QUANTITATIVE ANALYSIS OF HYDROGEN GAS FORMED
BY AQUEOUS CORROSION OF
METALLIC URANIUM

by

Jacqueline Fonnesbeck

Engineering Division
Argonne National Laboratory-West
P. O. Box 2528
Idaho Falls, ID 83403-2528

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

QUANTITATIVE ANALYSIS OF HYDROGEN GAS
FORMED BY AQUEOUS CORROSION OF METALLIC URANIUM

Jacqueline E. Fonnesbeck
Argonne National Laboratory-West
P.O. Box 2528
Idaho Falls, Idaho 83401
(208)533-7163

ABSTRACT

Three unirradiated EBR-II blanket fuel samples containing depleted uranium metal were corrosion tested in simulated J-13 well water at 90°C. The corrosion rate of the blanket uranium metal was then determined relative to H_2 formation. Corrosion of one of the samples was interrupted prior to complete oxidation of the uranium metal and the solid corrosion product was analyzed for UO_2 and UH_3.

I. INTRODUCTION

The effects of aqueous corrosion of metallic uranium is an important parameter in understanding the degradation of spent nuclear fuel (SNF) during interim and extended storage. Apart from the effects on radionuclide release, aqueous corrosion produces hydrogen (H_2), a flammable gas, and uranium hydride (UH_3), and pyrophoric solid.

The results of the experiment described in this paper were used to define some of the parameters that can affect hydrogen and UH_3 production when uranium based metallic fuel comes in contact with water. These tests involved submerging unirradiated, unalloyed uranium in simulated J-13 (SJ-13) well water and accelerating corrosion by raising the temperature to 90°C.
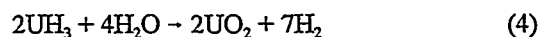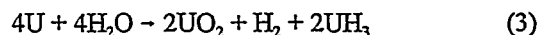
Headspace gas pressure was first measured and then collected to determine gas composition by Gas Mass Spectrometry (GMS) or Gas Chromatography (GC). Quantitative X-Ray Diffraction (XRD) analysis was used for corrosion product phase identification.

II. THEORETICAL BACKGROUND

There are two major modes of uranium aqueous corrosion. It has been shown that for oxygenated water, the uranium oxidizes preferentially via its reaction with elemental oxygen. This process is referred to as 'Oxic'.

$$U + O_2 + 2H_2O \rightarrow UO_2 + 2H_2O \qquad (1)$$
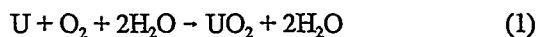
The second mode is referred to as 'Anoxic', by which the uranium is oxidized via hydroxyl ions formed during the hydrolysis of water at the uranium oxide surface.[2] However, the following reactions express the overall anoxic process,

$$U + 2H_2O \rightarrow UO_2 + 2H_2 \qquad (2)$$

$$4U + 4H_2O \rightarrow 2UO_2 + H_2 + 2UH_3 \qquad (3)$$

$$2UH_3 + 4H_2O \rightarrow 2UO_2 + 7H_2 \qquad (4)$$
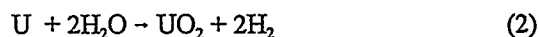
Both the oxic and anoxic reactions most likely occur simultaneously. However, the kinetics of the anoxic reaction are much faster than the oxic one. The principal difference between oxic and anoxic uranium corrosion is the formation of uranium hydride (UH_3) and hydrogen (H_2) in the latter.

Recent uranium corrosion studies of three irradiated EBR-II blanket fuel segments submerged in simulated J-13 well water showed that the rapid release of ^{137}Cs and ^{90}Sr after an initial slower leaching period can occur.[3] In addition, a vessel containing one of the segments became pressurized, so that when it was uncapped for sampling, gas and leachate spewed out. In all probability the gas

was hydrogen. When these tests were terminated, two out of the three corrosion products contained UH_3. The tests described below were performed with unirradiated samples to minimize any possible effects of irradiation, and were designed specifically to quantify hydrogen evolution throughout the corrosion process.

IV. EXPERIMENTAL

Three unirradiated EBR-II blanket fuel segments were sliced from a larger piece into approximately the same lengths. They each measured 1.11 cm in diameter with an average length of about 0.66 cm. Each segment was placed in individual 45 mL Parr pressure bombs equipped with gas sampling ports. Into each vessel was poured enough SJ-13 well water to equal a sample surface area to leachant volume (S/V) ratio of 12 m^{-1}. The initial pH of the SJ-13 well water was 8.65.

The SJ-13 water was pre-prepared and consisted of the compounds in concentrations listed in Table 1.

Table 1. Chemical additives for the SJ-13 well water.

Compound	Concentration mg/L
NaHC	180
$KHCO_3$	14
$CaCl_2 \cdot 2H_2O$	12.3
$Ca(NO3)_2 \cdot 4H_2O$	19.8
$CaSO_4 \cdot 2H_2O$	20.6
$MgSO_4 \cdot 7H_2O$	18
$SiO_2 \cdot H_2O$	85

The Parr pressure vessels were placed in a 90°C oven and allowed to accumulate pressure. Periodically, the vessels were sampled for gas using the apparatus shown in Figure 1. This is a photograph of the gas manifold onto which is attached a Parr pressure bomb, a 25 mL gas collection cylinder, two pressure transducers connected to a digital readout meter, and an outlet for evacuating the apparatus of residual gases between sampling intervals. The pressure range for the transducers were 0-50 psig and 0-500 psig respectively.

Initially, at each sampling interval, the vessels were opened and 4 mL aliquots of the SJ-13 water were taken to measure dissolved O_2 and the pH. The missing leachate was then replaced with fresh leachant and the vessels were recapped and again placed in the 90°C oven. The O_2 and pH measurements were discontinued after the first few sampling intervals for reasons discussed briefly in Section IV.

When the gas had been analyzed for composition, whether through GMS or GC, the moles of H_2 present were calculated taking into account that the total pressure shown on the meter was the sum of the partial pressures contributed by all gas species present in the headspace of the vessels. This phenomenon is defined mathematically by *Dalton's Law of Partial Pressures* which states that the partial pressure of each gas in an ideal gas mixture is equal to its mole fraction times the total pressure and is represented by the following expression:

$$P_H = X_H P \qquad (5)$$

where, in this case, P_H is the partial pressure of H_2 and X_H is the fraction of H_2 found in the gas sample when analyzed by GMS and GC.

Upon determining the partial pressure due to H_2, the number of moles of H_2 could then be calculated using the ideal gas equation defined as

$$P_H V = n_H RT \qquad (6)$$

From this data, the grams of uranium metal consumed by the corrosion process could also be directly calculated, assuming that equation (2) was obeyed and no UH_3 was formed.

V. RESULTS AND DISCUSSION

A. O_2 and pH Measurements of The SJ-13 Water

O_2 and pH measurements were taken of the SJ-13 water for the first several sampling periods. And, in order to have a baseline to compare with these results, the O_2 level and the pH was measured on a blank sample of the SJ-13 water. The initial O_2 level was 90.5% of air saturation and the pH was 8.65.

One can see from Table 2 that amount of O_2 decreased appreciably by the first sampling period nine days after the experiment had begun.

Although the overall O_2 concentrations in the leachates had dropped substantially from the baseline reading by day nine, they appeared to have leveled off after which no discernable decreases were observed. According to the reaction shown in equation (1), one would have expected the O_2 levels to continue to decline until all of the O_2 was consumed. The only conclusion drawn from these observations was that, although
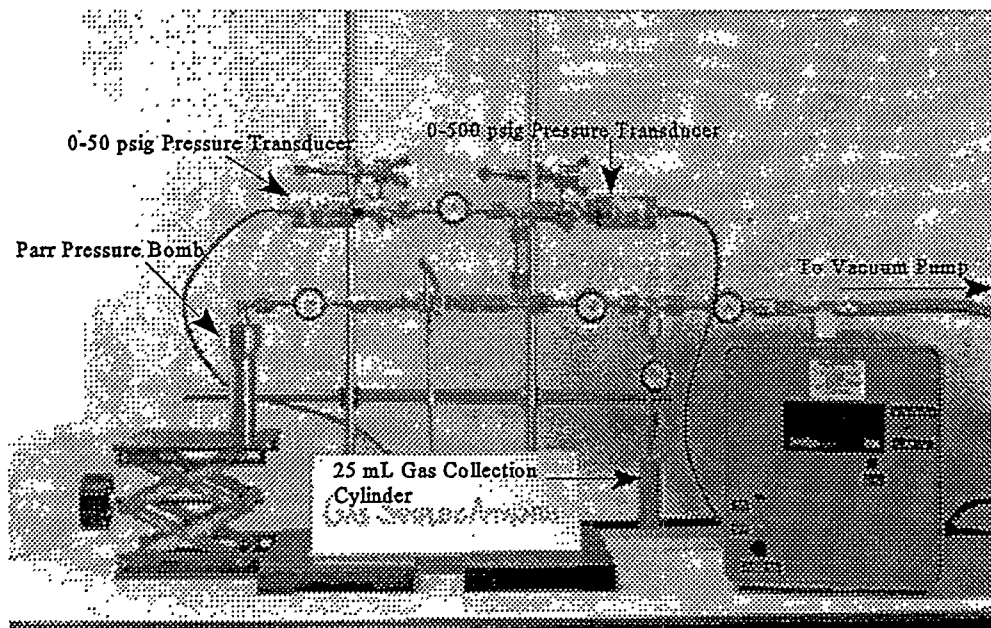
Figure 1. Gas Sampling Apparatus

Table 2. Dissolved O_2 measurements for the depleted uranium leachates.

Day	Sample 1		Sample 2		Sample 3	
	%O_2	mg O_2/ g H_2O	%O_2	mg O_2/ g H_2O	%O_2	mg O_2/ g H_2O
9	39.1	1.8E-2	33.5	1.5E-2	35.3	1.6E-2
14	54.9	2.5E-2	46.3	2.1E-2	47.0	2.1E-2
21	NA	NA	NA	NA	36.0	1.6E-2

Table 3. pH measurements of the leachates.

	pH of SJ-13 Aliquots (initial = 8.65)		
Day	Sample 1	Sample 2	Sample 3
9	9.95	10.21	10.02
14	10.38	10.21	9.92
21	NA	NA	9.84
23	10.38	10.38	9.87
81	NA	NA	9.79

precautions were taken to avoid exposing the leachates to air during sampling intervals, they nonetheless absorbed some atmospheric oxygen. To substantiate this hypothesis, a simple experiment was performed to roughly determine the rate of O_2 uptake in a sample of deaerated water. To retain experimental consistency, the same sampling techniques and environmental conditions were applied to the test water sample as was for the actual samples. Surprisingly enough, the rate of O_2 uptake was fairly rapid at 4.5×10^{-3} mg O_2/min or 3.3% O_2 saturation increase per minute (at 635.8 Torr and 12°C).

Table 3 shows the pH results. One can see that the pH rose significantly at the onset of the experiment and remained fairly constant afterwards.

This phenomenon was addressed by assessing the quality causing the increase in pH, ergo increase in basicity. First, the dynamics behind the change in pH could only be attributed to chemical events occurring within the vessels. These events include the reactions expressed in equations 1-4. Second, it is also known that the mechanism for UO_2 formation indicated in equations 1-4 involves the formation of OH^- ions.[2,4] Third, from this information, one can further consider that one of the fundamental definitions of a basic solution requires that it contains more hydroxyl ions (OH^-) than protons (H^+). And finally, one can deduce that there was an increase in OH^- content in the leachate, hence, an increase in pH. The limitation of pH increase indicated that a chemical equilibrium between leachate and uranium metal had occurred.

B. Oxygen Depletion From the Gas in the Vessel Headspace

The pressure changes in the vessels were measured over time and the gas product was analyzed for the first three sampling intervals by GMS. Ultimately however, all gas samples were analyzed by GC. During the first two sampling intervals (day 9 and 14), the three vessels were opened in order to obtain aliquots of the SJ-13 water (for both the pH and the dissolved O_2 measurements). On day 21, the third vessel alone was opened for sampling. And, again on day 23, all three vessels were again opened to obtain leachate samples. The first several times the gas product was analyzed, although hydrogen was present as the major component, nitrogen, oxygen, and trace argon, the main constituents of air, were also seen. This was not surprising considering that every time a vessel was uncapped for leachate sampling, air would fill the empty volume above the leachate thus reintroducing air into the vessel. However, over time, when the vessels were no longer uncapped for leachate sampling, the other gases were eventually diluted down to non-detectable limits. At this point, hydrogen was the only accountable gas present.

While yet detectable, O_2 and N_2 ratios found in the gas samples were significantly lower than normally found in air. The O_2/N_2 ratio in air is approximately 20:78 (0.256). Table 4 shows the average O_2 to N_2 ratios calculated from the data obtained during the first three gas sampling intervals. One can see that these values were appreciably lower than expected. Essentially, the O_2 had been 'removed' from the headspace above the leachates.

This data is evidence that O_2, which was reintroduced into the vessels each time they were opened for leachate sampling, was being consumed by the corrosion of uranium.

Table 4. Average O_2/N_2 mole percent ratios found in gas samples.

Day	Average O_2/N_2
9	0.003
14	0.001
21	0.002

C. Hydrogen Generation

Figure 2 shows the quantity of hydrogen produced throughout the course of the experiment. Notice that Samples 2 and 3 correlated quite closely in their behavior, whereas Sample 1 performed differently.
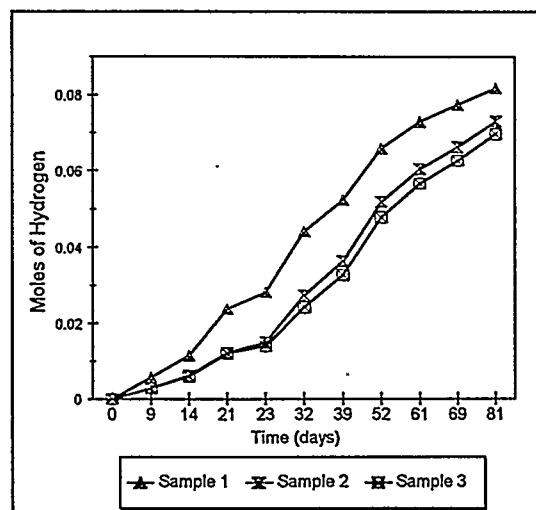

Figure 2. Moles of hydrogen

Initially, after day 9, H_2 production in Sample 1 was 50 % greater than in either Sample 2 or 3. However, by day 81, the accumulated amount of H_2 produced by Sample 1 exceeded Sample 2 by only 5 % and Sample 3 by 15 %. The rate of H_2 production in both Samples 2 and 3 had increased appreciably during this time.

D. Corrosion Rate of The DU Blanket Material

The hydrogen data was used to calculate the mass of uranium metal that had reacted in each sample assuming all of the H_2 was liberated as shown in equation (2). These results are listed in Table 5. After 81 days, it can be seen that, on average, three-quarters of the total uranium in these samples had corroded. However, these values are based upon the assumption that the only compound present in the reaction product was UO_2 and do not include the quantity of uranium metal that may have reacted to form UH_3. It is impossible to quantify UH_3 from the H_2 data alone. Therefore, if any hydrogen was present in the form of UH_3, then a negative bias would be associated with all of the calculated uranium values listed in Table 5.

Hence, going on the assumption that these numbers are accurate, Figure 3 represents the uranium corrosion mass curves for the three samples as well as the averaged linear regression curve from which has been derived a reaction rate of 32.2 $mg/cm^2/day$.

Table 5. DU corrosion data after 81 days.

Sample #	Original Weight (grams)	Mass of Uranium Corroded (grams)	Percent of Sample Corroded
1	11.996	9.7	80.9
2	12.029	8.7	72.3
3	11.123	8.3	74.5

Only the averaged data from day 9 through day 69 was included in the derivation of the regression curve because the H_2 production rate remained fairly constant during this time frame. Beyond day 69, the rate began to wane as shown by the graphed data.
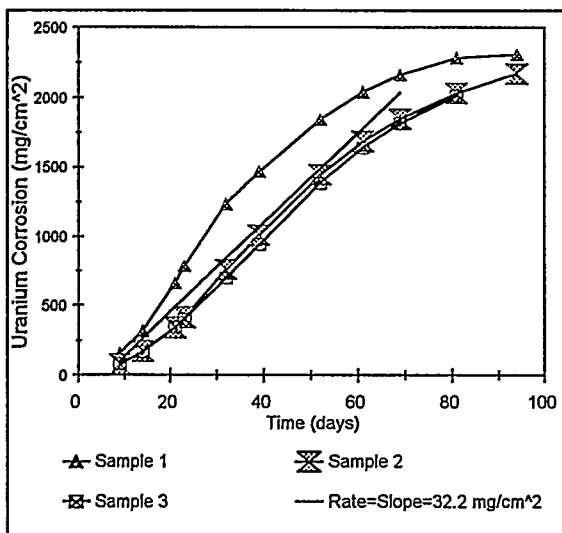

Figure 3. Uranium corrosion curves for the three DU segments

The calculated corrosion rate obtained from this work corresponds very closely to a compilation of uranium aqueous immersion studies conducted at temperatures below 302°C.[5] This yielded the following expression

$$\ln k = 22.34 - 7989T \qquad (7)$$

where k = U corrosion rate constant=1.4 mg/cm²/hr, and T = Temperature (K)=363.

The rate constant cited above is in close agreement with the rate determined from this study (1.34 mg/cm2/hr).

E. Analysis of Corrosion Product

Day 81 was the final gas sampling interval for the vessel containing sample number 3. Figure 3 shows that the uranium corrosion rates were essentially identical for both samples 2 and 3. Based upon this observation, the decision to terminate the gas sampling of one of the two samples was made. Sample 3 was chosen. The remaining two vessels were allowed to continue to further generate H_2. This process is still ongoing an will be stopped when all of the available uranium metal has oxidized. The choice to prematurely stop the experiment for only one sample was made to observe any differences that may exist between the partially and totally oxidized material.

After the contents of the vessel had been filtered and the oxidation product was still water saturated, its visual appearance was that of a dark, brown, clay-like substance. However, after drying in air for several days, the product was predominately a fine, black powder. A portion of this material can be seen in Figure 4. While most of the sample consisted of the black powder, there were pieces of agglomerated chunks which could be easily broken up. A very small piece of the original sample remained. This is consistent with the data in Table 5 since about 25 % was calculated to be yet uncorroded. However, the remaining sample retained its original cylindrical geometry and was completely covered by a solid black coating.

A small portion of the black powder (about 40 mg) was taken and further pulverized to a fine powder. This small sample was subsequently submitted for XRD analysis to determine the phases present within this product.

The resulting diffraction pattern shown in Figure 5 shows only UO_2 or U_3O_7 (UO_{2+x}). It is difficult to distinguish x-ray patterns of the oxides of uranium because they are very similar. And, even if other higher molecular weight uranium oxides were present in this sample, one could never resolve the peaks due to their broad nature.
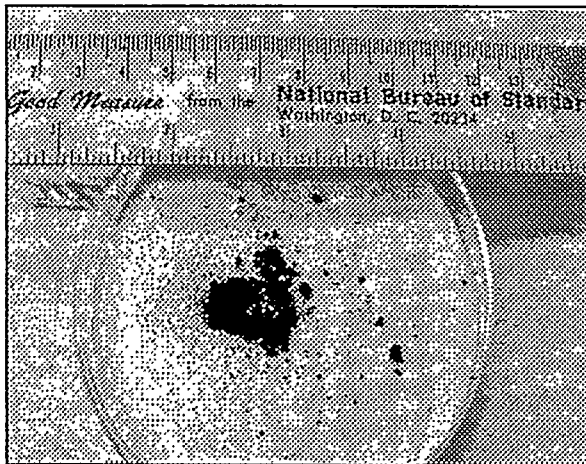
Figure 4. Corrosion product from Sample 3

It is also apparent that this sample contained no detectable UH_3. Gray reported only UO_2 product from the N-Reactor spent fuel flowthrough tests.[6] Yet others have reported the presence of UH_3 in the uranium aqueous corrosion product.[1,3] It is difficult to determine why uranium corrosion product sometimes contains UH_3, and other times none.
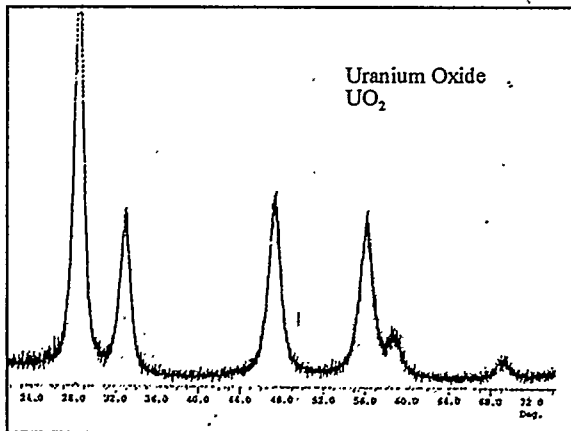

Figure 5. Uranium oxide XRD pattern

F. Mass Balance for Sample 3 Corrosion
   Product

Prior to the XRD analysis all of the solid material was weighed. The final weight was 12.4 g. As indicated from the XRD pattern in Figure 5, the corrosion product contained only oxide. It was now apparent that this sample contained no hydride, therefore, all of the uranium that had reacted should have converted to its respective oxide. Hence, the 8.3g

of uranium metal reported to have reacted by day 81 (Table 5) should have reacted stoichiometrically with water to form 9.42 g of UO_2. This would increase the total mass of the material to 12.24 g which translates to a gain of 1.12 g. The difference between the weighed value (12.4 g) and the experimental H_2 derived value (12.24g) is less than 1.5 %.

VI. CONCLUSION

Depleted, unirradiated uranium metal undergoes rapid anoxic oxidation on 90°C water. The average uranium corrosion rate of 1.34 mg/cm^2/hr obtained from these experiments coincides very closely with the average anoxic uranium corrosion rate of 1.4 mg/cm^2/hr determined by other researchers. The quantity of hydrogen produced during corrosion closely matched that predicted for anoxic corrosion. No uranium hydride was produced in the corrosion product of the sample analyzed.

It is shown that stoichiometric metal loss rate during uranium aqueous oxidation can be derived from hydrogen off-gas measurements. However, this is true only if the corrosion product does not contain UH_3.

REFERENCES

1. T.C. Totemeier, R.G. Pahl, S.L. Hayes, S.M. Frank, "Metallic Uranium ZPPR Fuel: Corrosion Characteristics and Corrosion Product Oxidation Kinetics", Argonne National Laboratory, Idaho Falls, Idaho (1997).

2. C.A. Colmenares, "Oxidation Mechanisms and Catalytic Properties of the Actinides", *Prog. Solid St. Chem.*, 15, 257 (1984).

3. J. E. Fonnesbeck, J. R. Krsul, S.G. Johnson, "EBR-II Blanket Fuel Leaching Test Using Simulated J-13

Well Water," *Proc. Third Topical Meeting on DOE Spent Nuclear Fuel and Fissile Materials Management*, Charleston, SC, September 8-11, 1998, 2, p. 715, American Nuclear Society, La Grange Park, Illinois (1998).

4. S. Orman, "Oxidation of Uranium and Uranium Alloys," *Physical Metallurgy of Uranium Alloys.* J.J.

   Burke, ed. 815-833, Brook Hill Publishing Company (1974).

5. B. Hilton, "Review of Rate of Reaction of DOE Spent Nuclear Fuel in Oxygen, Water Vapor, and Water. PART I" Report No. NSNF-195 (2000). IN PRESS.

6. W.J. Gray and R.E. Einziger, "Initial Results from Dissolution Rate Testing of N-Reactor Spent Fuel Over a Range of Potential Geologic Repository Aqueous Conditions", Pacific northwest national Laboratory, Richland, Washington (1998).

ARGONNE
NATIONAL
LABORATORY

Intra-Laboratory Memo

March 3, 2000

TO: Valerie Gaines · PRS, ANL-E

FROM: Tami Taylor · ED Publication Representative

SUBJECT: Publication for Clearance

The publication titled, "QUANTITATIVE ANALYSIS OF HYDROGEN GAS FORMED BY AQUEOUS CORROSION OF METALLIC URANIUM" has been enclosed (three copies) with the necessary form for review and clearance.

Thank you for your prompt assistance.

Enclosure

Distribution
Author
Publication File A-JF-003
RF