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**URANIUM/WATER VAPOR REACTIONS IN
GASEOUS ATMOSPHERES**

R. L. Jackson
J. B. Condon
L. M. Steckel

July 1977

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OAK RIDGE, TENNESSEE**

prepared for the **U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION**
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Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
Price: Printed Copy \$3.50 ; Microfiche \$3.00

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Date of Issue: July 18, 1977
Distribution Category: UC-4 & UC-25

Report Number: Y-2078

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Prepared for the US Energy Research
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Under US Government Contract W-7405-eng-26

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ABSTRACT

Experiments have been performed to determine the effect of varying humidities, gaseous atmospheres, and temperatures on the uranium/water vapor reaction. A balance, which allowed continuous in-system weighings, was used to determine the rates of the uranium/water vapor reactions at water vapor pressures of 383, 1586, and 2853 Pa and at temperatures of 80, 100, and 150° C in atmospheres of hydrogen, argon, or argon/oxygen mixtures. Based on rate data, the reactions were characterized as hydriding or nonhydriding. Hydriding reactions were found to be preferred in moist hydrogen systems at the higher temperatures and the lower humidities. The presence of hydrogen in hydriding systems was found to initially inhibit the reaction, but causes an acceleration of the rate in the final stages. In general, reaction rates of hydriding systems approached the hydriding rates calculated and observed in dry hydrogen. Hydriding and nonhydriding reaction rates showed a positive correlation to temperature and water vapor pressure. Final reaction rates in moist argon/oxygen mixtures of 1.93, 4.57, and 9.08 mole percent oxygen were greater than the rates observed in moist hydrogen or argon. Final reaction rates were negatively correlated to the oxygen concentration.

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SUMMARY

The reactions of uranium in moist atmospheres of argon, hydrogen, and argon/oxygen mixtures were studied at temperatures of 80, 100, and 150° C. Water vapor pressures of 383, 1586, and 2853 Pa were used in this study. Results of the experiments indicated that:

1. There were no simple quantitative relationships between the water vapor pressures and the uranium reaction rates in moist argon or moist hydrogen systems.
2. There were no simple quantitative relationships between temperatures and the uranium reaction rates in moist argon or moist hydrogen systems.
3. Hydrogen initially inhibited the uranium/water vapor reaction, but accelerated the weight-gain rates in the final stages due to hydriding.
4. Uranium hydriding reactions in moist hydrogen were favored by a high temperature and low humidity.
5. Uranium-reaction rates in moist argon/oxygen mixtures were negatively correlated to the oxygen concentration.
6. Uranium-reaction rates in the presence of low levels of moist oxygen were higher than the rates in hydrogen or argon under the same conditions of humidity and temperature.

These experiments confirm the conclusion reached by other researchers that the oxidation of uranium is a complex reaction. A description of the reactions under the various gaseous atmospheres is offered to clarify some of the conflicting reports in the literature.

INTRODUCTION

It is well known that oxygen and water vapor can inhibit the hydriding reaction of uranium. The presence of either of these gases in the parts-per-million range can modify reaction rates considerably. Compensations can be made in hydriding-rate calculations for these low levels of oxygen or water contamination;¹ however, with increasing levels, the oxidation reaction becomes an important factor.

A survey of the literature involving the oxidation of uranium reveals major conflicts in theories and results. Variations in sample purity and preparation have been shown to have only a minor effect on the oxidation rates of uranium under humid conditions,^{2,3} but differences in the experimental procedures and detail have proven to be the more crucial factors in evaluating the existing literature.

Bennett, et al,⁴ have shown that the presence of water, while increasing oxidation at 100 - 200° C, is without significant influence at 50, 70, and 300° C. Baker, et al,⁵ have shown that the reaction rate of the uranium/water vapor system is dependent on the water vapor pressure up to saturated water conditions, but showed no difference in the rates on immersion versus saturated conditions.

There is general agreement that the presence of oxygen and hydrogen has severe effects on the oxidation of uranium in water vapor. The relative influence of each of these gases individually on the oxidation reaction as well as the mechanism that controls the reaction continues to be a source of conflict. Several theories on the mechanism have been proposed. Orman, et al,^{6 - 8} proposed a mechanism which is controlled by hydroxide ion diffusion through a protective oxide layer. Draley⁹ theorizes that the mechanism is controlled by the hydrogen damage arising from hydrogen that is produced as a product in the reaction:

According to Draley, hydrogen causes rupturing in the oxide layer which results in increased corrosion.

Kondo, et al,¹⁰ proposed a mechanism of "hydride fracture" in which growth and fracture of uranium hydride play vital roles in determining the oxidation rate. Waber¹¹ introduces a "hydroxide" mechanism and postulates that the principal role of the corrosion of uranium is attributed to the formation of the hydroxide of uranium.

There has been little conclusive evidence to support any one of these theories over the others. True quantitative studies are lacking at present. The purpose of this investigation, conducted at the Oak Ridge Y-12 Plant,^(a) is to provide a qualitative description of the uranium/water vapor/hydrogen reaction at temperatures of 80, 100, and 150° C and relative

(a) Operated by the Union Carbide Corporation's Nuclear Division for the US Energy Research and Development Administration.

humidities of 12% (383 Pa), 50% (1586 Pa), and 90% (2853 Pa). A description of the effect of oxygen on the oxidation of uranium in a 383-Pa water-vapor-pressure environment at 80° C is offered which can be used to clarify some existing theories.

URANIUM/WATER VAPOR REACTIONS IN GASEOUS ATMOSPHERES

PRESENTATION OF EXPERIMENTAL WORK

Materials

Uranium samples were of rolled foil shaped into concave discs. The geometric surface area for all samples was an average of 24.4 cm². Major impurities found by chemical analysis of the uranium foil are listed in Table 1. All other elements were either below the level of detection by spark-source spectroscopy or below 10 wppm.

Table 1
URANIUM ANALYSIS RESULTS

Element	Concentration (wppm)
Carbon	98
Iron	85
Silicon	60
Aluminum	38
Nitrogen	10
Oxygen	<< 100

The uranium samples were rolled into a cylindrical configuration and cleaned immediately before admission to the test chamber, using the following method: (1) pickle the sample at 80° C in a 1:2 nitric acid solution; (2) ultrasonically clean the sample in the same acid solution at room temperature for two minutes; (3) rinse the sample, using demineralized water, and (4) provide a final rinse and dry the sample, using ethyl alcohol. There were small variations in the sample weights due to etching of the samples.

Initial heat treatment consisted of: (1) a prehydriding step, (2) an alpha anneal, (3) a beta quench, (4) a gamma quench, or (5) a prehydride-and-anneal sequence.

Prehydriding and annealing operations were done after the cleaning sequence in the test chamber. Quench operations were done prior to cleaning outside of the test chamber.

Gamma-quench heat treatments consisted of heating the sample for one hour in a high vacuum (1.3×10^{-3} Pa) at 825° C, followed by a rapid water quench. Beta-quench heat treatments of samples consisted of heating for one hour at 750° C in a high vacuum followed by a rapid water quench. Alpha-anneal heat treatments were performed by heating the samples to 630° C in a high vacuum in the test chamber and holding at this temperature for one hour immediately prior to beginning the selected test.

Prehydriding was performed on samples which were to be tested in moist hydrogen and was always performed after the cleaned and weighed samples were in the test chamber. In practice, the test chamber was evacuated and backfilled with Serfass hydrogen, and the sample area was then heated to 150° C until hydriding started. Hydriding was indicated by a weight gain in the sample. The test chamber was then evacuated to a high vacuum (1.3×10^{-3} Pa), cooled to <50° C, backfilled with hydrogen, and reweighed to detect any actual weight gain associated with this step.

The argon gas was of 99.997% purity. The hydrogen (99.5% pure) was passed through a palladium diffuser to obtain the gas in ultrahigh purity. Analysis of the oxygen/argon mixtures revealed oxygen levels of 1.93, 4.57, and 9.08 mole percent (mol %).

Instrumentation

Relative-humidity levels were determined by using a moisture-sensing cell.^(b) The humidity levels were created by passing a gas stream through water vapor. Flow rates through the humid gas stream, combined with a dry gas stream were varied to control the humidity level.

These studies were performed in a Mettler Thermoanalyzer DTA-TGA balance, Model TA-1.

Test Procedure

Samples which were cleaned by the previously described cleaning procedure were placed in a quartz crucible of sufficient depth (59 mm) to allow for containment of the reaction products. The test chamber was backfilled with argon during admission of each sample in an effort to minimize oxidation. After loading, the test chamber was evacuated to 1×10^{-5} torr (1.3×10^{-3} Pa) and the sample weight recorded. The test chamber was then backfilled with argon, an argon/oxygen mixture, or hydrogen, and the corresponding gas with a given moisture content was allowed to flow through the test chamber. Total system pressure in the test chamber was maintained at one atmosphere. Samples were reweighed at this point. The test chamber was then heated to the selected temperature (80, 100, or 150° C) and the weights recorded continuously. The length of the experimental runs varied, depending on whether a reaction rate was judged to be essentially stable relative to change in the reaction-rate characteristics. The average run lasted about 300 minutes (5 hr). Due to laboratory restrictions, several of the hydrogen tests were interrupted with an evacuation to a high vacuum, backfilled with argon, then continued on the following day.

Upon completion of each test, the test chamber was evacuated to 1.3×10^{-2} Pa (1×10^{-4} torr), backfilled with argon, and heated to 500° C. After stabilization of the weight at 500° C, the chamber was cooled to room temperature and the final sample weight was recorded. It was assumed that any weight loss during this step was due to dehydriding of the sample. Data were collected and analyzed using a Control Data Corporation time-share computer and a program that calculated rates from average values spread over a five-point span.

Results

Tests using the prehydride, alpha-anneal, and beta-quench treatments revealed problems in reproducibility as well as exotherms, accompanied by rapid weight gains. The duration and

(b) A product of Hydrodynamics, Inc.

intensity of the exotherm exhibited no dependence on the experimental conditions, such as sample preparation and temperature. The gamma-quench treatment was found to be the most reliable.

Weight-gain curves for uranium in moist gases yielded distinctively different patterns, depending primarily upon whether the selected gaseous atmosphere was hydrogen, argon, or an argon/oxygen mixture. In moist argon, the weight gain, with respect to time, was linear, as noted in Figure 1. This relationship corresponds to rate curves (dw/dt) which reach constant values, as the graph of Figure 2 reveals, and is indicative of the absence of hydriding. No weight loss occurred on heating the sample to 500°C in argon.

Figure 1. WEIGHT GAIN OF URANIUM IN MOIST ARGON (383 Pa WATER VAPOR) AS A FUNCTION OF TIME AND TEMPERATURE.

Curves characteristic of the uranium/water vapor/hydrogen systems did not reach a constant rate of weight gain (Figure 3). These hydriding curves did show a period of weight-gain inhibition characterized in the initial portion of the curve in Figure 3. The final portion of the curve indicates an acceleration due to hydriding. When the observed rates followed this type of behavior, the sample always lost weight on the final 500°C treatment, indicating the presence of hydride. Delays in the onset of the reactions observed in the weight-gain curves were not reproducible and showed no simple relationship to a time base.

Figure 2. RATE OF WEIGHT GAIN OF URANIUM IN MOIST ARGON (383 Pa WATER VAPOR). (Sample Area, 24.4 cm²)

Figure 3. RATE OF WEIGHT GAIN OF URANIUM IN MOIST HYDROGEN (383 Pa WATER VAPOR) AT 100°C. (Accelerating Rate is Indicative of the Hydriding Reaction; Sample Area, 24.4 cm²)

Figure 4 compares the oxidation rates of uranium in moist hydrogen and moist argon. Initially, the reaction is inhibited in moist hydrogen; but, after 10 ks, proceeds at a rate exceeding that in moist argon. Those cases having the highest reaction rates approached the expected "pure hydriding" rates proposed by Condon and Larson,¹ as seen in Figure 5. The rates were slightly lower than would be expected in pure, dry hydrogen. According to the hydriding model mentioned earlier, additions of small amounts of water should decrease the rate of hydriding. These results justify the assumption that hydriding is the dominating reaction that proceeds in the uranium/water vapor/hydrogen system when the typical accelerating rate (Figure 3) is observed.

Figure 4. WEIGHT GAIN OF URANIUM IN MOIST HYDROGEN AND MOIST ARGON (383 Pa WATER VAPOR) AS A FUNCTION OF TIME. (At 80°C)

The presence of hydrogen in the uranium/water vapor system did not always cause a hydriding reaction (Table 2). All tests done in a 383-Pa water vapor pressure environment with hydrogen yielded hydriding reactions. Likewise, all trials at 150°C were hydriding

Figure 5. RATE OF WEIGHT GAIN OF URANIUM IN MOIST HYDROGEN (383 Pa WATER VAPOR) AS A FUNCTION OF TEMPERATURE. (Sample Area, 24.4 cm²)

Table 2
TENDENCY OF URANIUM TO UNDERGO
HYDRIDING REACTIONS IN MOIST
HYDROGEN

Temperature (°C)	Water Vapor Pressure (Pa)		
	383	1586	2853
80	H(1)	NH	NH
100	H	NH	NH
150	H	H	H

(1) H - a hydriding system; NH - a nonhydriding system.

runs. This result leads to the assumption that there are critical values of humidity and temperature which will permit hydriding. It can also be assumed that in this critical region the reaction mechanism is different from the mechanism of the reaction of a nonhydriding system.

The water/oxidation reaction is not a simple one. A simple kinetic order or a single activation energy cannot be used on this system. The Arrhenius plot (Figure 6) and the plot of log pressure of water vapor versus log rate of weight gain (Figure 7) illustrate that the kinetics under consideration are complex in nature.

The hydriding reaction involves at least a two-stage sequence. Tests which were interrupted and held overnight exhibited a severe reduction in the rate on resuming the following day. The rate slows down due to a possible rearrangement of the product layer or additional oxidation from the residual water or oxygen in the argon system. On exposure to moist hydrogen, the rate subsequently returned to the previous linear value. Figure 8 shows how a uranium/water vapor/hydrogen system is affected by an overnight interruption. A plateau-and-rise sequence, as indicated in Figure 8, was also noted in all hydriding runs. This observation is supportive of the theory that the uranium/water vapor/hydrogen reaction occurs in at least two stages. The overall effect of the plateau/rise sequence is to yield an apparent linear-rate value for hydriding.

Reactions of the uranium/water vapor/oxygen system were characterized by rate curves similar, in some respects, to both the hydriding and nonhydriding curves. An initial decrease in the rate values occurred in the 9.08 and 4.57 mol % oxygen-in-argon runs. This initial rate decrease was also detected in most of the previously described hydriding runs, and was

followed by a period of linear rates in all runs. The oxygen runs ended in a leveling off of the rate values, which is characteristic of nonhydriding systems. The initial rate (illustrated in Figure 9) at which the reaction proceeds was found to be directly proportional to $\sqrt{P_{O_2}}$. This relationship leads to the conclusion that either the oxygen involved in the reaction is elemental oxygen, or that the reaction which takes place initially is chemisorption rather than adsorption. The final rates of uranium oxidation for all of the tests in moist argon/oxygen mixtures used in this investigation were higher than the rate in moist argon. Figure 10 gives a full description of this result. The diagram of Figure 10 indicates that moist oxygen does increase the uranium oxidation rate, while moist hydrogen decreases the rate (though it has been shown that the rate in hydrogen will eventually supersede the rate in argon). The final rates of oxidation also show a linear dependence on the initial oxygen pressure. This dependence is emphasized in Figure 11. The higher percentages of oxygen generate the greatest inhibition factor which, in turn, yields the lowest final rate. A complete listing of the results of these experiments is given in Table 3.

DISCUSSION OF RESULTS

The results of these experiments help in understanding why the uranium/water vapor reaction has eluded a concise description up to this point. At temperatures of 80, 100, and 150°C, the uranium/water vapor reactions in argon and hydrogen have been shown to be complicated. The reaction rate is dual in nature and highly sensitive to variations in the experimental conditions. A qualitative survey of the relationship between weight

Figure 6. ARRHENIUS PLOT FOR URANIUM CORROSION RATES IN MOIST ARGON. (Sample Area, 24.4 cm²)

Figure 7. RATE OF WEIGHT GAIN OF URANIUM IN MOIST ARGON AS A FUNCTION OF TEMPERATURE AND WATER VAPOR PRESSURE. (Sample Area, 24.4 cm²)

Figure 8. EFFECT OF AN INTERRUPTION ON THE RATE OF WEIGHT GAIN OF URANIUM IN MOIST ARGON (383 Pa WATER VAPOR) AT 80° C. (Sample Area, 24.4 cm²)

gain and time for the three temperatures under study (Figure 1) would indicate some temperature dependence of the reaction. (The higher the temperature the greater the weight gain.) A close look at the Arrhenius plots (Figure 6) does not support a quantitative theory of temperature dependence. The same is true for the water vapor pressure-and-oxidation rate relationship. The oxidation rate increases as the pressure of water vapor increases. A simple quantitative relationship does not exist, as revealed in Figure 7.

Figure 9. INITIAL RATE OF REACTION OF URANIUM IN MOIST OXYGEN (383 Pa WATER VAPOR) AT 80° C AS A FUNCTION OF THE OXYGEN PRESSURE.

Depending on the test conditions, hydrogen in the uranium/water vapor system can either enhance the reaction rate or be ineffectual in accelerating the rate. The data of Table 2 show that, in a low water vapor pressure (<1.58 kPa) as well as of a high temperature (>100° C), the presence of hydrogen causes the hydriding reaction to become prevalent. Nonhydriding rates will prevail in systems with a high water vapor pressure and at low temperatures.

Figure 10. RATE OF WEIGHT GAIN OF URANIUM IN MOIST ARGON, HYDROGEN, AND ARGON/9 mol % O₂ AT 80° C. (Moisture Content, 383 Pa; Sample Area, 24.4 cm²)

One advantage of the procedure and equipment in this study is the use of a balance which gives continuous weight values of the reaction products. Spalling presented no problem because the product was contained in a deep crucible. Initial weight changes were recorded which have been ignored in many studies. These weight changes provide valuable information on the intermediate steps which will be necessary for determining the rate-controlling steps. The moist hydrogen and moist argon/oxygen mixture runs were both characterized by initial inhibitions in the weight gain. Several theories have been proposed to quantify this event. Grimes¹²

Figure 11. FINAL RATES OF WEIGHT GAIN OF URANIUM IN MOIST OXYGEN (383 Pa WATER VAPOR) AT 80° C AS A FUNCTION OF THE INITIAL OXYGEN PRESSURE. (Sample Area, 24.4 cm²)

Table 3
RESULTS OF THE REACTION OF URANIUM IN MOIST ARGON, HYDROGEN, AND OXYGEN/ARGON MIXTURES

Trial Number	Gaseous Atmosphere	Temperature (° C)	Water Vapor Pressure (Pa)	Heat Treatment	Initial Sample Weight (g)	Rate of Weight Gain (μg/s)	Weight Loss (or gain) on Dehydrating (mg)	Permanent Weight Gain (mg)
3034	Hydrogen	80	383	Prehydride	3.704	1.02	38.3	31.7
3054	Hydrogen	80	383	Prehydride, α Anneal	3.7795	0.89	53.4	13.9
3144	Hydrogen	80	383	α Anneal	2.9400	1.25	31.9	13.7
305	Hydrogen	80	383	Prehydride	3.855	0.18	45.4	10.6
625	Hydrogen	80	383	β Quench	2.986	0.12	35.9	5.9
695	Hydrogen	80	383	β Quench	3.7197	0.13	(0.2)	1.7
775	Hydrogen	80	383	γ Quench	3.7134	1.40	9.9	37.8
1185	Hydrogen	80	1586	γ Quench	3.0855	0.27	(0.3)	6.4
1255	Hydrogen	80	2853	γ Quench	2.6756	0.47	(0.2)	7.8
705	Argon	80	383	β Quench	3.6608	0.25	0	3.3
735	Argon	80	383	γ Quench	3.45005	0.23	0	3.0
1125	Argon	80	1586	γ Quench	3.3588	0.50	0	3.7
1275	Argon	80	2853	γ Quench	3.6898	0.63	0	10.2
3184	Hydrogen	100	383	α Anneal	3.809	3.28	46.1	9.5
655	Hydrogen	100	383	β Quench	3.4942	15.9	41.4	14.9
715	Hydrogen	100	383	γ Quench	2.939	22.0	28.1	13.2
1205	Hydrogen	100	1586	γ Quench	2.9825	1.15	0.1	41.5
1265	Hydrogen	100	2853	γ Quench	2.7098	1.36	0	22.6
725	Argon	98	383	γ Quench	3.519	0.33	0	5.2
1135	Argon	100	1586	γ Quench	3.2649	1.19	0	16.0
1285	Argon	100	2853	γ Quench	3.5237	1.43	0.2	24.0
3154	Hydrogen	150	383	α Anneal	3.9787	0.92	38.5	6.2
3164	Hydrogen	150	383	No Anneal, No Prehydride	4.1364	6.58	49.6	5.2
645	Hydrogen	150	383	β Quench, Prehydride	3.7520	49.0	45.7	4.7
775	Hydrogen	150	383	γ Quench	3.1919	1.13	39.7	3.4
1755	Hydrogen	150	1586	γ Quench	3.2071	28.6	37.4	18.2
1765	Hydrogen	150	2853	γ Quench	3.6837	51.6	42.8	22.2
765	Argon	150	383	γ Quench	3.2437	0.53	0	6.0
1745	Argon	150	1586	γ Quench	3.6414	2.20	0.2	33.7
1775	Argon	150	2853	γ Quench	2.5726	2.75	0.3	40.1
1325	1.93% O ₂ in Ar	80	383	γ Quench	3.7536	0.37	0	4.7
1335	4.57% O ₂ in Ar	80	383	γ Quench	3.8085	0.35	0.1	4.0
1345	9.08% O ₂ in Ar	80	383	γ Quench	2.995	0.33	0.1	4.0

has theorized that this initial period is one of a protective film formation, with the reaction rate becoming very nearly linear with respect to time after an oxide film of 3000 Å in thickness has developed. Leibowitz¹³ has determined that the rate changes markedly in the uranium/oxygen system after an average of 50 $\mu\text{g O}_2/\text{cm}^2$ has been consumed. The results and nature of this study cannot be conclusive in determining what type of relationship exists between inhibition and surface thickness or rate. Figure 10 does show that the change in reaction rates is much more pronounced in the moist argon/oxygen systems than in the moist hydrogen system. Also, the higher concentrations of oxygen show the more severe change in reaction rates. This change is, in fact, an acute or abrupt change, which supports the "oxygen consumption" theory of several investigators. Baker⁵ has stated that oxygen does effect a decrease in the corrosion rate until hydrogen has consumed all of the available oxygen. The change in rate after this consumption is immediate. The results of this study show that the characteristics of the rate curve for the moist argon/oxygen systems after this rate reversal is clearly the same as in the moist argon system (Figure 10).

Results of this study and others indicate that the uranium/water vapor reaction warrants further investigation to resolve the areas of conflict that continue to exist concerning reaction mechanisms and characterization.

CONCLUSIONS

The uranium/water vapor reaction has been shown to be highly dependent on the gaseous atmosphere of the environment. The rate curves observed in this study are distinct for moist argon, hydrogen, and the argon/oxygen systems. This unique character suggests that the reactions are different for the particular gas(es) involved.

Certain conclusions are the same for all of the uranium/water vapor reactions performed in this study. There is a temperature dependency, although results of this study indicate that this is not a simple one. Reaction rates were also shown to be dependent on the humidity. The conclusion reached from these studies is that the relationship between temperature, water vapor pressure, and the reaction rate is complex.

Hydriding occurs in the uranium/water vapor/hydrogen system under favored conditions. The water vapor pressure and temperature are the determining factors. Low humidity and high temperature are the favored conditions. Further studies must be conducted to describe the quantitative relationship between the two conditions. Hydrogen initially inhibits the reaction rate of the uranium/water vapor system, but final rates are greater than the rates in moist argon.

Oxygen initially inhibits the uranium/water vapor reaction, and the greater the oxygen concentration the more severe the inhibition. This period of the reaction, characterized by a decrease in the rate, has been described as indicating an oxygen consumption phase. The effect of oxygen at later stages of the reaction is a leveling off of the reaction rate. This result is identical in characteristic to the final stages of the reaction in moist argon. The reaction rates for the moist argon/oxygen systems in this study were slightly higher than the reaction rates for the moist argon systems. Present studies indicate that oxygen has a total

effect of increasing the reaction rate. Other investigators have stated that oxygen inhibits the reaction. Possibly, if oxygen concentrations are greater than those used in this study, the system will lose the ability to recover from the effects of oxygen and show a total system inhibition. Further studies will be necessary to investigate this possibility.

The results of this study help to clarify the reaction characteristics of the uranium/water vapor reaction under the influence of argon, hydrogen, and argon/oxygen atmospheres.

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