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PARTICULATES GENERATED DURING THE AIR OXIDATION OF URANIUM

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PARTICULATES GENERATED DURING THE AIR OXIDATION OF URANIUMINTRODUCTION

The release and entrainment of radioactive species from overheated fuel elements constitutes one of the potential hazards in the production and use of nuclear fuels. The resulting hazard from such an incident may vary drastically, depending on a number of variables such as fuel element composition, cladding, irradiation level, temperature, time at temperature, air velocities, containment facilities and atmospheric conditions. The effects of temperature, fuel element composition and irradiation level have been investigated⁽¹⁻⁷⁾ with respect to the percent of radioisotopes released. However, in addition to the information of this type, a knowledge of the physical and chemical nature of the released material could add significance to predictions of the hazards ensuing from nuclear incidents of this type.

One of the important physical properties in size distribution of particles generated from overheated fuel elements. Particles with which fission products may be associated will be carried in the gas stream and travel through reactor channels or be retained at the fuel element site, depending to a degree on particle size. Surface contact interactions, agglomeration, adsorption and release of fission gases will also be influenced by particle size. Knowledge of particle sizes and an understanding of particle interactions will permit more realistic estimates of the consequences of a fuel element incident.

Limited data exist on the physical nature of oxides formed from uranium oxidizing in air. Adley et al.⁽⁸⁾ generated an aerosol of U_3O_8 particles for

testing filter efficiencies. In their study they heated uranium metal turnings by electrical resistance and obtained a uranium oxide fume of submicron particles. A median particle size of 0.07μ in diameter was obtained on a count basis, whereas the mass median diameter was 0.5μ . This same group⁽⁹⁾ analyzed building air in work areas where uranium oxide and uranium were being processed and determined mass median diameters from 0.9 to 3.0 for various operations. The most abundant size particle observed in this case was approximately 0.018μ in diameter, although greater than 99 percent of the particle mass was believed associated with particles greater than 0.75μ . Hellyer⁽¹⁰⁾ on oxidizing a 1" diameter uranium rod at 250 C and an air velocity of 4000 cm/sec, concluded that 99 percent of the oxide particle mass would be in the greater than 10μ diameter size range. Megaw et al.⁽¹¹⁾ determined particle size distributions for uranium oxides produced in air and carbon dioxide from 400 to 1000 C. Mass median diameters from 10 to 500μ were obtained on air oxidation of large (1 kilogram) specimens in a vertical tube at velocities from 70 to 240 cm/sec. This research by Megaw et al. appears to be the most detailed study of uranium oxide particle entrainment in regard to fission product release to the environs. Parker et al.⁽⁶⁾ have quoted values of 50 to $100 \text{ \AA}$ for the diameter of particles collected on filters during the oxidation of irradiated uranium at 1200 C and above. Optical microscopic analyses in this case showed agglomerates of these submicron species into particles 0.3 to 1.0μ in size. Parker et al.⁽⁷⁾ also determined the size distribution of sublimed species formed during the high temperature melting of UO_2 in air, carbon dioxide and helium. Number median diameters of 0.1, 0.04 and 0.015μ were observed during heating in air, carbon dioxide and helium, respectively. These experiments were performed at low air

velocities (0.15 to 2.5 cm/sec) and aerodynamic entrainment of particles larger than a few microns in diameter was not likely.

The present study was initiated to determine the physical nature of oxide particles formed on oxidizing uranium specimens of the type used in fission product release tests^(1,2) at this laboratory. A few additional experiments were performed with irradiated specimens in an attempt to determine the amounts of certain radionuclides found associated with various particulate size fractions.

OBJECTIVE

The objective of this research was to provide information on the nature of oxide particles formed from unclad uranium oxidizing in air, as affected by temperature and air velocity. Many of the experiments employed a low air velocity (8.3 cm/sec) to allow possible correlation with fission product release experiments^(1,2) performed at this velocity.

SUMMARY

The following observations and data were obtained from sedimentation and microscopic analyses of particles formed on air oxidation of 0.69 X 1.9 cm long uranium cylinders at furnace temperatures of 400, 600, 800, 1000 and 1200 C.

1. The physical nature of the uranium oxide formed changes from fine, black, platelet-like particles (400-600 C) to coarse, coke-like granules (600-800 C), and finally to a dense, columnar, needle-like structure remaining largely intact at 1000-1200 C. There is a general increase in oxide particle size with increasing temperature.
2. Less than four percent of the oxide formed at 400-1200 C was in the less than 10 μ particle size range in any of the cases investigated. Mass

- median diameters of approximately 100 and 160 μ were determined for oxide residues at 400 and 600 C. At 800 C and above, 75 percent or more of the mass was associated with particles greater than 250 μ in diameter.
3. At air velocities of 8.3 cm/sec and lower, the quantity of particulate oxide reaching a point 20" downstream was greatest at 1200 C. The entrained oxide in this case consisted primarily of agglomerates of individual particles from 0.015 to 0.5 μ in diameter, believed to arise from sublimation of UO₃. As air velocities are increased, aerodynamic entrainment of somewhat larger particles over-shadows release by direct volatilization.
  4. At temperatures of 400, 600 and 800 C, the average diameter of oxide particles reaching a point 20" downstream was on the order of 2 to 5 μ at an air velocity of 8.3 cm/sec.
  5. Specimens oxidizing at 1000 to 1200 C give rise to few micron size oxide particulates during heating. On rapid cooling stresses within the system, result in projection of micro and macroscopic particulates at high velocities.

EXPERIMENTAL METHODS

Uranium Specimens

The specimens used were beta-heat-treated cylinders 0.64 X 1.9 cm long, weighing approximately 11.5 grams. Prior to oxidation, the specimens were polished with 4/0 emery paper.

Apparatus

Oxidations were performed in a 1-1/16" Mullite combustion tube passing in a large resistance heated furnace. The furnace was track-mounted and

could be rolled over the tube section containing the specimen for rapid heating and cooling. Specimens were placed in a short section of quartz tubing and positioned at a fixed distance from the downstream collection filter. Specimens were brought up to temperature in He, held at the fixed temperature in air for the specified time and quenched in air or He. Temperatures were recorded with a Pt vs Pt - 13 percent Rh thermocouple located 12mm from the upstream edge of the test specimen in a quartz thermowell and therefore represent furnace rather than specimen temperatures.

Particle Collection and Sedimentation

Oxide particulates were collected on membrane or glass filters located 51, 102, or 204 cm (20, 40, 80") downstream from the oxidizing specimen. Membrane filters were used for ease in optical microscopic counting of the deposited particles. Glass filters were used at increased air velocities where the gas stream temperature was sufficient to decompose the membrane filters.

Samples for electron microscope examination were collected by electrostatic precipitation. Prepared grids were mounted directly on the collector which consisted of a thin tantalum or stainless steel tube.

Sedimentation experiments using oxide residues were carried out in a 106 cm sedimentation column consisting of a 5 cm inner column surrounded by a 10 cm outer water column. Oxide was introduced into the inner column and collected in a balance pan suspended below the exit end. The balance pan was supported on a cantilever whose deflection was sensed by a linear motion transducer. This balance had a sensitivity of 1 mg. The less than 60 mesh fraction of the bulk oxide was used in the sedimentation experiments to permit greater sensitivity in weight determinations.

Association of Radionuclides With Specific Particle Size Fractions

Oxidation of irradiated uranium specimens was performed in a horizontal quartz furnace heated by an induction coil. The system was composed of the quartz furnace surrounded by a graphite susceptor and a ceramic reflector all encompassed by the induction coil. Temperature recordings were from a thermocouple in a quartz thermowell 12mm upstream from the specimen. The particle collection system was a 5-stage inertial impactor, the fifth stage being an MSA type glass filter. A controlled air leak arrangement upstream from the impactor served to maintain a chosen air flow through the furnace and impactor. All experiments were performed at an air velocity of 8.3 cm/sec past the specimen with an impactor flow rate of 16 liters per minute. Particles were collected on xylene-rosin coated microscope slides in the first four stages.

RESULTS AND DISCUSSION

Physical Nature of Oxide Residues

The trend of increased particle size with increased temperature was evident in all experiments. The change from a finely divided, porous, platelet-type structure (400, 600 C) to coarse, coke-like granules at 800 C and to a dense, adherent, laminar needle structure (1000-1200 C) is depicted in Figures 1 and 2. During the early stages of oxidation at 400-800 C, the oxide builds up on the specimen surface, then gradually begins to sluff off on extended oxidation. At 1200 and 1000 C, the oxide remains largely intact throughout the course of oxidation and fractures primarily on rapid quenching. Rapid air cooling of incompletely oxidized specimens at 1200 and 1000 C results in the breakdown of the normally intact oxide, as shown in Figure 1.

This is possibly due to both thermal stresses and the formation of oxides of lesser density between the unoxidized metal and the dense, adherent oxide film.

Physical Nature of Entrained Oxide Particulates

Figure 3 illustrates the type of submicron particles obtained from a specimen oxidizing at 1200 C and an air velocity of 8.3 cm/sec. The individual submicron particles vary in size from approximately 0.015 to 0.2 μ in diameter. Chain-like agglomerates of these smaller particles were seldom greater than 0.5 μ in length during short sampling periods. Figure 3 shows particles collected during a three-minute sampling period. The reason for the difference in appearance of particulates collected on SiO and carbon-coated grids, as shown in Figure 3, is not known. Since the particles were collected directly on the SiO or carbon-coated grids, the different appearance may be in part due to the differences in electrical conductivity of the two collecting media. At 1200 C, there were usually a few discrete micron-sized particles observed by optical microscopy having average diameters of about 2-5 μ when sampling was continued during cooling. If collection were stopped prior to cooling, essentially no particles greater than 1 micron were observed. This emphasized the fact that the greater than 1 micron diameter particles observed arose on rapid quenching of the specimen. Particles collected at 800 C and below were of the general type pictured in Figure 2. Electron micrographs of entrained particles at 800 C and below showed an absence of the small, spherical, submicron species present at 1000 and 1200 C. Assuming these submicron species arise from the condensation of sublimed UO_3 , one would predict a large decrease in their concentration with decreasing temperature. From the vapor pressure equation for UO_3 over U_3O_8 ⁽¹²⁾

$$-\log P_{(atm)} = - \frac{(1.856 \pm 0.016) 10^4}{T} + 6.928 \pm 0.103$$

* 6 min in air at 1200°C   24 min in air 1200°C   24 min in air at 1200°C
Cooled in He   Cooled in He   Cooled in Air

5 hrs in air at 1200°C   60 min in air at 1000°C   60 min in air at 1000°C
Cooled in air   Cooled in He   Cooled in Air

60 min in air at 800°C   60 min in air at 600°C   60 min in air at 400°C
Cooled in He   Cooled in He   Cooled in He

* All specimens brought up to a temperature in a He atmosphere-held in air for the stated times - quenched in He or air.

FIGURE 1

Appearance of the Oxides Formed when 0.64 x 1.9 cm Long Uranium Cylinders are Oxidized in Air

1200°C > 60 Mesh 7X   800°C > 60 Mesh 7X   400°C > 60 Mesh 7X

1200°C < 60 Mesh 11X   800°C < 60 Mesh 11X   400°C < 60 Mesh 11X

1200°C < 60 Mesh 35X   800°C < 60 Mesh 35X   400°C < 60 Mesh 100X

FIGURE 2

Photomicrographs of Sieve Sized Oxides Formed at Various
Temperatures During Uranium Oxidation in Air

Particles Collected on a Silicon Monoxide Coated Grid

Particles Collected on a Carbon-Coated Grid

FIGURE 3

Electron Micrographs of Particles Collected by Electrostatic
Precipitation 20" Downstream from a Specimen Oxidizing at 1200°C

the vapor pressure at 1200, 1000, 800, 600 and 400 C would be 2×10^{-6} , 3×10^{-8} , 4×10^{-11} , 5×10^{-15} and 2×10^{-21} atmospheres, respectively.

As the collision frequency and coagulation rate are functions of the square of concentration, few observable ($> 10^0 \text{ \AA}$) size particles would be expected at temperatures less than 800 C under the conditions of the present experiments.

Particulate Size Distributions (Oxide Residues)

The size distributions of the unentrained oxide particles at various temperatures are shown in Figure 4. These data are from sedimentation of the less than 60 mesh (246 μ) fraction of oxide residues sieved for three minutes. Sieving was performed to increase the sensitivity of the weighing of the mass fractions of the smaller particles. Sieving time was limited to three minutes to reduce attrition.

The size distribution of oxide residues formed at 1000 and 1200 C are not comparable with those at 800 C and below, since at the higher temperature the oxide particles arise during fracturing on cooling. When these specimens are observed in the furnace prior to cooling, the oxide appears to be a single bulk mass. Another effect observed was that the degree of fracturing depended on the degree of oxidation. Even on complete oxidation, up to 98 percent of the oxide mass remained intact on rapid quenching in helium in some cases. Figure 5 illustrates the difference in the particle size distribution of the less than 60 mesh oxide when specimens oxidizing at 1000 and 1200 C were rapidly cooled in air and helium. These plots cannot be extrapolated over the larger particle size region, since up to 98 percent of the mass can be associated with one large piece of oxide having centimeter dimensions. The general effects of temperature, air velocity and coolant atmosphere are presented in Table I.

FIGURE 4

Size Distribution of Oxide Residues when Specimens are Quenched in
an Inert Atmosphere

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FIGURE 5

Effect of Coolant Atmosphere on Oxide Particle Size Distribution for Specimens Heated at 1200 and 1000 C

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TABLE I

EFFECT OF TEMPERATURE AND COOLANT ATMOSPHERE
ON THE SIZE DISTRIBUTION OF OXIDE RESIDUES

<u>Temp.</u> <u>C</u>	<u>Sample</u>	<u>Time</u> <u>(Min)</u>	<u>Air Velocity</u> <u>cm/sec</u>	<u>Cooling</u> <u>Conditions</u>	<u>Weight Percentage of</u> <u>Total Oxide Less</u> <u>Than 60 Mesh (246μ)</u>
1200	A-12-2	24	8.3	He	2.8
	A-12-3	24	66.4	Air	21.7
	A-12-4	24	66.4	Air	21.8
	A-12-5	24	66.4	Air	20.2
	A-12-9	*60	66.4	Air	4.0
	A-12-10	*60	33.2	Air	1.7
	A-12-12	24	8.3	Air	38
1000	A-10-11	60	8.3	Air	4.3
	A-10-3	60	66.4	Air	11.8
	A-10-4	60	66.4	He	8.2
	A-10-5	60	33.2	He	11.0
	A-10-6	60	33.2	Air	7.0
800	R-8-7	60	12.5	Air	40
	A-8-3	60	33.2	He	9.5
	A-8-1	60	66.4	He	7.0
	A-8-2	60	66.4	He	9.0
600	A-6-1	60	66.4	He	51
	R-6-7	60	8.3	Air	70
400	A-4-1	60	66.4	He	86
	A-4-3	60	66.4	Air	86

*Complete Oxidation

The effect of the degree of oxidation on the resultant particle size distribution was not determined but would be expected to have an effect at lower temperatures where thermal cycling occurs. At a furnace temperature of 400 C, for example, specimen temperatures have been observed to increase to 800 C during thermal cycling. As this effect can occur several times prior to complete oxidation, the frequency and maximum temperature rise would alter the ultimate size distribution. The observed thermal cycling is believed due to poor heat transfer through the oxide coating which builds up on the sample. When the temperature increases, this thermal insulating material disrupts and the temperature recedes.

Entrained Particulates

Data on the size distributions of entrained particles reaching a point 51 cm (20") downstream from the oxidizing specimens are presented in Table II. The optical microscope counts are for a linear dimension in one direction, no attempt being made to obtain average particle areas or volumes. The irregularity of particles would suggest that the effective spherical particle settling diameters of these particles would be much less than the measured values. This was evidenced by particles as large as 40 μ in diameter being found 51 cm downstream at air velocities of 8.3 cm/sec. The maximum diameter of a spherical particle of density 7.3 g/cm³ which would reach this point would be about 7 μ in diameter.

Much of the oxide entrained at 1000 and 1200 C arises during rapid cooling of specimens oxidizing at these temperatures. A comparison of the amounts of material entrained during the oxidation and cooling periods is given in Table III.

TABLE II

SIZE DISTRIBUTION OF ENTRAINED OXIDE PARTICLES 51 cm
DOWNSTREAM FROM URANIUM SPECIMENS OXIDIZING IN AIR

Run	Temp.	Air Velocity	Percentage In Given Size Range (microns)			
<u>No.</u>	<u>C</u>	<u>cm/sec</u>	<u>(1-4)</u>	<u>(4-8)</u>	<u>(8-12)</u>	<u>> 12</u>
12-16	1200	8.3	65	15	17	3
A-12-3	1200	66.4	17	30	29	24
10-3	1000	12.5	87	7	5	1
A-10-5	1000	33.2	68	18	8	6
A-10-2	1000	66.4	30	37	27	5
8-1	800	8.3	48	14	22	16
8-3	800	83	28	21	33	17
7-1	700	3.6	48	28	17	7
7-2	700	12.5	27	24	23	26
7-3	700	12.5	61	22	12	6
6-2	600	8.3	79	11	8	2
6-3	600	12.5	52	24	17	8
4-3	400	8.3	70	22	6	2
4-7	400	12.5	65	29	6	1

TABLE III

COMPARISON OF THE AMOUNTS OF URANIUM OXIDE ENTRAINED
DURING OXIDATION AND COOLING

<u>Run No.</u>	<u>Temperature C</u>	<u>Velocity cm/sec</u>	<u>Time At Temperature</u>	<u>Cooling Time</u>	<u>µg U 51 cm Downstream</u>
12-49	1200	8.3	20 min	- - -	72
12-49	1200		- - -	20 min in air	110
A-12-4	1200	66.4	24 min	- - -	1950
A-12-4	1200	66.4	- - -	10 min in air	1800
A-10-2	1000	66.4	60 min	- - -	22
A-10-2	1000	66.4	- - -	10 min in air	527

The cooling rate at 1200 C was 320 C/min the first minute, dropping off to about 10 C/min at 10 minutes. The total temperature drop was from 1200 C to 360 - 380 C in a 10 minute cooling period. The coolant rate at 1000 C was 200 C/min the first minute, dropping off to about 10 C/min at 10 minutes. The temperature in this case dropped from 1000 C to 270 C in the 10 minute period.

Quantity of Uranium Oxide Entrained

The amount of entrained oxides collected on filters downstream from the specimen was determined by fluorometric uranium analyses and are presented in Table IV. The effects of air velocity, temperature and distance from specimen to collection point are evident.

Rate of Oxide Entrainment

The rate of oxide entrainment was investigated at 1200 C at an air velocity of 8.3 cm/sec. This was to further substantiate that entrainment

TABLE IV

AMOUNT OF AIR ENTRAINED OXIDE ON FILTERS

<u>Run No.</u>	<u>Time (min)</u>	<u>Temp. C</u>	<u>Air Velocity cm/sec</u>	<u>Distance of Specimen to Filter (cm)</u>	<u>µg of U on Filter</u>	<u>Percentage of Total Oxide</u>
A-12-1	24	1200	8.3	51	165	0.0018
A-12-2	24	1200	8.3	51	119	0.0013
12-24	24	1200	8.3	51	200	0.0021
12-29	25	1200	8.3	51	160	0.0017
12-53	24	1200	8.3	102	152	0.0016
12-56	60	1200	8.3	204	150	0.0013
12-10	24	1200	33.2	51	1380	0.014
A-12-5	24	1200	66.4	51	2250	0.024
A-12-6	60	1200	66.4	51	2700	0.023
A-10-1	60	1000	8.3	51	11	0.0001
10-18	45	1000	8.3	51	20	0.0002
10-19	45	1000	33.2	51	88	0.0009
10-21	45	1000	33.2	51	44	0.0005
A-10-4	60	1000	66.4	51	1095	0.012
A-10-3	60	1000	66.4	51	1065	0.012
10-22	45	1000	83	204	140	0.0015
8-6	45	800	8.3	51	1.8	0.00002
8-8	60	800	8.3	51	2.7	0.00003
8-7	45	800	12.5	51	3.8	0.00004
8-9	60	800	33.2	51	53	0.0006
A-8-4	60	800	33.2	51	56	0.0006
A-8-1	60	800	66.4	51	1455	0.016
A-8-2	60	800	66.4	51	3240	0.034
6-2	80	600	8.3	51	6.2	0.0001
6-3	80	600	8.3	102	4.3	0.00006
6-4	80	600	8.3	204	6.6	0.0001
A-6-1	60	600	66.4	51	3450	0.049
6-7	80	600	83	204	410	0.006
4-7	60	400	8.3	51	2.1	0.0002
4-1	600	400	8.3	51	25	0.0005
4-3	120	400	8.3	204	1.2	0.0001
A-4-2	120	400	16.6	102	19.5	0.0017
4-2(1)	120	400	16.6	204	3.5	0.0003
A-4-1	420	400	66.4	51	4300	0.068
4-2(2)	120	400	83	204	134	0.012

of oxide at this temperature was from a sublimation process. The rate is fairly uniform with time, and specimen to collector distance has little effect, as shown in Table V.

TABLE V
RATE OF URANIUM OXIDE ENTRAINMENT

Temperature: 1200 C
Air Velocity: 8.3 cm/sec

<u>Sample No.</u>	<u>Time In Air (min)</u>	<u>Distance of Specimen To Filter (cm)</u>	<u>µg of U</u>	<u>Rate of Entrainment µg U/min</u>
A-12-13-1	60	51	180	3.0
A-12-13-2	60	51	210	3.5
A-12-13-3	60	51	240	4.0
12-49-1	5	51	78	15
12-49-2	5	51	59	12
12-49-3	10	51	82	8.2
12-49-4	20	51	72	3.6
12-49-5	40	51	270	6.8
12-49-6	Cooling 20 min	51	110	5.1
12-56-1	4 min in He	204	1.4	0.35
12-56-2	5	204	24	4.8
12-56-3	5	204	26	5.2
12-56-4	10	204	33	3.3
12-56-5	20	204	130	6.5
12-56-6	40	204	180	7.2
12-56-7	20	204	140	7.0
12-56-8	120	204	900	7.5
12-56-9	120	204	830	6.9
12-56-10	87	204	400	4.6
12-56-11	180	204	960	5.3

On the basis of Stokes' Law, few spherical particles of density 7.3 g/cm³ and diameters greater than 1µ could reach a point 204 cm downstream. No micron and larger size particles were observed in samples taken

at this point and examined by optical microscopy. From the equilibrium vapor pressure equation⁽¹²⁾ for UO_3 over U_3O_8 the rate of uranium entrainment would be calculated as 48.4g of U/min if the gas stream were saturated. The observed rate of about 7.4g/min is consistent with these values, considering plate-out of uranium oxide in the tube and incomplete saturation of the air stream. Preferential plate-out of sublimed oxide on the furnace tube occurred at 1000 - 1150 C in the region between 13 and 18 cm downstream from the specimen. A concentration of sublimed oxide corresponding to a rate of entrainment of 3.24g U/min would cause equilibrium saturation at the average temperature of 1075 C. Preferential plate-out in this narrow temperature band is attributed to this saturation effect. At distances further downstream the original molecular species have had time to condense and grow to a size where diffusion is limited. The narrow band of plated oxide when analyzed contained up to twice as much uranium as that deposited on the filters downstream, and was an iridescent yellow-green in color.

Filter Efficiency

The efficiencies of MSA absolute filters and Type AA Millipore filters were tested in a few cases only to assure that no appreciable particle penetration was occurring. The data for penetration at 1200 C presented in Table VI show efficiencies greater than 99.7 percent, based on assumed 100 percent collection efficiencies for the one stage caustic scrubber or electrostatic precipitator backing the filters. The limited data suggest that the electrostatic precipitator is more efficient for removing those particles which penetrate the filter than the wet-scrubber.

TABLE VI
PENETRATION THROUGH FILTERS

<u>Filter</u>	<u>Sample</u>	<u>Velocity cm/sec</u>	<u>µg U on Filter</u>	<u>µg U in Scrubber</u>	<u>Percentage Penetration</u>
MSA	A-12-4	66.4	3750	0.9	0.02
MSA	A-12-3	66.4	697	1.8	0.2
MSA	A-12-5	66.4	2700	0.05	0.002
MSA	A-12-6	66.4	2250	0.18	0.008
MSA	A-12-9	66.4	1650	0.23	0.01
MSA	A-12-10	16.6	1350	0.15	0.01
Millipore	12-54	8.3	170	0.44*	0.25
Millipore	12-57	8.3	1690	2.0*	0.12

*Collected by electrostatic precipitation.

Chemical Composition of Oxides

Only qualitative type X-ray analyses of the oxide samples were performed. In all cases in the 400-1200 C range the oxide appeared to be U_3O_8 with less than one percent of lower oxides. Electron diffraction analyses of the submicron species collected at 1200 C gave little information on the true composition. Difficulty was experienced in getting good diffraction patterns, and it was first thought that the material might be amorphous UO_3 . Further work suggested that the microcrystalline character of the oxide deposit was causing the diffuse lines observed. Megaw⁽¹¹⁾ studied the composition of oxides produced at temperatures up to 1000 C and concluded that between 600 and 800 C the oxide is essentially all U_3O_8 . At 1000 C he reports some evidence for the presence of lower oxides, and analyses of various particle size fractions showed the deficiency in oxygen to occur in the larger size particles. He expressed the possibility that the lower oxide content of the larger particles could be from unoxidized uranium originating during the disrupting of the intact oxide coating

on cooling. It was noticed in the present study that the oxide metal interface of incompletely oxidized specimens had a film of oxide quite different from the bulk oxide. This may be an oxide having an oxygen to uranium ratio of less than 2.67 which could be flaked off during rapid cooling.

Discussion of Uranium Oxide Size Distribution Relating to Fission Product Release

A few experiments were performed to determine the size of particulates with which certain entrained fission products were associated when released from oxidizing uranium specimens. These experiments were at 1200 C and an air velocity of 8.3 cm/sec. The fission products and uranium oxide are found associated with submicron particles at this temperature as anticipated from unirradiated oxidation experiments. Results are presented in Table VII. Further research on particle size-fission product association was discontinued but deserves some comment on the basis of the present knowledge of uranium oxide particulate size distribution.

It would appear that at temperatures of 1000 C and above, fission product release from uranium oxidizing in air is primarily a volatilization process although aerodynamic entrainment of fission product-bearing uranium oxide particles can occur during cooling. At 800 C and below the substantial release of nonvolatile fission products observed by Hilliard⁽¹⁾ compared to their release at 1200 C suggests that sublimation is no longer the main mechanism for release. If sublimation were the main source of released material, one would expect an exponential increase with increasing temperature which was not observed. As air velocities are increased, aerodynamic entrainment of microscopic particles becomes more and more important; thus, an appreciable release of nonvolatile fission products could be expected at low temperatures due to this mechanism.

TABLE VII

FISSION PRODUCT-PARTICLE SIZE DISTRIBUTION 51 cm
DOWNSTREAM FROM AN URANIUM SPECIMEN OXIDIZING IN AIR

Temperature: 1200 C
 Air Velocity: 8.3 cm/sec

Relative Percentage Deposition
 Within Inertial Impactor

<u>Impactor stage</u>	<u>MMD*(μ)</u>	<u>Te¹³²</u>	<u>I¹³¹</u>	<u>Cs¹³⁷</u>	<u>Zr-Nb⁹⁵</u>	<u>Ba-La¹⁴⁰</u>	<u>Uranium</u>
<u>C-1-1</u>							
1	>3	0.3	3.4	0.3	0.2	0.1	
2	3	0.3	3.0	0.3	0.2	0.1	
3	2	0.4	2.7	0.4	0.3	0.2	
4	1	0.7	3.1	0.6	0.6	0.5	
(MSA Filter)	<1	98.3	87.7	98.4	98.7	99.1	
<u>C-1-2</u>							
1	>3	0.3	1.8	0.3	0.2	0.2	5.4
2	3	0.3	1.1	0.3	0.3	0.2	3.2
3	2	0.5	1.5	0.4	0.4	0.3	2.1
4	1	0.7	1.4	0.7	0.6	0.5	2.7
(MSA Filter)	<1	98.2	94.2	98.3	98.5	98.8	87.6
<u>C-1-3</u>							
1	>3	0.3	2.1	0.5	0.2	0.1	
2	3	0.3	2.2	0.5	0.2	0.2	
3	2	0.6	3.2	0.9	0.4	0.4	
4	1	0.7	3.3	1.1	0.5	0.5	
(MSA Filter)	<1	98.1	89.2	97.0	98.7	98.8	

* Mass median diameter for particles of density 7.3 gm/cm³.

CONCLUSION

The effect of temperature on the nature of oxide formed from uranium oxidizing in air is pronounced, there being an increase in particle size with increasing temperature over the range 400 to 800 C. At 1000 C and above the oxide formed remains largely intact, giving rise to few micron size particles during the heating period. In relating these facts to fission product release it would be anticipated that the effect of air velocity on the release of fission products would be more pronounced at lower temperatures.

Only a fraction of those oxide particles of apparent entrainable size become airborne, emphasizing the possible effects of fuel element geometry and orientation. This stability of a mass of fine particles is an important factor to consider in a system where localized high air velocities or explosions might occur. This material once dispersed by a sudden rise in air stream velocity could remain suspended for extended periods of time. Deposition of uranium oxide and fission products on experimental apparatus points out the importance of the location of the fuel element during an overheating incident.

In conclusion particulate entrainment and deposition, fuel element geometry, orientation and location are variables which may have an important effect on fission product release. These variables along with effects of temperature, fuel element composition, cladding, air velocities and irradiation level compose a very complex system. Since little research to date has dealt with deposition parameters, this area merits added consideration.

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