cell, the specimen was weighed on a shielded analytical balance and placed in a zirconia boat prior to insertion in the horizontal furnace.

5.1 The Horizontal Tube Furnace

The trace level runs and all of the "incomplete-oxidation" runs were conducted in a silica tube heated by a horizontal tube furnace (Fig. 1) containing a platinum resistance element. A platinum-platinum-10% rhodium thermocouple enclosed in a protective silica tube was placed near the sample to control and record the furnace temperature. The boat was inserted into a helium-filled silica furnace tube and helium flow was continued to sweep out the tube. The pre-heated furnace was then rolled on a track over the specimen and the furnace tube was maintained at the required temperature for the period of the oxidation. After a prescribed heating time the furnace was rolled away from the sample, the specimen was cooled in helium and finally the boat and residue were removed for chemical dissolution of the specimen.

In these experiments the uranium was not completely oxidized and therefore the remaining metal was determined chemically by dissolving in HCl and titrating U^{+4} with Cr^{+6} .

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Figure 4
FLOW DIAGRAM OF FISSION PRODUCT RELEASE APPARATUS

The fission product adsorption train was essentially that used in previous work⁵ except that a hot charcoal trap was used instead of a wet alkaline scrubber, to collect iodine. Several "Millipore" filter papers were used in series to collect particulate material such as uranium oxide and oxides of ruthenium, tellurium, cesium, etc.

5.2 The Vertical Furnace and Thermobalance Apparatus

The vertical furnace (Fig. 2) required for the continuous recording thermobalance, comprised a "Mullite" tube 1-1/4" O.D. and 20" long with pyrex fittings fused to the ends. Some difficulty was encountered with Mullite in completing material balances. A part of the cesium and ruthenium was suspected of being retained in the surface of the porcelain and strontium recovery was also in doubt. To check on this possibility, one furnace tube, after it had been washed with 2 M NaOH, concentrated HNO₃, 2 M NH₄F-HF and HNO₃ containing NaBrO₃, was pulverized in a hammer mill and submitted for radiochemical analysis. It was found to contain about 0.5% of the total Ru content of an irradiated specimen and 12% of the Cs content.

In order to obtain a suitable frictionless gas seal on the furnace, the suspension wire was passed through a constriction between two "Magnehelic" pressure gauges having a range of 0 to 1" of water. Helium was introduced through the top opening at a rate of about 150 cc/min to give a positive pressure of 0.4" of water while a vacuum applied to the exit end of the fission product collection train, following the cold charcoal trap, gave a negative pressure of approximately 0.1" of water at the lower opening. Thus a controlled leak of helium into the furnace tube was maintained to insure containment of fission product gases and exclusion of air during the oxidation or melting experiments.

5. G. W. Parker, et. al., op. cit.

Figure 2

FURNACE AND THERMOBALANCE ARRANGEMENT FOR URANIUM
OXIDATION IN STEAM WITH FISSION PRODUCT COLLECTION TRAIN

- 1 HOT Cu TURNINGS
- 2 ROTAMETER
- 3 PRESSURE GAUGE
- 4 VACUUM GAUGE
- 5 PINCH CLAMP
- 6 CONDENSER
- 7 BOILER
- 8 HEATING TAPE
- 9 THERMOCOUPLE WELL
- 10 CRUCIBLE & SAMPLE
- 11 Pt-10% Rh FURNACE WINDING
- 12 Pt SUSPENSION
- 13 THERMOBALANCE
- 14 HEAT LAMP
- 15 CONDENSATE BULB
- 16 COLD TRAP -80°C
- 17 MILLIPORE FILTER HOLDER
- 18 CHARCOAL TRAP AT -225°C
- 19 THERMOCOUPLE WIRE
- 20 COLD TRAP -195°C
- 21 HEATING MANTLE

In most of the experiments conducted in this apparatus, the samples were contained in a 2-1/4" long alumina extraction thimble and were allowed to oxidize completely except for the steam experiments. This is in contrast to those conducted in the open boat and horizontal tube furnace. In practice it was found that an air flow rate of 300 cc/min. or velocity of 120 cm/min. (STP) in the horizontal furnace produced an oxidation rate equal to or greater than that produced by 600 cc/min. in the vertical furnace with the specimen contained in the deep thimble. Since the two systems differed so widely in the amount of surface of metal or oxide directly exposed to the flowing furnace atmosphere, it is not surprising that some differences in results were encountered.

5.3 Radiochemical Material Balances

A simple procedure based upon complete recovery of all products released from the combustion boat or crucible was used to obtain radiochemical material balances. After establishing the fission product inventory in a series of specimens from repeated analyses considerably more confidence could be placed in a set of results which accumulated a high percentage of the expected inventory. These analyses were made after the metal residue was dissolved and the furnace tube and associated equipment were carefully leached with acids, bases and fluoride-containing reagents. The rare gas samples were simply compared by a total ionization method to obtain relative percentages. The filter papers used were sectioned and dissolved after an initial ionization measurement. The hot charcoal iodine trap could be assayed directly if only I^{131} were present by means of a gamma spectrometer. If the charcoal contained any particulate activity it was chemically leached for wet analysis.

6.0 FISSION PRODUCTS RELEASED ON MELTING IRRADIATED URANIUM
IN AN INERT ATMOSPHERE.

The most important previous studies of the release of fission products accompanying the melting of irradiated uranium in an inert atmosphere were carried out at the Argonne National Laboratory by Feder⁽⁶⁾ and co-workers. A series of experiments was performed to demonstrate the feasibility of uranium decontamination by melting irradiated uranium in an inert atmosphere in contact with various ceramic adsorbents. High release rates of the halogens, rare gases, cesium and strontium were reported by these investigators. Comparison of fission product release in an inert atmosphere with results obtained in oxidizing atmospheres should serve to indicate which fission products depend on oxide formation for vaporization, such as ruthenium, and which are suppressed by the presence of oxygen, e.g., strontium. Several melting experiments in helium were performed, one in the horizontal, silica tube furnace and the others in the thermobalance apparatus. The latter experiments were performed principally for the purpose of observing rare gas release and recovery of fission products that deposited in the furnace tube and tubing connecting the furnace to the filters and charcoal trap was not attempted. The results of these experiments are displayed in Table I. A striking difference is noted between the high rare gas release values obtained in these experiments with uranium irradiated to 0.2% burn-up and the value obtained by Hilliard⁽⁷⁾ (10% release) in helium at trace irradiation level. This discrepancy suggests the possibility of trapping xenon or krypton in oxide crystals or other defects in the uranium at low concentrations because of their large atomic radii and low solubility in metals. At higher

6. L. Burris, H. M. Feder, S. Lawroski, W. A. Rodger and R. C. Vogel,
"The Melt Refining of Irradiated Uranium: Application to EBR II, Fast
Reactor Fuel," Nuclear Science and Engineering 6, 493-495 (1959).

TABLE I
ACTIVITY RELEASED BY MELTING IRRADIATED URANIUM*
IN HELIUM

Max. Furnace Temp. °C.	% U. Oxidized	Location of Activity	Gross γ	Percent of Total Activity Released				
				Xe-Kr	I	Te	Cs	Sr
1200**	4.1	Total	0.4	97.7	47.0	0.6	2.0	0.9
1170-	0.9	Filters	-	-	0.7	-	-	-
Cycled		Charcoal	-	-	25.3	-	-	-
		Total	-	98.9	26.0***	-	-	-
1180-	3.9	Filters	-	-	17.3	-	-	-
Cycled		Charcoal	-	-	24.8	-	-	-
		Total	-	97.1	42.1***	-	-	-
1250	15.3	Filters	-	-	1.6	-	-	-
		Charcoal	-	-	21.0	-	-	-
		Total	-	99.6	22.6***	-	-	-
1400	2.6	Filters	-	-	5.1	-	-	-
		Charcoal	-	-	78.3	-	-	-
		Total	-	-	83.4***	-	-	-

* 0.2 at. % burn-up.

** This run performed with the uranium contained in a boat in a horizontal tube furnace. The other runs were carried out in the thermobalance apparatus (Figure 2).

*** Iodine release values probably low because no effort was made in these experiments to recover iodine or other activity deposited in the furnace or tubing connecting the furnace to the filters and charcoal trap.

concentrations of the rare gases, they apparently cannot be retained by the trace amounts of oxides present in the molten metal. An alternate explanation is that the small amount of rare gases produced by the trace level irradiation only slightly exceeded the solubility of the gases in molten uranium at the temperature of the experiment (1215°C) while at 0.2 at. % burn-up, the amount of rare gases greatly exceeded the solubility value in liquid uranium.

An interesting release-rate curve for the rare gases observed on melting and cooling irradiated uranium in helium is shown in Figure 3. Use of a sensitive in-stream counter permitted observation of details of the rate of gas release apparently unreported previously. Among the interesting points shown in Figure 3 are the large fraction of the gas content of the irradiated uranium released rapidly on melting, the accelerated releases at the freezing point and the $\beta - \alpha$ inversion temperature (660°C) and finally the accelerated release obtained on cooling the sample rapidly, presumably due to a "squeeze-out" effect accompanying the increase in uranium density. The lack of a noticeable increase in release rate at the $\beta - \alpha$ inversion temperature may be attributed to the small density difference between these two forms of uranium. The percent gas release values noted in Figure 3 were determined by means of ionization chamber readings on cold charcoal traps in the same manner that released rare gases accompanying oxidation of uranium were measured. It should be noted that the temperatures shown at the top of Figure 3 were measured gas temperatures rather than uranium specimen temperatures which accounts, at least in part, for the discrepancy between the observed temperatures at the freezing point and the $\beta - \alpha$ inversion temperature as compared to literature values for these points noted in the drawing.

7. R. K. Hilliard, "Fission Product Release From Uranium Heated in Air,"
HW-60689, August 3, 1959.

Figure 3
RELEASE OF FISSION GAS (Krypton-85) FROM IRRADIATED URANIUM (0.2% Burn-up) MELTED
IN FLOWING HELIUM

7.0 OXIDATION OF URANIUM IN AIR AT HIGH TEMPERATURES.

Each atmospheric environment of uranium has its unique characteristics of oxidation rate and type of oxide formed upon which the amount of fission products diffused and vaporized through the oxide layer depend. Since the most likely mode of fission product release from a loss-of-coolant reactor accident would involve uranium in contact with air at high temperatures, the oxidation of uranium in air and the resultant fission product release were investigated first. Less attention was directed toward elucidation of reaction kinetics than in some previous investigations^{8,9}. The extensive kinetic studies by Vogel, et al,⁹ have shown in much detail the mechanism of ignition and self-heating in uranium and uranium alloys. Hilliard⁸ reported the results of an investigation of the oxidation of unirradiated uranium in air similar in many respects to the present investigation and the results of the parallel studies appear to agree satisfactorily. Hilliard also reported⁷ results of fission product release studies of uranium irradiated at trace level and heated in air.

Hilliard's data⁸ showed a linear relationship between the log of air velocity and oxidation rate. A limited investigation performed with the thermobalance apparatus using air flow rates of 300, 600 and 1000 cc per minute (measured at room temperature) at 1000, 1200 and 1400°C showed the expected increase in oxidation rate with increasing air flow velocity.

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8. R. K. Hilliard, "Oxidation of Uranium in Air at High Temperatures," HW-58022, December 1958.
 9. T. G. Schnizlein, P. J. Pizzolato, H. A. Porte, J. D. Bingle, D. F. Fischer, L. W. Mishler, and R. C. Vogel, "Ignition Behavior and Kinetics of Oxidation of the Reactor Metals, Uranium, Zirconium, Plutonium, and Thorium, and Binary Alloys of Each," ANL-5974, April, 1959.

The effect of varying surface area to weight ratio on oxidation rate was studied only in the open-boat horizontal tube furnace apparatus. Data obtained at a furnace temperature of 630° C are shown in Figure 4. Similar data obtained at 1000 and 1200° C are shown in Figure 5. It is clear from these data that even a small change in surface area to weight ratio produces a significant change in oxidation rate.

The effect of increasing temperature on oxidation curves for 1/4" by 11/16" cylinders (0.42 cm²/gm.) obtained by use of the thermobalance with an air flow rate of 600 cc/min., equivalent to a room temperature velocity of 220 cm/min. around the alumina thimble containing the uranium specimen, is shown in Figure 6. The variation in maximum oxidation rate with temperature is shown in an Arrhenius type plot, Figure 7. While the oxidation rate increased with air temperature much more uniformly than in CO₂, a maximum in the rate of oxidation was noted at 700°C, followed by a drop in oxidation rate until the temperature reached 800 or 900°C, where the regular increase in rate with temperature resumed. This behavior is probably related to the $\beta - \gamma$ transition discussed in the section on oxidation of uranium in CO₂. Under the conditions prevailing in these experiments, approximately 30 minutes was required to oxidize 1/2 of the uranium specimen at 800°C while at 1200° C the time was reduced to about 6 minutes.

Irradiated uranium (0.2 at. % burn-up) specimens oxidized more rapidly than did unirradiated specimens when exposed to air under the same conditions in the thermobalance apparatus. Data obtained in air at 800°C are compared in Figure 8 with similar oxidation data obtained in CO₂-helium and steam-helium mixtures. A similar comparison at 1000°C is shown in Figure 9, and Figure 10 displays the data obtained at 1200°C. It should be emphasized that the temperatures reported

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Figure 4
EFFECT OF SURFACE AREA TO WEIGHT RATIO
ON OXIDATION OF URANIUM IN AIR AT 630° C

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Figure 5
EFFECT OF SURFACE AREA ON OXIDATION RATE
OF URANIUM IN AIR

Figure 6
OXIDATION OF URANIUM IN AIR

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Figure 7
OXIDATION RATES FOR URANIUM
IN AIR AND CO₂-HELIUM MIXTURE

Figure 8

COMPARISON OF OXIDATION RATES OF IRRADIATED AND UNIRRADIATED URANIUM IN AIR (600cc/min), CO₂-HELIUM MIXTURE (150-450 cc/min) AND STEAM-HELIUM MIXTURE AT 800°C

Figure 9
COMPARISON OF OXIDATION RATES OF IRRADIATED AND UNIRRADIATED
URANIUM IN STEAM, AIR, AND CO₂ AT 1000°C
(600 cc/min Flow Rate)

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Figure 10
COMPARISON OF OXIDATION RATES OF IRRADIATED AND UNIRRADIATED URANIUM IN STEAM, AIR, AND CO₂ AT 1200°C

here are gas temperatures to which the uranium was exposed rather than uranium specimen temperatures. Data indicating the extent of the self-heating effect obtained on heating uranium in air are reported elsewhere in this document. Possible explanations of the difference in oxidation rates between irradiated and unirradiated uranium are discussed in connection with CO_2 oxidation data.

Data obtained in the horizontal tube furnace (Fig. 1) provided a comparison of the rates of oxidation of irradiated and unirradiated uranium in air at 1000°C (Fig. 11) and 1200°C (Fig. 12) under different experimental conditions than the comparisons discussed above, and it is clear that these data substantiate the data obtained in the thermobalance apparatus (Fig. 2). The comparison between oxidation data obtained with unirradiated uranium in air and a steam-air mixture shown in Figures 11 and 12 is discussed in another section of this report.

7.1 COMPOSITION OF OXIDES FORMED ON BURNING URANIUM METAL IN AIR AT $800 - 1400^\circ\text{C}$.

Previous investigators have generally ignored the composition of the uranium oxides formed by the incomplete oxidation of the metal in air as opposed to the composition after complete oxidation. Hilliard⁽⁸⁾ reported in his work that the weight ratios observed indicated only U_3O_8 was formed at temperatures above 300°C . Hilliard's results for partially oxidized uranium were based upon the weight of the metal residue left after carefully removing the oxide by scraping followed by dissolution of the remaining oxide in nitric acid and he apparently did not identify the oxide layer.

In the work contemplated here, it was decided that the mechanical method could not be applied because of the expected hazardous radiation level and, therefore, a method useful for remote operation was devised. The process developed required the chemical treatment of a mixed metal and oxide residue with strong

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Figure 11
RELATIVE RATE OF OXIDATION OF $\frac{1}{4}$ in. x $\frac{11}{16}$ in.
CYLINDER OF IRRADIATED AND NON-IRRADIATED
URANIUM IN AIR AND STEAM MIXTURE AT 1000°C

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Figure 12
RELATIVE RATE OF OXIDATION OF $\frac{1}{4}$ in. x $\frac{11}{16}$ in.
CYLINDER OF IRRADIATED AND NON-IRRADIATED
URANIUM IN AIR AND STEAM MIXTURE AT 1200°C

hydrochloric acid which did not attack the uranium oxides but vigorously dissolved the remaining metal to form a green solution of UCl_4 . It was then only necessary to determine the amount of UCl_4 in solution by titration with standard dichromate solution. In order to check the method with unirradiated uranium, a comparison was made which required weighing both the oxides and metal residue as well as treating both with acid and performing the titration.

Surprisingly, the weights obtained for the amounts of metal consumed and the amount of oxide formed did not indicate the formation of stoichiometric U_3O_8 . This result led to the further heating of the previously formed oxide at $600^\circ C$ in air to constant weight at which time the gain in weight accurately corresponded to the composition of U_3O_8 . The results of three series of experiments with uranium specimens having different surface to weight ratios are tabulated in Table II in which the percent of the oxide formed as UO_2 was calculated. The data showed about 70% of the oxide to be UO_2 at the end of the first 5 minutes, and a gradual decrease to ~20% UO_2 after 1 hour. The terms used in the calculation are defined below.

To Calculate the Weight of UO_2 and U_3O_8 Formed:

Values Obtained by Direct Weighing:

W_0 = Wt. of U sample before oxidation

W_1 = Wt. of U sample after oxidation

W_2 = Wt. of U and reburned oxides

Let: X = Wt. of U remaining after oxidation

Y = Wt. of UO_2 formed during oxidation

Z = Wt. of U_3O_8 formed during oxidation

$U/UO_2 = a$; $3U/U_3O_8 = b$; $U_3O_8/3UO_2 = c$

Then: $W_0 = X + aY + bZ$

$W_1 = X + Y + Z$

$W_2 = X + cY + Z$

In the results reported from experiments based on complete oxidation, both the gravimetric ratios and x-ray and optical diffraction data support the composition of the final oxide as U_3O_8 .

X-ray examination⁽¹⁰⁾ of a section of oxide film that flaked off of a 1/4 x 11/16" uranium specimen that had been oxidized in air for 10 minutes at 1000°C showed an interesting difference in composition between the side adjacent to the uranium and the outside. The inner side was predominately UO_2 while the outside gave an x-ray pattern⁽¹¹⁾ identified at $UO_{2.92}$. It has generally been assumed that U_3O_8 is the only oxide formed in this temperature range although Waber⁽¹²⁾ has reported data indicating other oxides formed in the temperature range 185 to 275°C.

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10. R. E. Thoma, Oak Ridge National Laboratory, Private communication.
 11. H. R. Hoekstra and S. Siegel, Argonne National Laboratory, Private communication to R. E. Thoma.
 12. James T. Waber, "A Review of the Corrosion Behavior of Uranium" LA-2035, December, 1958.

TABLE II
COMPOSITION OF MIXED URANIUM OXIDES FORMED
BY INCOMPLETE OXIDATION IN AIR AT 1000°C.

No.	Time @ 1000° Min.	$W_2 - W_1$ Grams	W_0 Grams.	$W_1 - W_0$ Grams.	$W_2 - W_0$ Grams.	Wt. UO_2 Grams.	Wt. U_3O_8 Grams.	% of Oxide as UO_2
<u>Area/Weight = 0.74 cm²/gm.</u>								
1	10	0.0188	1.4058	0.1316	0.1504	0.476	0.500	48.8
2	15	0.0106	1.3684	0.1751	0.1857	0.268	0.933	22.3
3	20	0.0096	1.3970	0.1805	0.1901	0.043	0.999	19.6
<u>Area/Weight = 0.53 cm²/gm.</u>								
4	5	0.04	4.7188	0.1756	0.2156	1.01	0.316	76.2
5	10	0.0562	4.7183	0.2689	0.3251	1.42	0.566	71.5
6	15	0.0518	4.6769	0.3501	0.4019	1.31	1.179	52.6
7	20	0.0463	4.6275	0.4058	0.4521	1.17	1.78	39.7
8	30	0.0381	4.7159	0.4791	0.5372	0.964	2.53	27.6
9	40	0.0404	4.6723	0.5489	0.5893	1.02	2.81	26.6
10	60	0.0422	4.6659	0.6491	0.6913	1.07	3.43	23.8
<u>Area/Weight = 0.42 cm²/gm.</u>								
11	5	0.0422	10.4367	0.23	0.2722	1.068	0.667	61.6
12	10	0.0823	10.5005	0.4055	0.4878	2.083	0.950	68.7
13	10	0.0728	10.2686	0.4211	0.4939	1.843	1.383	57.1
14	10	0.0767	10.3687	0.4019	0.4786	1.942	1.167	62.5
15	10	0.0806	10.3704	0.4001	0.4807	2.04	1.050	66.0
16	20	0.106	10.2987	0.6402	0.7464	2.688	2.033	56.9
17	30	0.1213	10.3906	0.7957	0.917	3.071	1.782	63.3
18	40	0.1327	10.4369	1.0058	1.1385	3.359	3.192	51.3
19	40	0.1235	10.3384	1.0063	1.1298	3.126	4.183	42.8
20	50	0.0951	10.2722	1.1992	1.2943	2.407	5.917	28.9

7.2 VOLATILIZATION OF URANIUM OXIDE.

When irradiated uranium was burned in air, CO_2 , or steam at 1200°C , colored particles were deposited on filter paper in the effluent gas stream (see Figure 13). Before analytical data on the filters became available, it was thought that the deposit might be due to fine particles of uranium oxide produced directly in the burning process or to volatilization of uranium oxide at the high temperature produced in the sample by heat from the oxidation reaction. To test the second possibility, an experiment was performed to determine the amount of uranium oxide volatilized by heating in a stream of air at approximately 1600°C , a temperature that could be reached in a sample burning rapidly in a gas stream at 1200°C . The uranium oxide used in this experiment was produced by burning normal uranium in CO_2 at 1400°C and then raising the temperature to 1600° until the weight of the oxide dropped to the approximate value calculated for UO_2 . The sample of oxide, weighing 11.744 gms. and contained in a porous alumina thimble, was lowered into the furnace, heated to 1550°C , and weighed continuously by means of the thermobalance while an air flow of 600 cc per minute was maintained and the temperature increased to a maximum of 1600° over a period of 100 minutes. The weight changes recorded by the thermobalance are shown in Table III. During the last 25 minutes of the heating period, a side arm consisting of a three foot length of 10 mm tubing having a glass wool plug in the exit end was connected near the top of the furnace tube. The only other outlet from the furnace tube was the small tube at the top of the quartz attached to the furnace through which the suspension wire passed. Since this outlet was much smaller than the side arm connection, most of the air flowing through the furnace probably passed through the side arm during the period it was connected to the furnace tube.

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Figure 13
MILLIPORE FILTER SHOWING SMOKE LIKE PARTICLES
FROM BURNED HANFORD URANIUM

TABLE III
WEIGHT CHANGES RECORDED FOR URANIUM OXIDE HEATED
IN AIR AT 1550° to 1600° C. (600 cc/min., air flow).

Time Minutes	Total Wt. Change Milligrams	Weight Change Initial Wt. Gms./Gm.	Rate of Weight Change Mg/min.
5	+5.5	+0.0004	+1.1
10	-3.5	-0.0003	-1.8
15	-17.5	-0.0015	-2.8
20	-33.0	-0.0028	-3.1
25	-49.5	-0.0042	-3.5
30	-69.5	-0.0059	-4.0
35	-88.5	-0.0075	-3.8
40	-109.5	-0.0093	-4.2
45	-131.5	-0.0112	-4.4
50	-153.5	-0.0131	-4.4
55	-177.5	-0.0151	-4.8
60	-194.5	-0.0166	-3.4
65	-209.5	-0.0178	-3.0
70	-219.5	-0.0187	-2.0
75	-229.5	-0.0195	-2.0
80	-239.5	-0.0204	-2.0
85	-249.5	-0.0212	-2.0
90	-259.5	-0.0221	-2.0
95	-269.5	-0.0229	-2.0
100	-281.5	-0.0240	-2.4
105	-291.5	-0.0248	-2.0
110	-302.5	-0.0257	-2.2

After the oxide sample was heated for 110 minutes, the thimble was raised to the cool part of the tube and the furnace was allowed to cool to room temperature. A black crystalline coating was found on the platinum suspension wire to a height of about 6 inches above the sample. A ring of black material was observed in the interior of the furnace tube below the top of the furnace. A thin brown film was also observed in the quartz attachment at the top of the furnace tube. No colored material was observed in the side arm except a very slight coloration on the glass wool plug. The acid-soluble material in the furnace tube, including the quartz attachment, and that on the platinum suspension wire, was dissolved in nitric acid and submitted for analysis. The side arm and glass wool plug were like-wise treated with nitric acid and the resulting solution was submitted for analysis. Approximately 40 mg of uranium was recovered from the furnace tube while only 0.03 mg was found in the side arm. The uranium oxide remaining in the thimble at the close of the experiment was submitted for x-ray examination and found to be largely U_3O_8 and the remainder was $UO_2 + x$. Some of the material from the platinum suspension wire used in a similar experiment was identified as pure U_3O_8 .

It was apparent from the high rate of weight loss that the sample was not pure UO_2 , as had been assumed from the final weight of the oxide in the burning experiment. Probably upon heating in air at the beginning of the experiment there had been weight gain due to re-oxidation at a temperature much lower than $1550^{\circ}C$. Data reported by Ackerman¹³ show that UO_2 , the only stable oxide of uranium at $1600^{\circ}C$., has a vapor pressure of approximately 10^{-5} mm. of Hg at this temperature. Therefore, it seems unlikely that the observed rate of weight loss, or the amount

13. R. J. Ackerman, "The High Temperature, High Vacuum Vaporization and Thermodynamic Properties of Uranium Dioxide," ANL-5482, Sept. 14, 1955.

of uranium found deposited in the furnace tube could be due to volatilization of UO_2 . However, since most of the sample was apparently U_3O_8 , the fact that the total weight loss (302.5 mg.) was much greater than can be accounted for by the uranium recovered (40 mg) indicates that U_3O_8 was probably decomposing according to the following simplified equations:

Volatilization of uranium oxide under the conditions of the experiment could also occur according to the equation:

Brewer¹⁴ has estimated that at 1600° K, the pressure of UO_3 over $\text{UO}_{2.25}$ to $\text{UO}_{2.62}$ is 10^{-5} atmospheres and over pure UO_3 the estimated value is 10^{-4} atmospheres at this temperature. The statement is also made¹⁴ that, in the presence of an appreciable oxygen pressure, UO_2 will react to form UO_3 and thus UO_2 will appear to be more volatile. Brewer states¹⁴ that UO_3 will decompose on condensation on somewhat cooler surfaces to form oxygen and an oxide having a composition between UO_2 and $\text{UO}_{2.62}$, depending upon the oxygen pressure. Our results, however, indicate that the decomposition product is U_3O_8 ($\text{UO}_{2.67}$), at least under the conditions prevailing in our experiment.

7.3 SELF HEATING OF URANIUM FROM HEAT OF REACTION.

The extent of self heating of unirradiated uranium resulting from its oxidation in air and oxygen was determined at 1100°, 1200° and 1400°C in an experimental arrangement comparable to that in which the partial-oxidation release experiments

14. L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, "The Thermodynamic Properties and Equilibria at High Temperatures of Uranium Halides, Oxides Nitrides, and Carbides," EC-82, Sept. 20, 1945.

were carried out (Figure 1). A thermocouple junction was placed in a hole in the specimen and both gas and sample temperatures were continually recorded during heating in helium and during admission of a measured flow of air or oxygen. An optical pyrometer was also used to observe the temperature transients beyond the range of the platinum-rhodium thermocouple. Typical temperature rises observed are shown in Table IV.

Sample No. 5, while burning in a very high flow rate of oxygen reached an incandescent temperature of 2650°C and vaporized approximately 100 mg. of uranium oxide. Examination of the collected material on the filter (Fig. 14) by means of the X-ray diffraction technique showed the oxide to be U_3O_8 . The samples burned in oxygen at a low flow rate which reached only 1450°C and the one in air at 1400°C which reached 1575°C also vaporized a small amount of oxide (less than a milligram).

Recently reported UO_3 vapor pressure data⁽¹⁵⁾ shown in Table V along with similar data for UO_2 and metallic uranium¹⁶ at the same temperature, support the belief that uranium was volatilized as UO_3 in these experiments, possibly due to the reaction shown in equation (3) above, and subsequently reverted to U_3O_8 at a lower temperature.

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15. R. J. Ackerman, R. J. Thorn, Carl Alexander and Marvin Tetenbaum, "Free Energies of Formation of Gaseous Uranium, Molybdenum and Tungsten Trioxides", J. of Physical Chem. 66, 350, (March) 1960.
 16. J. J. Katz and Eugene Rabinowitch "The Chemistry of Uranium-Part 1", NNCES Vol. VIII - 5, McGraw-Hill Book Co., New York, N. Y., (1951).

Figure 14
MILLIPORE FILTER FROM OXIDATION OF UNIRRADIATED
URANIUM IN OXYGEN AT 1200°C

TABLE IV
SELF HEATING OF URANIUM BY HEAT OF REACTION IN AIR AND O₂

Sample No.	Initial Temp. of Uranium °C.	Maximum Temp. Observed During Oxidation, °C.		
		400 cc/min. Air	300 cc/min. O ₂	3000 cc/min. O ₂
1	1100	1250	-	-
2	1200	1375	-	-
3	1200	-	1450**	-
4	1400	1575*	-	-
5	1400	-	-	2650**

* Smoke Pattern of U₃O₈ obtained on the filter.

** Heavy plate-out of U₃O₈ obtained on filters.

TABLE V
VAPOR PRESSURES OF URANIUM AND URANIUM OXIDES

Temp. °K	Pressure mm. Hg.		
	Uranium ¹	UO ₂ ²	UO ₃ ³
2200	5×10^{-2}	3×10^{-3}	53.2
1900	2×10^{-3}	1×10^{-5}	1.12
1700	1×10^{-4}	1×10^{-7}	0.08
1500	3×10^{-6}	1×10^{-8}	2.7×10^{-3}
1375	2×10^{-7}	-	2.0×10^{-4}

1. In vacuo, data from Katz and Rabinowitch (Ref. 16).
2. In vacuo, data from Ackerman (Ref. 13).
3. In 0.2 atm. O₂, data from Ackerman, Thorn, et al. (Ref. 15).

8.0 FISSION PRODUCT RELEASE FROM URANIUM HEATED IN AIR.

The accumulated data on fission product release from both trace level and highly irradiated uranium may be seen most readily in Tables VI to IX and in Figures 15, 16 and 17.

Comparisons between results at trace level in Table VI and the irradiated level (0.2% burn-up) in Table VII indicate a high degree of similarity in rate of fission product release except for cesium, strontium, and barium. Ruthenium appears to exhibit a burn-up effect although tellurium does not. Oxidation rates for the irradiated and unirradiated metal shown in Figures 11, and 12 at 1000°C and 1200°C, respectively, show a much greater difference than was noted in the thermobalance data. The rates of fission product release on a time scale are shown most clearly in Figures 15 and 16, which are highly generalized curves based on the best fit of the tabulated information.

In Table VIII, release results obtained in an air-steam mixture containing 12 parts by volume of water vapor to 1 part of air show that this atmosphere gave release results comparable to those obtained in air at a flow rate of 300 cc/min., equal to that of air in the steam-air mixture.

Table IX and Figure 17, present results obtained in the thermobalance apparatus which provided limited availability of oxygen because of an experimental condition requiring a deep thimble for retention of the burned oxide. The results on complete oxidation show only one strong trend not indicated previously in that ruthenium release is markedly enhanced.

The strontium and cesium data shown in Table IX are inconsistent with the data shown in Tables VI and VII, and has called our attention to the possibility of chemisorption of released fission-cesium and strontium in the Mullite tube. Possible errors in the release results from this phenomenon will be eliminated in subsequent experiments.

TABLE VI
FISSION PRODUCT RELEASE FROM
TRACE IRRADIATED URANIUM HEATED IN AIR

Sample Number	Time Min.	% U Oxid.	PERCENT OF TOTAL ACTIVITY RELEASED							
			Xe-Kr	G γ *	I	Te	Cs	Ba	Ru	Zr
FURNACE TEMP. 1000°C.										
4-2-1	10	25.6	55.6	4.8	8.0	6.5	0.63	0.005	0.22	-
4-3-1	60	72.0	86.7	3.32	35.0	13.6	4.4	0.07	1.12	-
FURNACE TEMP. 1200°C.										
4-6-1	10	34.6	54.2	2.65	31.8	37.9	-	0.011	0.163	0.009
4-6-2	50	91.7	80.6	9.48	92.4	66.3	-	0.01	0.61	0.007

* Gross gamma activity.

TABLE VII
FISSION PRODUCT RELEASE FROM
IRRADIATED URANIUM INCOMPLETELY OXIDIZED IN AIR

Sample Number	Time Min.	Percent U Oxid.	Percent of Total Activity Released								
			Xe-Kr	G y *	I	Te	Cs	Ru	Zr	Ce	Sr
FURNACE TEMP. 1000°C.											
5-7-1	< 1	11.1	-	0.009	3.1	-	0.01	0.004	0.003		
4-20-1	10	46.9	~ 100	0.6	-	-	2.4	0.1	0.0007	0.0001	0.05
4-15-1	20	53.2	~ 100	0.1	67.3	-	2.8	0.13	0.005	0.008	0.055
4-16-1	40	86.9	~ 100	0.8	79.5	-	18.4	5.2	0.018	0.006	0.05
FURNACE TEMP. 1200°C.											
5-8-1	< 1	25.0	-	0.22	12.5	-	1.62	0.019	0.17		
7-23-1	5	43.6	97.7	0.12	31.9	8.1	18.5	0.035	-	-	0.024
7-27-1	8	66.2	99.2	0.24	23.3	12.7	14.5	0.16	-	-	0.028
4-20-2	10	94.0	100.	0.145	-	-	11.2	0.51	0.05	0.06	2.7
8-7-1	10	68.0	98.7	0.7	39.9	24.8	17.1	0.22	-	-	0.6
8-11-1	12	77.5	99.8	3.5	46.4	23.0	-	-	-	-	0.9
8-27-1	15	72.0	99.8	0.55	52.8	51.6	28.6	4.3	-	-	3.1
9-8-1	15	64.8	99.6	1.15	71.5	68.0	13.65	2.0	-	-	1.1
9-9-1	20	65.4	99.4	0.7	57.3	71.3	13.0	1.8	-	-	0.85
9-15-1	30	72.3	-	1.48	62.1	77.4	19.2	2.34	-	-	1.77

* Gross gamma activity.

TABLE VIII
FISSION PRODUCT RELEASE FROM
TRACE IRRADIATED URANIUM HEATED IN AIR-STEAM MIXTURE

Sample Number	Time Min.	% U. Oxid.	PERCENT OF TOTAL ACTIVITY RELEASED					
			Xe-Kr	G γ^*	I	Te	Cs	Ru
FURNACE TEMP. 1000°C.								
4-27-1	11	17.1	4.7	0.51	4.3	1.8	0.77	0.44
4-28-1	40	25.0	5.5	0.32	4.9	6.2	0.41	0.16
5-12-1	60	41.5	-	0.32	2.74	4.7	0.23	0.02
FURNACE TEMP. 1200°C.								
5-5-1	10	13.0	25.8	8.9	8.6	6.5	1.6	0.04
5-6-1	40	28.1	65.0	5.9	45.5	41.6	5.8	0.32
5-11-1	61	49.4	-	4.9	46.7	60.4	6.9	4.0

Steam: Air Volume Ratio was 12:1 @ 20° C. Air = 300 cc/min.

* Gross gamma activity.

Figure 45
RATE OF VOLATILIZATION OF FISSION PRODUCTS
FROM IRRADIATED URANIUM IN AIR AT 1000°C

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Figure 16
RATE OF VOLATILIZATION OF FISSION PRODUCTS
FROM IRRADIATED URANIUM AT 1200°C IN AIR

TABLE IX

DISTRIBUTION OF ACTIVITY RELEASED BY COMPLETE OXIDATION OF IRRADIATED URANIUM* IN AIR

Run No.	Temp. °C.	Location of Activity	PERCENT OF TOTAL ACTIVITY RELEASED								
			Xe-Kr	G γ	I	Cs	Ce	Te	Ru	Zr	Sr***
H68	800	Furnace		1.33	2.4	0.036	0.001	0.56	24.7	0.035	0.02
		Filters		2.68	2.2	0.008	-	0.47	47.8	0.010	-
		Hot Charcoal		1.15	43.4	0.016	-	1.85	-	-	-
		Total	-	5.16	48.0	0.060	0.001	2.88	72.5	0.05	0.002
H81	1000	Furnace		2.3	3.9	0.37	0.0012	55.1	49.6	0.004	0.0017
		Filters		3.1	4.9	0.07	0.0009	24.7	27.7	0.011	0.0004
		Hot Charcoal		1.3	82.2	-	-	-	-	-	-
		Total	97.1	6.7	89.4	0.44	0.002	79.8	77.3	0.015	0.002
H83	1200	Furnace		2.5	25.2	13.44**	0.0005	40.5	21.2	0.011	0.018
		Filters		7.5	1.3	0.50	0.0001	55.4	63.8	0.002	0.002
		Hot Charcoal		0.5	63.3	-	-	-	-	-	-
		Total	99.2	10.5	89.8	13.94	0.0006	95.9	85.0	0.013	0.020
H32	1200	Furnace		2.34	2.70	15.54**	0.03	84.0	59.8	0.075	0.005
		Filters		0.83	0.05	0.01	-	0.06	18.3	-	-
		Hot Charcoal	-	0.05	96.4	0.03	-	-	0.1	-	-
		Total	-	3.22	99.2	15.58	0.03	84.1	78.2	0.075	0.005

* 0.2 at. % burn-up.
Air flow 600 cc/min. Experiments performed in thermobalance apparatus.

** Values corrected for chemisorption in porcelain furnace tube.

*** Values probably low due to chemisorption effect.

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Figure 17
FISSION PRODUCT RELEASE FROM
IRRADIATED URANIUM (0.2 % Burn-Up)
OXIDIZED IN AIR AT DIFFERENT TEMPERATURES

8.1 Particulate Material Collected During High Temperature Oxidation of Uranium.

The nature and size of airborne particles from a melt-down incident are questions of foremost interest to a hazard evaluation. The first indication of visible particles released from the oxidation of irradiated uranium occurred in the "run-away" oxidation experiment, Run 4-21-1, Table X. The resulting filter paper was coated with uranium oxide as shown by a photograph (Figure 13). A photograph of a portion of this paper taken with an oil-immersion optical microscope showed agglomerates of U_3O_8 in the particle size range 0.3 to 1.0 micron (Fig. 18). In attempting to duplicate the "run-away" effect, oxygen at 1200°C was used to burn a uranium specimen and resulted in production of a comparable amount of oxide (Fig. 14). Examination of this material by means of an electron microscope, using the carbon replica method, showed it to consist of small, spherical particles approximately 50 to 100 angstroms in diameter. A photograph of the particles at 20,000 x magnification is shown in Fig. 19. Filters obtained by oxidation of irradiated uranium were also examined by this process. All of these examinations showed the same range of particle sizes, 50-100 Å. A number of experiments with irradiated uranium produced slightly darkened filters, but accurate chemical determinations of the amount of uranium involved were not obtained. Some estimates were of the order of 100 micrograms of U_3O_8 on the darkest filters. At present there is no reason to suppose that the fission product activities were not closely associated with the U_3O_8 .

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Figure 20
ALUMINUM-CLAD URANIUM SPECIMEN AFTER
OXIDATION IN AIR

TABLE XI
EFFECT OF ALUMINUM CLADDING ON RATE OF OXIDATION OF METALLIC URANIUM IN AIR.

Run No.	<u>Furnace Temp. 800°C.</u>		<u>Rate of Oxidation mg/cm²/min.</u>	
	Time (Min.)	U/Al Weight Ratio	With Al	Without Al
1-22-1	20	8.16	30.1	
1-26-1	20	4.92	33.4	
1-26-2	20	5.14	37.4	
1-26-3	20	6.61	<u>34.0</u>	
			Av. 32.9	Av. 38.1

<u>Furnace Temp. 1000°C.</u>				
1-29-1	20	6.14	11.3	
1-29-2	20	6.29	<u>14.5</u>	
			Av. 12.9	Av. 44.0
1-29-3	40	6.03	10.8	
1-29-4	40	6.27	<u>13.1</u>	
			Av. 12.0	Av. 33.4

8.2 Effect of Aluminum Cladding on Rate of Oxidation of Uranium In Air.

The effect of the addition of a loosely fitted aluminum tubular jacket on the rate of oxidation of uranium metal (unirradiated) was briefly compared with the observed rate of oxidation of unclad uranium. The results shown in Table XI indicate that at 800°C the effect of the aluminum is slight and results in a reduction in oxidation rate of about 18%.

At 1000°C the aluminum clad specimens oxidized at a rate equivalent to approximately 1/3 of the rate for unclad uranium. The increased effect at the upper temperature suggests that a significant amount of alloy formed which was absent at 800°C. In the photograph of one of the specimens, Fig. 20, a fine line of metallic aluminum can be seen deeply embedded in the uranium oxide.

From the hazards point-of-view, it might be concluded that the addition of the effect of the presence of aluminum, especially a bonded cladding, should suppress the oxidation rate and, consequently, the fission product release rate.

8.3 Comparison of the Windscale Incident Release With a Predicted Fission Product Spectrum.

In view of the significance of the Windscale incident in the field of reactor safeguards, it was of interest, although speculative, to derive some comparison of the results of the present investigation with the observed Windscale release values.

In order to carry out the comparison fall-out activity ratios found after the incident, reported by Booker⁽¹⁷⁾ and Chamberlain,⁽¹⁸⁾ were used and it was necessary to assume saturation concentration of all the short-lived fission products of interest. This assumption could be made with little likelihood of

Figure 19
ELECTRON MICROSCOPE PHOTOGRAPH AT 20,000 X OF
PARTICLES FROM OXIDATION OF UNIRRADIATED URANIUM
IN OXYGEN

Figure 18
PARTICLES FROM RUN NO. 4-21-1
AT 1000 X MAGNIFICATION

TABLE X

FISSION PRODUCT RELEASE FROM HIGHLY SELF-HEATED*
IRRADIATED URANIUM OXIDIZED IN AIR AT 1200°C.

(Run 4-21-1)

G γ	I	PERCENT OF TOTAL ACTIVITY RELEASED					
		Cs	Ru	Zr	Ce	Sr	Pu
0.82	82.3	60.3	1.8	0.04	32.7	15.8	3.5
PERCENT OF TOTAL ACTIVITY COLLECTED ON FILTER**							
0.19	0.17	14.0	0.07	0.02	9.8	0.65	0.1

* One anomalous run of more than 20 at 1200°C. Possible explanation in uncertain high air flow. Observed to produce incandescence and visible oxide smoke. Maximum temperature reached > 1800°C.

** Millipore filter 0.8 micron pore diameter. Heating time: 20 min.

error; however, in the case of cesium it was necessary to assume an average irradiation time which was chosen simply by trial and error on the basis of the best agreement with the other calculated activity ratios.

After making the above-mentioned assumptions and setting the iodine activity as unity, the other fission product concentrations were calculated from the proportion of their fission yield to that of I-131, with corrections for decay and percent saturation. Inspection of fission product release data obtained at 800, 1000, and 1200°C in air showed that the data at only one temperature gave a readily apparent fit with these ratios and that was at 1200°C; however, since the percent of uranium oxidized had been found to control ruthenium release, it was necessary to select from the data on incomplete oxidation a condition showing a low ruthenium release and a high cesium release. The data obtained when 75% of the uranium was oxidized at 1200°C met these requirements. The results of this comparison are given in Table XII.

Since the maximum temperature observed by optical pyrometer during the Windscale fire was 1300°C, it appears that the 1200° indicated by this comparison is credible. It is significant that while tellurium and cesium were released in fairly high percentages, their effect on the nature and extent of the biological hazard created was almost insignificant when compared to I-131, as indicated by the published fall-out data.

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17. D. V. Booker, "Physical Measurements of Activity in Samples from Windscale" AERE-HP/R-2607 - October, 1958.
 18. A. C. Chamberlain, "Relation Between Measurements of Deposited Activity After the Windscale Accident of October, 1957," AERE-HP/R-2606, September, 1958.

TABLE XII
ANALYSIS OF WINDSCALE FISSION PRODUCT RELEASE

Nuclide Observed	Activity Ratio From Fallout Filter Samples ¹	Approx. Ratio in Fuel on Oct. 11. Assume 360 d. Irrad. ² (I ¹³¹ = 1.0)	Calculated Percent of Total Released Based on 70% ⁴ For I ¹³¹	Predicted Percent of Total Released Assuming Average Temp. of 1200°C. ⁵
I ¹³¹	100	1.0	70	~ 70
Te ¹³²	58	0.75 ³	55	~ 70
Cs ¹³⁷	2.6	0.08	15	~ 18
Sr ⁸⁹	1.0	1.6	1.1	~ 2
Ru ¹⁰³	2.0	1.0	1.4	~ 1.7
Zr ⁹⁵	0.1	2.2	0.3	~ 0.04

1. Data from Booker⁽¹⁷⁾ and Chamberlain⁽¹⁸⁾

2. Fission yield x % saturation.

3. Ratio includes decay from October 7.

4. Based on ~ 75% Oxidation.

5. Maximum reported was 1300°C.

9.0 RATE OF OXIDATION AND COMPOSITION OF OXIDES FORMED IN CO_2 AT HIGH TEMPERATURES.

The oxidation of uranium in CO_2 has been studied by several British investigators,^{19, 20, 21, 22} undoubtedly because of the extensive use of CO_2 as the coolant in natural uranium gas-cooled reactors. The earlier studies were made in the temperature range 175 to 700°C, while the most recent study²² covered the range 500 to 1000°C and included a determination of the effect of water vapor on the reaction rate. The present study extended the temperature range of the U- CO_2 reaction to 1400°C and provided data on the oxidation of uranium in CO_2 diluted with helium in the temperature range 700 to 1400°C. In addition, irradiated samples have been oxidized in CO_2 and CO_2 -helium mixtures to determine the effect of irradiation on reaction rate.

Data from a preliminary study of the reaction of CO_2 with a uranium cylinder 1/4" O.D. x 11/16" long, weighing 10.612 grams initially, are shown graphically in Fig. 21 where the gain in weight in grams per gram of uranium at 600, 700 and 800°C is plotted against time in minutes. The graph shows that the rate of weight increase in CO_2 at 600°C and 700°C was approximately the same as in the impure helium at these temperatures. However, there was a rapid increase in oxidation rate soon after the partially oxidized sample was exposed to CO_2 at 800°C. This appears to confirm the observation reported by Antill et al.²² that there was a large increase in oxidation rate when the sample surface temperature reached 775-781°C, which is quite close to reported values for the temperature of the β - γ uranium transition, 772 to

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19. R. A. U. Huddle, TRDC P.36, May 7, 1954.
 20. D. R. Silvester, AERE-M/R-2437.
 21. J. E. Antill, et al., AERE-M/M-168, 1957.
 22. J. E. Antill, et al., AERE-M/R-2524, March 1958.

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Figure 21
OXIDATION OF URANIUM IN CO₂
AT DIFFERENT TEMPERATURES

to 774°C.²³ The practical importance of these data is that a layer of UO_2 which is formed on the surface of uranium by low temperature reaction with CO_2 will not appreciably retard the oxidation of uranium in CO_2 if the temperature rises to approximately 775°C. The temperature of the uranium undoubtedly went much higher than the gas temperature as a consequence of the rapid oxidation rate. It did not appear experimentally feasible to simultaneously record both the temperature and weight of the specimen in our experiments or to control the temperature of the uranium. The previous investigators explained the large increase in reaction rate at the transition temperature on the basis that a certain amount of atomic matching exists between β uranium and the oxide film and that this is destroyed by the transition, resulting in a less adherent film. The present investigation does not throw additional light on the mechanism of this effect, but it does seem reasonable to assume that a volume change in the uranium accompanying the phase transition could cause breaks in the oxide film, exposing additional uranium surfaces to the oxidizing gas. Walker reported²⁴ the observation of cracks in the surface of γ -annealed uranium and increased escape of gas attributed to these cracks. This may help to explain the greater reactivity at 775°C. The oxide formed at this temperature by oxidation of uranium in CO_2 was observed to be granular material having a low bulk density.

Data on the oxidation of uranium cylinders, of approximately the same dimensions given above, in helium- CO_2 mixtures are shown graphically in Figure 22. These data and the corresponding rate curves shown in Figure 23 and Figure 24 provide

23. W. A. Maxwell, "Metals for Nuclear Reactors," Technical Editor, American Society for Metals, Cleveland, Ohio, 1959.

24. J. F. Walker, IGR-TN/W-1046, 1959.

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Figure 22
OXIDATION OF URANIUM IN CO₂ DILUTED
WITH HELIUM

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Figure 23
OXIDATION OF URANIUM IN HELIUM-CO₂ MIXTURES
AS A FUNCTION OF TIME AND TEMPERATURE

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Figure 24
RATES OF OXIDATION OF URANIUM IN CO₂
MIXED WITH HELIUM AS A FUNCTION
OF TIME AND TEMPERATURE

further confirmation of the importance of the β - γ transition temperature in the oxidation of uranium with CO_2 . It seems probable that the sudden increase in the oxidation rate observed in the experiment carried out with a gas temperature of 750°C , after 20 minutes of exposure to CO_2 , resulted from heating of the uranium by the heat of oxidation to a temperature of 772°C or higher. However, Figure 24 shows that in all experiments in the range 750 to 1000°C , the oxidation rate showed an initial decrease and then increased to a maximum rate. This behavior can be explained by assuming that after the oxide layer reaches a certain thickness it sloughs off leaving the uranium with an increased surface area. This would result in an increased reaction rate and consequently an increased heat release rate which would raise the temperature of the uranium and produce a further increase in reaction rate. The 60 and 100 minute oxidation rates (Figure 23) reached a maximum at 775° and then showed a decrease with increasing temperature from 800 to 1000°C , in agreement with the findings of Antill²², but the data in Fig. 22 show that at 1200 and 1400°C the reaction rate was higher than at 1000°C , possibly due either to a change in the nature of the oxide layer formed or to the increased rate of diffusion of CO_2 through the protective oxide coating at the higher temperatures. The oxide formed at 1000°C and higher temperatures was observed to be more dense and adherent than that formed at 800°C . The data in Figures 22, 23, and 24 serve to emphasize the fact that different factors were operating to influence the rate of oxidation of uranium in this temperature range. It is also clear from Fig. 7, that an Arrhenius type of plot does not give a meaningful value for the heat of oxidation of uranium in CO_2 in these experiments.

A comparison of oxidation rates obtained with normal and irradiated (0.2 % burn-up) uranium at 1000° and 1200°C with a CO_2 flow rate of 600 cc/minute is shown in Figures 9 and 10. A similar comparison in CO_2 diluted with helium at 800°C is

shown in Figure 8. It is apparent that changes of an undefined nature in the irradiated uranium make it more susceptible to oxidation than unirradiated uranium. A possible explanation of the increased oxidation rate at temperatures below the melting point of uranium is provided in this statement in Maxwell's "Metals for Nuclear Reactors"²³ ".....experiments show that high irradiation embrittles uranium and leads to spontaneous splitting and fracturing. This might readily be due to a network of microscopic cracks, formed during irradiation, which propagate along certain crystallographic planes during phase transformations." However, the comparison between irradiated and unirradiated uranium in CO₂ at 1200°C shows that this statement does not provide an adequate explanation of the observed facts since it seems unlikely that such effects would persist in melted uranium. This behavior could be due to imperfections in the oxide produced by oxidation of irradiated uranium resulting from the presence of fission product atoms. Such imperfections could lead to cracking and diminished protectivity of the oxide layer over the uranium. The data in Figures 8, 9 and 10 clearly show that oxidation rates obtained with unirradiated uranium cannot be applied directly to predictions of the behavior of highly irradiated uranium present in operating reactors. More data to provide a correlation between burn-up and oxidation rates appear to be highly desirable.

Data on the oxidation of uranium in undiluted 98-99% CO₂ at different temperatures and flow rates are shown graphically in Figure 25. It is not clear why the increased flow rate at 1400°C produced a decreased oxidation rate while at 1200°C the higher flow rate did result in an increased oxidation rate, as expected. It seems probable that the oxidation rates observed in the temperature range 800 to 1400°C were determined by the rate of diffusion of CO₂ through the oxide layer, and that this rate varied not only with the temperature but also with

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Figure 25
OXIDATION OF URANIUM IN CO_2

the density of the oxide. It is possible that the oxide coating formed at a higher flow rate at 1400°C was slightly more dense than that formed at the lower flow rate. Both of the 1400°C oxidation curves showed a sharp decrease in oxidation rate as the weight increase in grams per gram of uranium approached the value for UO_2 (0.1345), indicating that UO_2 was the reaction product. However, there was a further slow increase in weight which can presumably be attributed to conversion of UO_2 to a higher oxide by the 1% oxygen present in the impure, commercial grade CO_2 used in these experiments. Some U_3O_8 plus $\text{UO}_{2.17}$ was reported present in the product formed at 1400°C. X-ray diffraction examination¹⁰ of the product formed at 1200°C showed it to be $\text{UO}_{2.15}$.

The behavior of the sample exposed to CO_2 at 800°C is more difficult to understand. Instead of levelling off at a weight gain corresponding to UO_2 , the weight increase reached a maximum at 0.147 grams per gram of U, equivalent to an oxygen to uranium molar ratio of 2.19, and then decreased slowly. In a similar experiment the maximum in the weight increase curve was equivalent to a 2.25 molar ratio, corresponding to the reported²⁵ oxide U_4O_9 while others showed a maximum molar ratio of 2.32, near the reported²⁶ upper limit of the UO_2 - UO_{2+x} solid solution range. Although no completely adequate explanation of the observed facts can be given at present, it appears that an oxide of higher oxygen content than UO_2 can be formed by the rapid oxidation of uranium by CO_2 but that this oxide is not stable at 800°C and reverts slowly to UO_2 . The reversion appeared to be more rapid in CO_2 than in helium but insufficient data were obtained to be conclusive on this point. An apparently analogous oxidation curve was reported for

25. M. Hering and P. Perio, Bull. Soc. Chim. de France, 1952, Fasc. 3-4, p. 351.

26. F. Gronvold and H. Haraldsen, Nature 162, 69 (1948).

the oxidation of MnO to Mn_3O_4 by Muan and Hahn.²⁷ One of the conditions that they postulate as necessary for this type of behavior, i.e., compositional variations in one of the structures involved in the equilibrium, is supplied in our case by $UO_2 - UO_{2+x}$ solid solutions. However, in our experiments the temperature of the uranium varied during the course of the oxidation due to the heat of reaction while the MnO oxidation study was carried out at constant temperature. The formation of metastable phases in heterogeneous reactions is said²⁷ not to be unusual.

9.1 RELEASE OF FISSION PRODUCTS FROM URANIUM OXIDIZED IN CO_2

No trace level fission product release experiments were conducted in an atmosphere of carbon dioxide. Oxidation of irradiated uranium (0.2 % burn-up) in CO_2 at 800, 1000, and 1200°C in the thermobalance apparatus (Figure 2) gave release data contained in Table XIII. The data showed a decidedly lower release of cesium and ruthenium than was observed in air at these temperatures. Cesium released in CO_2 at 1200°C was lower than that in air by a factor of about 10 while ruthenium release was lower by a factor of approximately 50. This fortunate reduction did not hold for iodine or tellurium as these were released to about the same extent that they were in air. Dilution of the CO_2 with 3 parts of helium by volume resulted in iodine and tellurium release values only slightly lower than those obtained in undiluted CO_2 .

In considering the results in Table XIII it should be kept in mind that the commercial grade CO_2 gas used in these experiments probably contained 1 to 2% of O_2 which may have been sufficient to affect the extent of release of the more readily oxidized elements such as iodine and tellurium.

27. A. Muan and W. C. Hahn, Jr., J. Phys. Chem. 63, 1826 (1959).

TABLE XIII

DISTRIBUTION OF ACTIVITY RELEASED BY OXIDATION OF IRRADIATED URANIUM *

IN CO₂ ** OR CO₂-HELIUM MIXTURE

Sample No.	Atmosphere	Location of Activity	Temp. °C.	% Uranium Oxidized	Percent of Total Activity Released								Rare Gases
					Gross γ	I	Cs	Ce	Te	Ru	Zr	Sr	
67	CO ₂ -Helium	Furnace	800	100	0.27	1.62	0.015	0.0005	1.39	0.039	0.044	-	Not Det.
		Filters	"		0.03	0.46	-	-	0.07	0.000	-	-	
		Hot Charcoal	"		0.42	3.76	0.002	0.0003	0.39	0.002	-	-	
		Total	"		0.72	5.84	0.02	0.001	1.85	0.04	0.044	-	
82	CO ₂	Furnace	1000	100	0.042	3.7	0.0023	0.0003	24.3	0.074	0.002	0.001	75.3
		Filters	"		0.022	4.8	0.0001	-	14.3	0.002	-	-	
		Hot Charcoal	"		0.660	76.3	-	-	-	-	-	-	
		Total	"		0.72	84.8	0.0024	0.0003	38.6	0.076	0.002	0.001	
62	CO ₂ -Helium	Furnace	1200	90	0.540	2.24	0.925	0.0003	85.2	-	0.59	0.012	Not Det.
		Filters	"		0.006	1.14	0.003	-	10.0	-	-	-	
		Hot Charcoal	"		0.093	65.0	0.0004	-	-	-	-	-	
		Total	"		0.64	68.4	0.93	0.0003	95.2	-	0.59	0.012	
31	CO ₂	Furnace	1200	100	6.23	51.4	1.7	0.002	65.0	1.4	0.09	0.01	Not Det.
		Filters	"		0.095	0.64	0.002	-	44	0.05	-	-	
		Hot Charcoal	"		1.25	0.64	-	-	-	0.5	-	-	
		Total	"		7.58	52.7	1.7	0.002	69.4	1.95	0.09	0.01	
84	CO ₂ ***	Furnace	1200	100	3.96	7.7	1.7	0.0032	45.4	27.5	0.015	0.20	99.2
		Filter	"		10.00	2.9	0.09	0.0007	50.6	65.8	0.005	0.09	
		Hot Charcoal	"		0.59	74.0	-	-	-	-	-	-	
		Total	"		14.6	84.6	1.8	0.004	96.0	93.3****	0.020	0.29	

* 0.2% Burn Up

** 600 cc/m in CO₂ Flow rate; 150 cc/min CO₂ - 450 cc/min helium flow rates.*** Approximately 10% of the Uranium was oxidized by accidental admission of air at the beginning of this run. After the completion of the CO₂ oxidation, high velocity helium (125 ft/min) was passed through the apparatus for 30 minutes.

**** Average of two analyses. High results possibly due to unusual conditions mentioned in the text.

In one experiment, No. 84 in Table XIII, ruthenium was almost fully released under unusual conditions. The sample was partially oxidized in air at the beginning of the experiment and after completion of the oxidation in CO_2 , a high velocity stream of helium was passed through the apparatus for 30 minutes. This combination of conditions produced high release values of several nuclides and an especially high ruthenium release as compared to the normal CO_2 oxidation (Run No. 31) at 1200°C . All of the filters used in experiment No. 84 including, in order, a 3.0 micron Millipore, a 0.4 micron Millipore, a Whatman filter, a 0.4 micron Millipore and another Whatman filter, contained ruthenium indicating extremely small particles of ruthenium. This fact, in addition to its observed solubility, suggests that ruthenium probably volatilized as RuO_4 . The filters are shown in Fig. 26.

10.0 RATE OF OXIDATION AND COMPOSITION OF OXIDES FORMED IN STEAM AT HIGH TEMPERATURES.

Several investigators have studied the oxidation of uranium in steam because of interest in water cooled reactors fueled with uranium^{28, 29, 30, 31}. The earlier studies were performed at temperatures below 600°C , but a more recent study reported by Hopkinson³¹ covered the temperature range 160 to 1400°C . He found maxima in the attack of uranium by steam at about 300°C and 750°C , which he did not attempt to

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28. T. Wathen, BR-233, "Corrosion of Uranium Metal in Air and Steam at Various Temperatures," May 1943.
 29. J. J. Katz, and E. Rabinowitch, "Chemistry of Uranium," NNES, Vol. VIII, p. 167, McGraw-Hill, 1951.
 30. R. A. U. Huddle, AERE-M/R-1281. "The Uranium-Steam Reaction," 1953.
 31. B. E. Hopkinson, AERE-M/R-1281A. "The Kinetics of the Uranium-Steam Reaction," January, 1957.

Figure 26
SERIES OF FILTER PAPERS FROM RUN 84 OXIDATION OF IRRADIATED
URANIUM IN CO₂ AT 1200° C

explain. The 300°C maximum is probably due to hydride produced by H₂ released by the U-H₂O reaction. The finely divided UH₃ will react with steam at this temperature releasing 3.5 moles of H₂ per mole of UO₂ formed for further reaction with uranium. The maximum at 750° C is undoubtedly connected with the β-γ uranium transition, and is discussed elsewhere in this report. (See section on oxidation of uranium in CO₂). Hopkinson also observed that above about 880° C a protective scale was formed on the uranium due to coalescence of the oxides so that the rates of oxidation observed above 880° C were smaller than those found between 200° C and 880° C.

The purpose of the present investigation was to study the oxidation of unirradiated and irradiated uranium specimens in steam under the same conditions used for the oxidation of uranium in CO₂ and air so that a direct comparison of oxidation rates in the different atmospheres and at different temperatures could be made. This study was limited to the temperature range 800 to 1400° C and was designed to provide data which may aid in estimating the consequences of a loss-of-coolant reactor accident rather than as a systematic study of the kinetics of the uranium-steam reaction. Fission product release resulting from the partial oxidation of irradiated uranium (0.2 % burn-up) in steam was determined at 800, 1000, and 1200° C. The experimental arrangement used to obtain oxidation data and fission product release data with irradiated uranium is shown in Figure 2. Helium was used to sweep air from the furnace prior to introduction of the uranium specimen into the high temperature region of the furnace tube and to carry water vapor from the controlled temperature water flask into the furnace. The steam flow rate was controlled by regulating the voltage applied to a heating mantle around the water flask and the fraction of the total helium flow passing through the water flask. Preliminary experiments were performed to determine the conditions

needed to give steam flow rates of 150 and 300 cc. per minute (calculated vapor volume at 25° C.), with equal total helium flow rates (measured at 25°C.). The fission product collection train was the same as that used for collecting fission products released by oxidation of uranium in air except for the condenser, bulb and cold traps needed to collect water after the vapor had passed through the furnace.

The effect of steam flow rate on the rate of oxidation of uranium at different temperatures is shown in Figures 27 and 28. It may seem surprising that the lower flow rates gave higher oxidation rates in this temperature range. This effect was undoubtedly due to the fact that the oxidation rate was controlled by the density of UO_2 rather than by the rate that the oxidizing agent was supplied. The sintering of UO_2 reported by Hopkinson³¹, Huddle³⁰ and others to be promoted by steam, apparently occurs at a rate proportional to the steam flow rate. Under the conditions prevailing in these experiments, sintering occurred at a lower temperature, at least as low as 800° C., than in Hopkinson's experiments (880° C). He used much larger steam flow rates than the maximum rate employed in the present investigation and also larger uranium specimens. The oxidation product at both 1000° C and 1400° C was identified by its x-ray diffraction pattern¹⁰ as essentially pure UO_2 ($UO_{2.005}$ at 1000° and $UO_{2.02}$ at 1400°), in agreement with Hopkinson's observations.

Inspection of the weight increase curves plotted in Fig. 27 and 28 show that in all experiments the initial rate was the maximum rate observed and that the rate became essentially constant for some time and then gradually decreased if oxidation proceeded for a long time. The high initial rate is, of course, due to the reaction of unprotected uranium with steam and the calculated rate of change was strongly dependent upon the time interval chosen for observation

Figure 27
EFFECT OF STEAM FLOW RATE ON OXIDATION
OF UNIRRADIATED URANIUM AT 1400°C

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Figure 28

EFFECT OF VARYING TEMPERATURE AND
STEAM FLOW RATE ON OXIDATION OF URANIUM
IN STEAM DILUTED WITH HELIUM

during the first few minutes. It was probably limited somewhat by the rate of response of the weight measuring system.

The linear part of the rate curve was explained by Hopkinson³¹ as follows: when the oxide reaches a certain thickness the stresses connected with film growth causes cracking but the oxide immediately adjacent to the metal remains intact. The oxidation rate, being controlled by diffusion through a layer of constant thickness, thus remains constant. Hopkinson offered no explanation for the decreasing rate that followed the linear portion of the rate curve that can be noted in some of his oxidation curves at higher temperatures. This effect may be due to the increasing thickness of loose oxide over the surface of the unoxidized uranium which could presumably sinter and provide an increased diffusion path length for steam.

Comparison of oxidation rates of irradiated and unirradiated uranium at 1000°C (Fig. 9) and at 1200° C (Fig. 10) show that the irradiated uranium burned more rapidly than unirradiated uranium at both temperatures in steam as in CO₂ and air. The comparison at 800° C (Fig. 8) was invalidated by a difference in steam flow rate. As noted previously, increasing the steam flow rate decreases the oxidation rate so it is not surprising that the irradiated uranium exposed to 440 cc. per minute steam flow rate as compared to 300 cc. per minute for the unirradiated uranium, showed the lower oxidation rate.

It may be noted that none of the specimens exposed to steam-helium mixtures at temperatures ranging from 800 to 1400° C burned completely although extrapolation of the data obtained at 1400° C indicates that complete oxidation probably would have been accomplished in 3 to 4 hours as compared to about 90 minutes in air at this temperature.

Data showing the effect of varying surface area to weight ratio on the rate of oxidation of uranium in a steam-air mixture are shown in Fig. 29. Since this ratio provides a direct measure of available surface area, the rate of oxidation of uranium would be expected to increase with increasing area to weight ratio as the data in Fig. 29 show. Since these data were obtained with the uranium contained in a boat in a horizontal furnace where the uranium specimen was more directly exposed to the flowing gas stream than in the thermobalance experiments discussed previously in this section, the data in Fig. 29 cannot be compared directly with the thermobalance steam-helium data. However, comparison between steam-air oxidation data and air oxidation data obtained under the same conditions, Figures 11 and 12, shows that there was a marked reduction in rate of oxidation when steam was the predominant gas to which the uranium was exposed as compared to exposure to air alone at the same temperature.

The steam oxidation data and the fission product release data in steam reported here, when compared with similar data obtained in air and CO_2 , show that the choice of water as the extinguishing agent in the Windscale incident, following the unsuccessful use of CO_2 , was extremely fortunate.

10.1 RELEASE OF FISSION PRODUCTS FROM URANIUM OXIDIZED IN STEAM

In the preceeding section of this report, it was pointed out that hydrogen was released when uranium reacted with steam at elevated temperatures. The hydrogen released at the surface of the metallic uranium diffused outward through the oxide coating around the uranium and probably helped to keep the oxide composition near the stoichiometric UO_2 ratio. High density UO_2 is generally produced by sintering the oxide in a hydrogen atmosphere at a temperature of approximately 1750°C but it appeared that in the presence of steam UO_2 sintered to form a dense, adherent oxide coating on uranium at temperatures as low as 800°C . This protective coating,

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Figure 29
OXIDATION OF URANIUM
IN A STEAM-AIR MIXTURE
FOR DIFFERENT AREA/WEIGHT RATIOS

not only reduced the extent of oxidation of the uranium due to the slow diffusion of water vapor through the uranium but also produced a barrier through which the fission products had to diffuse in order to reach the gas stream. It is not surprising, therefore, to find that release values obtained when uranium was partially oxidized in a steam atmosphere were much lower than the values observed when uranium was oxidized in air or CO_2 at the same temperature. Release data obtained at 800, 1000 and 1200°C, Table XIV, show that at 800°C iodine and the rare gases were the only released fission products found, while at higher temperatures tellurium was also released. The very high tellurium release noted at 1200°C, when compared to the iodine release at this temperature, suggests the possibility of the formation of a highly volatile form of tellurium under these conditions, such as H_2Te , but no corroborating evidence for the formation of such a compound was noted in these experiments. The very low release values for cesium, ruthenium and the rare gases in a steam atmosphere are especially noteworthy. The fact that low release values were found at 1200°C, except for tellurium, indicates that the protective oxide coating formed even over the surface of liquid uranium.

11.0 COMPARISON OF FISSION PRODUCT RELEASE FROM IRRADIATED URANIUM HEATED IN VARIOUS ATMOSPHERES.

A systematic comparison of the total fractional releases under various atmospheres is not possible with the limited data accumulated; however, some comparisons are presented which are of interest such as those in Table XV, summarizing results obtained under different conditions at 1200°C.

There seem to be no wide variations among various atmospheres in the release of iodine except for the low value in a steam atmosphere and in the release of tellurium except for the low value in a helium atmosphere. Ruthenium release was low in all cases except in air following or coincident with 100 percent

TABLE XIV

DISTRIBUTION OF ACTIVITY RELEASED BY OXIDATION OF IRRADIATED URANIUM*

IN STEAM DILUTED WITH HELIUM**

Sample No.	Location of Activity	Temp. °C.	% Uranium Oxidized	Percent of Total Activity Released							
				Gross γ	I	Cs	Ce	Te	Ru	Zr	Sr
70	Condensate	800	36	-	0.159	-	-	-	-	-	-
	Filters			-	0.045	-	-	-	-	-	-
	Hot Charcoal			-	0.134	-	-	-	-	-	-
	Total			0.002	0.34	-	-	-	-	-	-
80	Furnace	1000	34	0.111	3.54	0.036	0.007	2.0	0.022	0.04	0.02
	Condensate			0.024	1.52	-	-	-	-	-	-
	Filters			0.0001	0.01	-	-	-	-	-	-
	Hot Charcoal			0.001	0.11	-	-	-	-	-	-
	Total			0.14	5.2	0.036	0.007	2.0	0.022	0.04	0.02
61	Furnace	1200	65	0.140	1.48	0.152	0.00044	33.8	0.004	0.17	0.018
	Condensate			0.026	9.75	0.004	0.00007	4.5	-	-	0.0005
	Filters			0.030	2.25	0.048	0.00009	41.1	0.005	-	0.0002
	Hot Charcoal			0.002	1.82	0.015	-	-	-	-	-
	Total			0.20	15.3	0.22	0.0006	79.4	0.009	0.17	0.019

* 0.2% burn-up.

** Steam flow rate approx. 300 cc/min. and helium flow rate 300 cc/min.

TABLE XV

COMPARISON OF FISSION PRODUCT RELEASE FROM IRRADIATED
URANIUM* HEATED IN VARIOUS ATMOSPHERES AT 1200° C.

Atmosphere	Run No.	Time Heated (Min.)	Percent U Oxidized	PERCENT OF TOTAL ACTIVITY RELEASED						
				Xe-Kr	I	Te	Cs	Ru	Sr	Zr
Air	9-9-1	20	65.4	99.4	57.3	71.3	13.0	1.8	0.85	~ 0.05
Air	H-83	250	100	99.2	89.8	95.9	~ 14.0	85.0	-	0.01
CO ₂	H-31	630	100	~ 99	52.7	69.4	1.7**	1.95	0.01**	0.1
CO ₂ - Helium	H-62	410	90	-	68.4	95.2	0.93**	-	0.01**	0.6
Steam-Helium	H-61	123	65	-	15.3	79.4	0.2**	0.01	0.02**	0.2
Helium	8-12-1	148	4.1	97.7	47.0	0.6	2.0	-	0.9	-
Air***	4-6-2	50	91.7	80.6	92.4	66.3	~ 1.0	0.6	0.01	0.007

* 0.2 at. % burn-up.

** Release values probably low due to chemisorption in Mullite-porcelain furnace tube or Al₂O₃ crucible.

*** Trace-level irradiation.

uranium oxidation. Strontium release was quite low or negligible except in air and in helium.

Cesium release was highest in air with the attendant self heating by oxidation of uranium although it was released to an appreciable extent in all atmospheres at 1200°C. At trace level in air, cesium, ruthenium and strontium all showed appreciably lower releases than those found at the higher burn-up level.

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