Tech. Info. Files

BNWL-362
/

AEC
RESEARCH
and
DEVELOPMENT
REPORT

REACTION OF MOLTEN UO_2 WITH WATER

R. L. GIBBY

JANUARY, 1967

<i>L. Brown</i>	<i>30047</i>	<i>209E</i>	
<i>E. H. SHADE</i>	<i>31855</i>	<i>325</i>	<i>JUN 10 1967</i>

BATTELLE-NORTHWEST

BATTELLE MEMORIAL INSTITUTE / PACIFIC NORTHWEST LABORATORY

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

PACIFIC NORTHWEST LABORATORY

RICHLAND, WASHINGTON

operated by

BATTELLE MEMORIAL INSTITUTE

for the

UNITED STATES ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(45-1)-1830

PRINTED BY/ FOR THE U. S. ATOMIC ENERGY COMMISSION

3 3679 00060 5230

BNWL-362
UC-25, Metals, Ceramics
and Materials

REACTION OF MOLTEN UO_2 WITH WATER

By

R. L. Gibby

Ceramics and Graphite Research Section
Materials Department

January 1967

FIRST UNRESTRICTED
DISTRIBUTION MADE

MAR21 '67

PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U.S. Department of Commerce
Springfield, Virginia 22151
Price; Printed Copy \$3.00; Microfische \$0.65

REACTION OF MOLTEN UO_2 WITH WATER
R. L. Gibby

INTRODUCTION

The purpose of this study is to determine the amount of hydrogen that might be formed if the cladding of a fuel rod in the Plutonium Recycle Test Reactor (PRTR) should fail and molten UO_2 comes in contact with the primary coolant; also, to determine the resulting physical state of the UO_2 . The operation of the PRTR at high power density includes experiments in the Fuel Element Rupture Test Facility that involve a significant amount of molten UO_2 - PuO_2 fuel. Under normal conditions, the molten ceramic fuel is safely contained within a layer of solid fuel adjacent to the Zircaloy-2 cladding.

This document reports the results of preliminary attempts to obtain information concerning the interactions of molten UO_2 and water. Analytical calculations are useful in predicting what might happen after a sudden injection of UO_2 into the primary coolant; however, the calculations require information only available through experimental efforts.

SUMMARY

The reaction of molten UO_2 with water was investigated by allowing melted UO_2 samples to fall into water

heated to various temperatures. The tested UO_2 samples were analyzed for degree of oxidation by coulometric titration. Oxygen-to-metal ratios increased from an average initial value of 2.002 to values between 2.06 and 2.16, depending on the initial water temperature (30 to 250 °C). Water temperatures were arbitrarily selected to determine the effects of water temperature on the final results; the temperatures selected were much below those required for oxidation of UO_2 . The oxygen-to-metal ratio values correspond to a maximum hydrogen generation of 12 ml (STP)/g UO_2 , which is quite small. The only oxidation product determined from Guinier X-ray powder patterns was U_4O_9 . Attempts to measure simultaneous pressure transients, produced by evaporation and/or boiling of water in contact with the molten UO_2 , were generally unsuccessful.

Rapid injection of molten UO_2 into water did not produce a powdered end product; however, the quenched UO_2 was very friable and could be readily reduced to a coarse powder. Tyler screen analyses on three different powdered samples gave essentially identical average particle diameters of 0.062 cm.

EXPERIMENTAL PROCEDURE

MATERIAL

Uranium dioxide pellet samples were formed from reactor-grade natural UO_2 powder; standard pressing and sintering procedures were used. The pellets were ground to 1.3 cm diam by 1.3 cm long and faced to obtain flat parallel surfaces for electrical contacts.

The oxygen-to-metal ratio (O/M) was determined by coulometric titrations for each sample; the measured O/M values varied from 2.002 to 2.006.

Distilled water was used for the investigation; no attempt was made to degas the water because calculations indicated that the amount of dissolved oxygen in the water, even at one atmosphere oxygen overpressure at 25 °C (72 ppm O_2 dissolved in water), would not appreciably affect the final results.

EQUIPMENT

Experiments were performed in a high-pressure furnace capable of containing gas pressures in excess of 126 atm (Figure 1). Electrical power was furnished to the furnace interior through heavy-duty water-cooled copper leads, designed for high amperage operation, and through a set of 20-gage wires for 120 V power requirements. Special tungsten electrodes were connected to the heavy-duty leads to hold the sample in position for melting and, also, to serve as electrical contacts to the sample.

The entire furnace shell was water cooled; tantalum and tungsten heat shields were placed around the sample to minimize radiation heat-transfer to low-melting organic materials which

were also in the furnace. A quartz window at the front of the furnace permitted sample observation during melting.

Melting the UO_2 pellets required a combination of three different power supplies. A high voltage (1600 V max) power supply was used to overcome the high resistance of the UO_2 at room temperature. After the temperature of the sample reached about 600 °C, the power source was switched to a line voltage (120 V) supply and the sample temperature increased to about 1250 °C. Switching to a third power supply (low voltage, high current) permitted melting of the samples. An extremely useful amperage-control feature of the high-current power supply allowed controlled heating of the sample to the melting temperature, thus allowing more complete melting of the sample.

Water for the reaction was contained in a small (50 cm^3) stainless steel vessel (Figure 2). A nichrome wire, which was wrapped around the vessel, served as a heating element. An iron-constantan thermocouple was introduced through the side of the vessel and was used for temperature measurement. The millivolt output from the thermocouple was amplified and recorded on an oscillograph for a continuous water temperature history.

Water heated in the vessel, which is inside the furnace, vaporized and condensed on the furnace walls; therefore, water escaped from the vessel. To eliminate this problem, a thin aluminum membrane (0.005 cm thick) was fastened across the top of the

Neg. 0652526-1

FIGURE 1. High Pressure Furnace Arrangement for Molten UO₂ Experiments

Neg. 0652526-3

*FIGURE 2. Heated Water Vessel
with Aluminum Membrane*

water vessel. The membrane-covered vessel was filled with water through two small tubes that entered the vessel immediately below the membrane. During operation these tubes were plugged with Teflon stoppers to minimize water losses from the vessel. With the furnace pressurized to 67 atm, the water could be heated to 250 °C with only small water losses occurring. Since the vessel was filled at room temperature, heating caused volume expansion of the water, forcing water past the Teflon plugs into the furnace chamber; thus, complete containment of the water was not achieved by this method.

The furnace was pressurized with Ar-8% H₂ gas. A pressure transducer connected through a bridge-circuit amplifier to a strip-chart recorder provided continuous pressure readings. The overpressure of gas, besides allowing attainment of higher water temperatures without boiling, reduced the rate of UO₂ volatilization during melting; thus, minimizing darkening of the quartz window with UO₂ condensate.

A typical experimental run consisted of the following:

1. The furnace was purged for approximately an hour with the gas mixture and then pressurized to 67 ± 3 atm;

2. The temperature of the water was adjusted to the desired value with a rheostat in series with the power leads to the water-vessel heating element; and
3. The pellet sample was melted.

When melting occurred, the molten UO_2 readily penetrated the aluminum membrane and fell, still molten, to the bottom of the water vessel.

After each run, samples were obtained for chemical analysis to determine oxygen-to-metal ratios. Samples were taken from the UO_2 in the water vessel and from the unmelted UO_2 remaining on the tungsten electrodes; a comparison of these values was used to establish the degree of oxidation from reactions with the water in the vessel. Material remaining in the water vessel was dried and then placed in a small plastic vial. Shaking the vial reduced the UO_2 to a coarse powder, which was analyzed for particle size using Tyler sieves. For three different samples, the particle-size distribution and calculated

average particle diameter were so similar that additional samples were not tested.

Oxidation products were determined by X-ray diffraction using a Guinier power camera. This camera uses a focused beam of monochromatic $\text{CuK}_{\alpha 1}$ X-radiation and is more effective in distinguishing small quantities of second phase than, for instance, a Debye-Scherrer camera or a diffractometer.

RESULTS AND DISCUSSION

Data are tabulated in Table I according to sample weight and initial water temperature. Several attempts to measure molten UO_2 temperatures with an optical pyrometer and with tungsten-rhenium thermocouples were unsuccessful. However, molten UO_2 temperatures were calculated for several runs from water-temperature changes after sample injection and with the pertinent thermodynamic properties of UO_2 , including a calculated

TABLE I. Molten UO_2 - Water-Reaction Data

Melted UO_2 Weight g	Water Temperature, °C	ΔT , °C	Oxygen/Uranium		Calculated H_2 generation, ml (STP)/g UO_2
			Before	After	
0.756	27	5	2.002	2.058	4.5
9.37	28	73	2.005	2.080	6.2
0.571	100	5	2.002	2.077	6.2
1.126	105	15	2.004	2.082	6.5
7.705	110	61	2.012*	2.128	9.6
9.25	100	80	2.002	2.087	7.1
8.49	210	70	2.012*	2.155	11.9
11.381	255	49	2.029*	2.146	9.7
9.13	260	40	2.006	2.142	11.3

* Oxidation resulting from leakage of water into furnace chamber from water vessel.

heat of fusion.⁽¹⁾ The calculated temperatures varied from 3000 to 3300 °C, which are somewhat above the melting temperature of UO₂ (2800 °C).⁽²⁾ Above approximately 3100 °C, the vapor pressure of UO₂ is significant and results in considerable vaporization. Uniform deposits of UO₂ observed on the furnace walls after each experiment substantiate conclusions that UO₂ temperatures were above 3100 °C.

Small molten UO₂ samples did not oxidize as much as the large melts. This is surprising since one would expect the reaction to be surface-dependent; thus, small samples with higher surface-to-volume ratios should show higher oxygen-to-metal ratios. The observed result is apparently due to faster cooling rates for the small samples, and consequently, less time at higher temperatures where most oxidation should occur. The larger melts formed a single solidified mass on the bottom of the water vessel. All of the solidified melts were hollow and the microstructures hollow and the microstructures indicated rapid cooling progressed inward from the surface.

More oxidation occurred at higher water temperatures. The maximum water temperature experienced in this inves-

tigation was 300 °C; this temperature was maintained for only several seconds. Increasing the water temperature should enhance formation of vapor films over the cooling UO₂ surfaces, possibly reducing the effective thermal conductivity of the UO₂; thus allowing more time at high temperature for oxidation to occur. Because oxidation is most rapid at the higher temperatures, brief extensions of time at high temperature should reflect a noticeable increase in oxidation. In several cases, where the water was heated above 200 °C, vapor escaped into the furnace chamber; thus, some UO₂ oxidized before contacting the water. Oxygen analysis of molten UO₂ remaining on the tungsten electrodes after sample melt-down showed some oxidation. However, if it is assumed that the material that fell into the water was initially oxidized to the same extent as UO₂ remaining on the tungsten electrodes, oxidation was still greater in UO₂ samples dropped into the heated water.

Hydrogen-generation volumes were calculated from increases in oxygen-to-uranium ratios assuming the reaction

where x is the number moles of water reacting per mole of UO₂. The results compare favorably with measured hydrogen releases obtained by Liimatainen and Testa.⁽³⁾ In their work, UO₂

(1) Samuel Glasstone. Theoretical Chemistry, an Introduction to Quantum Mechanics, Statistical Mechanics, and Molecular Spectra for Chemists. D. Van Nostrand Co., Inc., New York, 1944. pp. 466-67.

(2) H. Hausner. "Determination of the Melting Point of Uranium Dioxide," Journal of Nuclear Materials, vol. 15, no. 3, pp. 179-83. 1965.

(3) R. C. Liimatainen and F. J. Testa. "Studies in TREAT of Uranium Dioxide Fuel," Section 5--Reactor Safety, Chemical Engineering Division Summary Report July-December 1964, edited by L. Baker, A. D. Tevebaugh. ANL-6925, p. 63. Argonne National Laboratory, Lamont, Illinois. 1965.

samples enclosed in an autoclave were rapidly melted by nuclear reactor transients. Hydrogen generation was calculated from off-gas analyses. At power transients sufficient to partially melt their samples, hydrogen-generation results compare favorably with those of this experiment. When some UO_2 vaporization occurred because of more powerful transients, the hydrogen generation was more than double that indicated by the present data.

Although the molten UO_2 solidified in a solid mass, the material was very friable. It was easily reduced to a powder by moderate agitation in a plastic vial. The average particle size was determined from Tyler sieve analysis using the Sauter mean-diameter equation

$$d_{sv} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \quad (2)$$

where, n_i = number of particles with diameter, d_i .

The equation was modified for use with weight fractions; thus, assumed the form

$$d_{sv} = \left(\sum \frac{w_i}{d_i} \right)^{-1} \quad (3)$$

where, w_i = fraction of particles of diameter d_i .

Derivation of Equation (3) from Equation (2) assumes that the powder is composed of uniformly dense, spherical particles. Although this assumption is not completely adhered to by the analyzed powders, the results calculated from Equation (3) are reasonable estimates for average powder diameters. The three powders that were analyzed for particle size and particle-size

distribution were nearly identical (Figure 3). The calculated Sauter mean diameters were 0.066 cm, 0.071 cm, and 0.074 cm. Because the results were so similar, other powders were not analyzed.

The attempts to measure pressure transients that accompany molten UO_2 injection into water were not successful. Thermal expansion of the argon atmosphere in the furnace during sample meltdown concealed pressure increases from water vaporization. Furthermore, the comparatively large volume of the furnace chamber would be

FIGURE 3. Particle Size Distribution of Quenched UO_2 Samples

expected to dampen any abrupt pressure rises. A much less compressible system would be necessary to obtain results that could be used in the analysis of pressure transients in a hard hydraulic system typical of reactor-coolant systems.

The X-ray diffraction data using the Guinier camera are shown for dif-

ferent final oxygen-to-uranium values in Table II. At oxygen-to-uranium ratios above 2.09, U_4O_9 was identified as the oxidation product. The U_4O_9 lines were diffuse and broad, indicating small particle size; consequently, the lines were difficult to distinguish from adjacent UO_2 lines.

TABLE II. A Comparison of X-Ray Diffraction Lines from Partially Oxidized UO_2 and Stoichiometric UO_2 and U_4O_9

X-Ray Diffraction Standards*				Oxidized Urania		
UO_2		U_4O_9		$UO_{2.09}$	$UO_{2.13}$	$UO_{2.16}$
I/I_0	$d, \text{\AA}$	I/I_0	$d, \text{\AA}$	$d, \text{\AA}$	$d, \text{\AA}$	$d, \text{\AA}$
100	3.157			3.15	3.15	3.15
		90	3.12			
48	2.735			2.72	2.73	2.72
		60	2.17			
49	1.934			1.93		
		90	1.918	1.92	1.92	1.92
47	1.649			1.648	1.646	
		100	1.636	1.643		1.64
13	1.579			1.577	1.577	1.575
		50	1.567			
9	1.368			1.366	1.366	1.366
		30	1.359			
18	1.255			1.251	1.253	1.254
		80	1.247			1.251
15	1.223			1.222	1.221	1.223
		80	1.215			1.219
13	1.1163			1.115	1.115	1.116
		100	1.110		1.112	1.112

* From ASTM X-Ray Powder Data File

DISTRIBUTION

<u>Number of Copies</u>		<u>Number of Copies</u>	
1	<u>Alkem</u> 7501 Leopoldshafen Karlsruhe, Germany W. Stoll	1	<u>Atomic International</u> B. R. Hayward
1	<u>Argonne National Laboratory</u> J. H. Kittel	4	<u>Battelle Memorial Institute</u> D. L. Keller S. W. Porembka (2) W. F. Heenan
1	<u>Associazione Euratom-ENEN</u> <u>Per I Reattori Veloci</u> Via Mazzini 2 Bologna, Italy F. Pierantoni	1	<u>Brookhaven National Laboratory</u> D. H. Gurinsky
5	<u>Atomic Energy Commission,</u> <u>Washington</u> Division of Reactor Develop- ment and Technology R. Grube J. M. Morrissey R. E. Olson J. M. Simmons M. J. Whitman	1	<u>Centre d'Etudes Nucleaires de</u> <u>Cadarache</u> Poite Postale No. 1 Saint-Paul-Lez-Durance, France Dr. B. Defreyn
3	<u>Atomic Energy Commission,</u> <u>Richland</u> Division of Reactor Develop- ment and Technology P. G. Holsted (3)	1	<u>Combustion Engineering, Inc.</u> J. C. Tobin
1	<u>Atomic Energy Research</u> <u>Establishment</u> Chemistry and Metallurgy Br. Fuels Development Branch Chalk River, Ontario, Canada J. A. L. Robertson	274	<u>Division of Technical Information</u>
4	<u>Atomic Energy Research</u> <u>Establishment</u> United Kingdom Atomic Energy Authority Harwell, Didcot, Berks, England P. Murray (3) L. E. Russell (1)	4	<u>Douglas United Nuclear, Inc.</u> T. W. Ambrose L. E. Kusler J. T. Stringer DUN File Copy
1	<u>Atomic Energy Commission</u> Brussels, Belgium AEC Representative	1	<u>European Atomic Energy Community</u> 51-53 Rue Belliard (Euratom) Brussels 4, Belgium Pierre Kruys
		1	<u>General Electric Company, APD</u> Special Purpose Nuclear Systems Operation P. O. Box 846 Pleasanton, California J. E. Van Hoomissen
		2	<u>General Electric Company</u> <u>Cincinnati</u> W. Briskin J. McGurty

<u>Number of Copies</u>		<u>Number of Copies</u>	
3	<u>General Electric Company Pleasanton</u> L. P. Bupp E. A. Evans A. I. Kaznoff	1	<u>University of Michigan</u> College of Engineering Ann Arbor, Michigan W. Kerr
6	<u>General Electric Company Richland</u> R. L. Dickeman T. W. Evans M. Lewis C. H. Shaw E. A. Smith GETA File Copy	2	<u>Westinghouse Bettis Atomic Power Laboratory</u> J. Belle B. Lustman
2	<u>General Electric Company San Jose</u> A. N. Holden M. F. Lyons	4	<u>Westinghouse Electric Corp.</u> Robert Allio A. A. Bishop A. Boltax N. R. Nelson
2	<u>Isochem, Inc.</u> H. H. Hopkins R. Y. Lyon	1	<u>Wright Air Development Center</u> AF Materials Laboratory Wright-Patterson AFB Dayton, Ohio S. W. Bradstreet
1	<u>Kerr- McGee Inds, Inc.</u> Oklahoma City, Oklahoma Harold Lambertus	43	<u>Battelle-Northwest</u> F. W. Albaugh H. J. Anderson R. J. Anicetti J. A. Ayres W. J. Bailey J. M. Batch C. H. Bloomster C. A. Burgess S. H. Bush J. A. Christensen F. G. Dawson D. R. de Halas R. L. Dillon P. L. Farnsworth M. D. Freshley R. L. Gibby (10) S. Goldsmith W. L. Hampson H. E. Hanthorn G. R. Horn H. Harty R. L. Junkins M. K. Millhollen R. E. Nightingale L. A. Pember W. E. Roake H. R. Wisely Technical Publications (2) Technical Information Files (5)
2	<u>NASA Lewis Research Center</u> A. F. Lietzke N. T. Saunders		
3	<u>Richland Operations Office</u> R. K. Sharp (2) Technical Information Library		
1	<u>Transuranium Institute (Euratom)</u> Karlsstrasse 42-44 Karlsruhe, Germany H. M. Mattys		
2	<u>Union Carbide Corporation (ORNL)</u> R. M. Carroll J. L. Scott		
1	<u>United Aircraft Corporation</u> Research Laboratory East Hartford, Connecticut G. H. McLafferty		
1	<u>University of Arizona</u> Nuclear Engineering Dept. Tucson, Arizona Monte V. Davis		