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Spent Nuclear Fuel Project Recommended Reaction Rate Constants for Corrosion of N-Reactor Fuel

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Page 1

Spent Nuclear Fuel Project Recommended Reaction Rate Constants for Corrosion of N-Reactor Fuel.

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W. J. F. J. J. J.

J.R. Frederick
6/11/98

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SPENT NUCLEAR FUEL PROJECT RECOMMENDED REACTION RATE CONSTANTS FOR CORROSION OF N-REACTOR FUEL

1.0 SUMMARY

The U.S. Department of Energy (DOE) established the Spent Nuclear Fuel Project (SNF Project) to address safety and environmental concerns associated with deteriorating spent nuclear fuel presently stored in the Hanford Site's K Basins. The SNF Project has been tasked by the DOE with moving the spent N-Reactor fuel from wet storage to contained dry storage in order to reduce operating costs and environmental hazards. The chemical reactivity of the fuel must be understood at each process step and during long-term dry storage.

Normally, the first step would be to measure the N-fuel reactivity before attempting thermal-hydraulic transfer calculations; however, because of the accelerated project schedule, the initial modeling was performed using literature values for uranium reactivity. These literature values were typically found for unirradiated, uncorroded metal. It was fully recognized from the beginning that irradiation and corrosion effects could cause N-fuel to exhibit quite different reactivities than those commonly found in the literature.

Even for unirradiated, uncorroded uranium metal, many independent variables affect uranium metal reactivity resulting in a wide scatter of data. Despite this wide reactivity range, it is necessary to choose a defensible model and estimate the reactivity range of the N-fuel until actual reactivity can be established by characterization activities.

McGillivray, Ritchie, and Condon developed data and/or models that apply for certain samples over limited temperature ranges and/or reaction conditions (McGillivray 1994, Ritchie 1981 and 1986, and Condon 1983). These models are based upon small data sets and have relatively large correlation coefficients.

R. J. Pearce conversely regressed a large number of uranium reactivity constants determined by many investigators over wide ranges of temperature and partial water pressure (Pearce 1989). The Pearce equations have lower correlation coefficients, because of the wide range of foundational data, than the McGillivray, Ritchie, and Condon equations. Nevertheless, Pearce's equations are considered more robust, since they cover a very wide range of moisture and temperature parameters. Despite the difference in correlation coefficients, all of these models give very similar calculational results.

The Pearce model has been chosen as the base case for modeling because of its robustness and simplicity. It represents average uranium reactivity values for unirradiated and uncorroded metal over wide reactivity ranges.

Until more characterization data becomes available, N-fuel reactivity modeling will use the Pearce-Arrhenius model with the pre-exponential factor increased by a factor of ten. An increase in the preexponential factor is justified by increases in the surface area from irradiation and corrosion processes.

Aqueous corrosion roughens and pits the metal surface and in oxygen limited environments creates uranium hydride as well as the oxides. This uranium hydride is incorporated into the metal surface as well as the oxide surface layer. According to Condon (1983), uranium hydride forms by interfacial precipitation within the first few microns of metal. Bloch and Mintz (1982) show that hydride precipitates at the surface of uranium metal and is not a bulk precipitation phenomena.

One may calculate a five to 20 fold increase in initial surface area resulting from surface alterations and the presence of hydride depending upon the initial assumptions. Tyfield (1988) shows an approximate order of magnitude increase in uranium metal reactivity for swollen fuel caused by irradiation effects. The combination of corrosion and irradiation could potentially increase the metal reactivity by a factor of 200 or more. It is believed that an overall average of 10 is an appropriate factor for N-fuel until more characterization data becomes available.

This factor of 10 will significantly increase the heat generation and hydrogen production rates within the MCO. Not enough N-fuel reactivity measurements have been made to determine if corrosion processes have changed the activation energy. When sufficient information becomes available from the characterization program, further changes to the pre-exponential factor and to the activation energy may be required. A more detailed discussion of these factors is found in Section 4.0.

2.0 RECOMMENDED RATE EQUATIONS

For ease of reference, the recommended rate equations for unirradiated and uncorroded uranium metal are gathered and summarized below. The derivations for these equations and expanded discussions occur in the appropriate sections. Units in these expressions refer to linear kinetics and are given in mg(wt gain)/cm²/hr unless otherwise noted.

P is the partial water pressure in kPa and T is in K.

1. Dry Air (<10-15 vppm H₂O)

$$\begin{aligned} \text{(Pearce 1989)} \quad (T < 597 \text{ K}) (R^2 = 0.86) \\ \text{Log K} = 8.9464 - 4638.2/T \end{aligned} \quad (1)$$

$$\begin{aligned} \text{(Pearce 1989)} \quad (T > 597 \text{ K}) (R^2 = 0.88) \\ \text{Log K} = 28.381 - 7\text{Log}[T] - 4638.2/T \end{aligned} \quad (2)$$

2. Moist Air

$$\begin{aligned} \text{(Ritchie 1986)} \quad (T < 373 \text{ K}) (11-75\% \text{ RH}) \\ \text{Log K} = 13.8808 - 5769.9/T \end{aligned} \quad (3)$$

$$\begin{aligned} \text{(Pearce 1989)} \quad (T < 373 \text{ K}) (100\% \text{ RH}) \\ \text{Log K} = 8.333 - 3730/T \end{aligned} \quad (4)$$

$$\begin{aligned} \text{(Pearce 1989)} \quad (373 < T < 463 \text{ K}) (<100\% \text{ RH}) \\ \text{Log K} = 10.566 - 4990/T + 0.3 \text{ Log}[P] \end{aligned} \quad (5)$$

$$\begin{aligned} \text{(Pearce 1989)} \quad (T > 463 \text{ K}) (<100\% \text{ RH}) \\ \text{Log K} = 6.1931 - 2963/T + 0.3 \text{ Log}[P] \end{aligned} \quad (6)$$

3. Oxygen Free Water Vapor

$$\begin{aligned} \text{(Ritchie 1981)} \quad (T < 373 \text{ K}) \\ \text{Log K} = 7.634 - 3016/T \end{aligned} \quad (7)$$

$$\begin{aligned} \text{(Pearce 1989)} \quad (T < 523 \text{ K}) \\ \text{Log K} = 4.33 - 2144/T + 0.5 \text{ Log}[P] \end{aligned} \quad (8)$$

$$\begin{aligned} \text{(Hayward 1994)} \quad (523 < T < 735 \text{ }^\circ\text{K}) (43-93 \text{ kPa H}_2\text{O}) \\ \text{Log K} = -22.915417 + (30066.5/T) - 9.119078 * 10^6/T^2 \end{aligned} \quad (9)$$

(Hayward 1994) ($735 < T < 923$ °K) (43-93 kPa H₂O)
 $\text{Log } K = -23.905197 + (42718.8/T) - 1.787581 * 10^7/T^2$ (10)

4. Carbon Dioxide

(Pearce 1989) ($723 < T < 945$ °K)
 $\text{Log } K = 6.746 - 5602/T$ (11)

(Pearce 1989) ($945 < T < 1173$ °K)
 $\text{Log } K = 10.221 - 8885/T$ (12)

3.0 GENERAL RATE EQUATIONS

3.1 PEARCE REVIEW, 1989

Many independent variables affect the observed reaction rates. The most important variables are temperature, diffusion rates, time, oxygen partial pressure, water vapor partial pressure, degree of corrosion, degree of irradiation-induced swelling, and the metal purity. N-Reactor fuel is not pure uranium metal but is, instead, an alloy with the following composition:

Al 700-900 ppm
Fe 300-400 ppm
C 365-375 ppm
Cu < 75 ppm
Si < 124 ppm
Ni < 100 ppm
Zr < 65 ppm
Cr < 65 ppm

No clear correlation or trend exists below 300 °C for a change in the corrosion rate with minor element concentrations. Above 500 °C, it has been shown that increasing the aluminum concentration leads to an order of magnitude increase in the corrosion rate.

Since the linear corrosion rate is related exponentially to the absolute temperature in an Arrhenius relationship, changes in temperature strongly affect the corrosion rate.

Time (or perhaps more accurately, the oxide thickness, which is a function of time) is also an important parameter affecting the corrosion rate. A typical corrosion rate, as a function of time graph, is presented in Figure 3-1.

Figure 3-1. Uranium Metal Corrosion as a Function of Time.

The corrosion rate is initially quite rapid with the weight gain raised to a power of 2 or 3 as a function of time. The gradual decrease in the corrosion rate from the initial very high value is caused by the growth of an oxide scale that restricts access of water and oxygen to the metal surface. This oxide scale eventually begins to slough off as the scale reaches 50-100 microns in thickness and eventually reaches an equilibrium thickness wherein its slough rate equals its formation rate. Beyond this point, the corrosion rate becomes constant and the curve becomes linear.

If corrosion rates are determined before the linear rate is established, the reported rate may be quite different than the true linear rate.

The oxygen partial pressure affects the reaction rate. The oxygen partial pressure effect can be divided into two factors. The first is the direct effect on the reaction of oxygen gas with uranium metal. The direct reaction rate due to oxygen is proportional to the square root of the oxygen pressure initially. As the surface begins to saturate, the oxygen reaction slows until

eventually the surface saturates and the reaction rate becomes insensitive to further oxygen pressure increases.

Oxygen exerts a strong indirect effect upon the water corrosion rate. Below 100 ppm oxygen for very pure metal, or 1000 ppm oxygen for metal containing 0.1% aluminum, water corrodes uranium metal at a very high rate. If the oxygen is increased significantly above these levels, the water corrosion rate is decreased by several orders of magnitude at ambient temperature, and the reaction is said to have become oxygen poisoned.

Water vapor also is absorbed upon the oxide surface in a Langmuirian fashion and between 2% relative humidity (RH) and 90% RH, the reaction rate only increases modestly. Above 90% RH, the reaction rate increases exponentially until it reaches the water saturation rate. The reaction rate of liquid water is essentially the same as the reaction rate of gas saturated with water vapor.

The degree of corrosion can affect the reaction rate by increasing the true reactive surface beyond the geometric surface, and by potentially altering the nature of the metal so that the activation energy is changed. This latter effect is not yet well documented experimentally.

The degree of irradiation induced swelling can also alter the reaction rate by increasing the true reactive surface area. This effect was noted by S. P. Tyfield (1988). M. J. Bennett's data for very swollen fuel elements showed significant changes to the activation energy as well (Bennett 1974).

Uranium metal purity also plays a role in the corrosion rate. Tyfield (1988) shows that 0.1 wt% aluminum decreases the low temperature corrosion rate by an approximate order of magnitude. Conversely, Schnizlein (1966) records an increase in the oxidation rate for 0.1 wt% aluminum alloyed uranium metal at or above 400 °C. No clear explanation is available for these conflicting trends, however, it may be noted that in the presence of water vapor, hydriding is the primary rate controlling corrosion mechanism below 400 °C, and oxidation is the primary rate controlling mechanism above 400 °C. The presence of aluminum may affect these mechanisms differently.

For all of these reasons, rate data from various authors may range over several orders of magnitude for a given temperature. The scatter in the rate constant data for dry air is illustrated in Figure 3-2.

Figure 3-2. Reaction Rate Constants in Dry Air.

Pearce reviewed data from many authors and regressed their data to obtain equations describing the rate constants as a function of temperature. These equations are presented below. Pearce's approach is useful for predicting an average reaction rate for uncorroded, unirradiated uranium metal, and in defining the range of measured reaction rate constants. All expressions refer to linear kinetics and the units of K are $\text{mg}(\text{wt gain})/\text{cm}^2/\text{hr}$.

Pressure (P) is the water vapor pressure in kPa.

1. Dry Air (<10-15 vppm H_2O)

$$\begin{aligned} (T < 597 \text{ }^\circ\text{K}) \\ \text{Log K} = 8.9464 - 4638.2/T \end{aligned} \quad (13)$$

correlation coefficient is ($R^2 = 0.86$)

$$\begin{aligned} (T > 597 \text{ }^\circ\text{K}) \\ \text{Log K} = 28.381 - 7\text{Log}[T] - 4638.2/T \end{aligned} \quad (14)$$

correlation coefficient is ($R^2 = 0.88$)

2. Moist Air

$$\begin{aligned} (T < 373 \text{ }^\circ\text{K}; 100\% \text{ RH}) \\ \text{Log K} = 8.333 - 3730/T \end{aligned} \quad (15)$$

$$\begin{aligned} (T < 463 \text{ }^\circ\text{K}; <100\% \text{ RH}) \\ \text{Log K} = 10.566 - 4990/T + 0.3 \text{ Log}[P] \end{aligned} \quad (16)$$

$$\begin{aligned} (463 < T < 605 \text{ }^\circ\text{K}; <100\% \text{ RH}) \\ \text{Log K} = 6.1931 - 2963/T + 0.3 \text{ Log}[P] \end{aligned} \quad (17)$$

3. Oxygen Free Water Vapor

$$\begin{aligned} T < 523 \text{ }^\circ\text{K} \\ \text{Log K} = 4.33 - 2144/T + 0.5 \text{ Log}[P] \end{aligned} \quad (18)$$

for 43 kPa steam at 523 °K to 93 kPa steam at 923 °K

$$\begin{aligned} (\text{Hayward 1994}) (523 < T < 735 \text{ }^\circ\text{K}) \text{ by regression analysis} \\ \text{Log K} = -22.915417 + (30066.5/T) - 9.119078 * 10^6/T^2 \end{aligned} \quad (19)$$

(Hayward 1994) ($735 < T < 923 \text{ }^{\circ}\text{K}$) by regression analysis

$$\text{Log } K = -23.905197 + (42718.8/T) - 1.787581 \times 10^7/T^2 \quad (20)$$

Equations 12 through 19 are displayed graphically in Figure 3-3. This figure shows that the water enhanced reaction rates are typically higher than the dry air rate below $330 \text{ }^{\circ}\text{C}$. Beyond $330 \text{ }^{\circ}\text{C}$, the dry air rate is faster than the moist air rate.

Figure 3-3. Dry Air, Moist Air, and Pure Water Reaction Rate Constants.

Equations 17, 18, and 19 are presented graphically in Figure 3-4. This graph shows that up to 90 kPa, the water corrosion rate of uranium metal is capped at 70 mg O₂/cm²/hr at 330 °C. The reduction in rate beyond 330 °C is attributed to two factors. The first is the instability of uranium hydride above this temperature, and the second is the decrease in lattice defects for uranium oxide formed at higher temperatures.

Figure 3-4 has important implications for the SNF Project since one may argue that in a pure water atmosphere at 1 bar or less pressure, the reaction rate does not increase over the temperature range 330-650 °C.

Figure 3-4. Water Corrosion Rates at 50-90 kPa.

5. Carbon Dioxide

The rate constants for reaction with carbon dioxide are:

$$\begin{aligned} (T = 723 < T < 945 \text{ }^{\circ}\text{K}) \\ \text{Log K} = 6.746 - 5602/T \end{aligned} \quad (21)$$

above 945 °K, a change in mechanism occurs possibly wherein carbon dioxide migrates through the oxide by gaseous diffusion.

$$\begin{aligned} (945 < T < 1173 \text{ }^{\circ}\text{K}) \\ \text{Log K} = 10.221 - 8885/T \end{aligned} \quad (22)$$

The rate constants for reaction of uranium metal with nitrogen are very low and not defined below 350 °C. At 800 °C, the rate constant is 4 mg (wt gain)/cm²/hr.

Rate constants for reaction of uranium nitride with oxygen and water vapor are not given by Pearce, but the statement is made that their reactivities to oxygen and water vapor are similar to the reactivities of uranium hydride.

4.0 EFFECTS OF IRRADIATION AND CORROSION

4.1 IRRADIATION EFFECTS

Uranium metal can be altered in a number of ways during reactor irradiation. These alterations affect the subsequent corrosion reactivity. During irradiation, the collision of high energy particles with the uranium nuclei can move the nuclei from their natural metallic lattice locations. From the energetic collisions, the uranium atoms gain a large amount of energy. If the displaced atom does not return to a natural lattice site, most of this energy is dissipated quickly as heat but a small fraction is retained. This means that these displaced atoms reside in a higher potential energy well and are therefore more chemically reactive than their counterparts that occupy natural lattice sites. Secondly, lattice defects increase the solubility and diffusivity of monatomic hydrogen within the metal, thereby increasing its aqueous corrosion rate.

Tyfield investigated the relationship between irradiation and uranium metal corrosion rates (Tyfield 1988). He assumed that the increase in reactivity exhibited by the irradiated metal could be correlated strictly to an increase in the metallic surface area and that the basic Arrhenius relationship could be modified from:

$$K_o = B * \text{Exp}[-E/RT] \quad (23)$$

to:

$$K_m = (V_i/V_o)_n * B * \text{Exp}[-E/RT] \quad (24)$$

Where K_o is the rate constant for unirradiated metal, K_m is the rate constant for irradiated metal, V_i is the irradiated volume, V_o is the unirradiated volume, and n is the index relating the ratio of surface areas to the ratio of volumes. Tyfield found $n = 6$ for the first linear reaction period, and 9 for the second.

Tyfield stated that a change in the activation energy as a function of irradiation induced swelling was theoretically possible, but found no experimental evidence for a change. Most of Tyfield's samples ranged from 0 to 20% swollen, with a few up to 33-43%. Since the preponderance of his samples were not highly swollen, this may have influenced his conclusions.

The data of Tyfield (1988), Zima (1960), and of Bennett (1974), all point to the conclusion that the activation energy is not significantly changed for material swollen 20 % or less. An analysis of Bennett's data however shows that the activation energies for 0%, 56%, and 79% swollen fuel are 16.9, 11.6, and 1.1 kCal/mole, respectively. One may therefore expect highly swollen fuel to exhibit quite different corrosion kinetics than unirradiated or low swollen fuel.

Since N-fuel swelling is not expected to exceed 10%, it is concluded that irradiation swelling will not change the activation energy for corrosion.

4.2 AQUEOUS CORROSION EFFECTS

Aqueous corrosion saturates the metal with monatomic hydrogen. Over time, this hydrogen precipitates as the hydride within the uranium metal surface and along the intergranular boundaries. The formation of hydride directly increases the reactive surface area since hydride has a specific surface area of 1 square meter per gram. Over long time periods, intergranular corrosion occurs as hydride forms in the grain boundaries. Extensive intergranular corrosion wedges the grains apart. These corrosion processes have the net effect of roughening the surface so that ridges, pits, cracks and hills appear on the surface. Surface roughening increases the surface area exposed to the corrosion process thereby increasing the corrosion rate.

Surface roughening also changes the activation energy for the corrosion process. Every metal atom is in a state of minimal strain energy when it occupies a metal lattice site and is completely surrounded by other metal atoms. As the corrosion process uncovers a given metal atom, its strain energy is proportional to the degree of uncovering. Therefore its strain energy is highest when it resides at the tip of a needle or along an acute ridge top. These highly strained atoms are much more reactive than atoms on a flat surface where they are at least 50% surrounded by other metal atoms.

All of these facts along with preliminary data from the characterization program indicate that the reactivity of corroded metal will be larger than for uncorroded uranium metal. Changes in reactive surface area can be accommodated by a simple multiplier used with the Pearce model. The irradiation/corrosion history of each fuel assembly or scrap fragment will be unique, and therefore, a different multiplier could be assigned to each sample. Characterization tests show that the multiplier value can range from 2 to 400. A value of 10 is reported as an average by the Characterization group.

Current characterization laboratory data shows an increase in the reactivity of the N-fuel that ranges from 2-400 times the reactivities predicted from the Pearce equations. From the quite limited characterization data obtained to date, an average factor of 10 may be used with the Pearce equations to describe the N-fuel. The maximum credible surface area that could be assembled in a given MCO is as yet uncertain.

5.0 MODELS THAT CAN BE CALIBRATED

Certain uranium corrosion models have been historically developed that use physical processes as their foundation. Ritchie and McGillivray assume that Langmuir absorption of gases at the uranium oxide surface controls the reaction rate. Condon develops a perfusion-precipitation model for the conversion of hydrogen gas to uranium hydride. Condon's model can be fitted to the water corrosion case by assuming that Langmuirian absorption of water vapor at the oxide surface is rate controlling.

Calibrateable models may prove useful, if the corrosivity of N-fuels proves to be markedly different than for uncorroded fuels. This usefulness stems from the fact that although Pearce needed hundreds of data points to build his regression model, a small number of experimental data points will allow a calibrateable model to describe N-fuel reactivity. For example, the Condon model requires only 5-6 data points to describe the reactivity of water vapor in oxygen-free gases over very wide temperature and relative humidity ranges.

The McGillivray model requires thermogravimetric analysis (TGA) as a function of water vapor partial pressure at five different temperatures to describe the reactivity of uranium with air at different relative humidities.

If the N-fuel corrosivity is markedly different than for unirradiated, uncorroded metal, and if the number of laboratory analyses are small, the use of these calibrateable models may be necessary.

5.1 RITCHIE'S REVIEW

Ritchie has shown that the corrosion rate can be represented by an Arrhenius equation of the form (Ritchie 1981 and 1986):

$$K = K_1 * \text{Exp}[-\Delta G/RT] \quad (25)$$

The Ritchie model is derived for both dry air and moist air oxidation processes. Below 100 °C in an oxygenated environment, the rate of oxidation of carefully prepared uranium samples is independent of humidity over wide ranges (4 - 90% RH).

Employing the simplest model of gas solid reaction, Ritchie proposes what appears to be a modified form of the Langmuir adsorption relationship to determine the dependence of the uranium-oxygen and uranium-water vapor reaction. According to the Langmuir theory of adsorption, the volume of adsorbed gas or vapor per unit mass of adsorbent is assumed to be proportional to the vapor pressure of the gas or vapor and the area of unreacted surface.

The relationship can be stated as:

$$V \propto P * S_{\text{unreacted}} \quad (26)$$

The unreacted surface can be determined from a knowledge of the volume of gas adsorbed to produce a monolayer on the adsorbent surface and the volume of gas actually adsorbed (V).

$$S_{\text{unreacted}} \propto V_{\text{max}} - V \quad (27)$$

then:

$$V \propto P * (V_{\text{max}} - V) \quad (28)$$

choosing the proportionality constant "b" with units 1/P

$$V = b * P * V_{\text{max}} - b * P * V \quad (29)$$

rearranging:

and

solving for V

$$V = b * P * V_{\text{max}} / (1 + bP) \quad (30)$$

where V is the volume of gas adsorbed per unit mass of adsorbent.

Inverting equation 30

$$1/V = (1 + bP)/b * P * V_{\text{max}} \quad (31)$$

If the rate of oxidation or of corrosion is proportional to the volume of adsorbed gas or vapor, by analogy, then equation 31 can be rewritten as:

$$1/k_p = (1 + b * P)/b * P * k_{\text{max}} \quad (32)$$

$$1/k_p = 1/b * P * k_{\text{max}} + 1/k_{\text{max}} \quad (33)$$

letting $1/b = \alpha$ where α is a constant independent of pressure

$$1/k_p = \alpha/P * k_{\text{max}} + 1/k_{\text{max}} \quad (34)$$

where k_p is the reaction rate constant at gas or vapor pressure "P" and $k_{\max}$ is the reaction rate constant as P goes to infinity.

Ritchie apparently uses a modified form of equation 34 reported as

$$1/k_p = 1/k_{\infty} + \alpha/P \quad (35)$$

where $k_{\max}$ does not appear as a coefficient of P.

In his 1986 paper, Ritchie describes a series of corrosion experiments carried out on a specimen of high purity depleted uranium. The paper is a report on the results of a combined experiment where the corrosion of uranium was studied as a function of relative humidity and sample surface preparation.

To evaluate humidity effects, the corrosion data from all surface treatment processes were averaged for each temperature condition and relative humidity.

To control relative humidity, Ritchie utilized saturated salt baths of NaCl, CaCl_2 , and MgCl_2 . By utilizing the boiling point elevation effect of the electrolyte solutions, Ritchie was able to control the relative humidity to three ranges: 17-19% RH, 23-32% RH and 74-75% RH for saturated solutions of CaCl_2 , $\text{Mg}(\text{Cl})_2$, and NaCl respectively. The results of the experiments are tabulated in Table 5-1 and plotted in Figure 5-1.

It can be seen from Figure 5-1 that when the natural log of the rate of corrosion is plotted against $1/T(^{\circ}\text{K})$ for a temperature range of 41 to 102 $^{\circ}\text{C}$, a straight line is obtained for relative humidities ranging from 17 to 75% where the relative humidities are averaged over the ranges 17-19% RH, 23-32% RH, and 74-75% RH (see Table 5-1).

Figure 5-1 Uranium Reactivity <100 °C (Ritchie 1986)

Table 5-1. Reaction Rates* versus Relative Humidity.

Temperature (°C)	Relative Humidity (%)		
	17 - 19	23 - 32	74 - 75
41	0.032	0.035	0.044
50	0.111	0.116	0.110
61	0.345	0.398	0.304
73	1.81	1.06	1.65
81	3.03	-	2.79
84	3.75	4.46	4.16
90	10.5	11.7	12.8
102	30.9	31.4	-

*Rate data in micrograms(wt gain)/cm²/hr

From the data in Table 5-1 and earlier literature data, Ritchie obtains the following correlation:

$$\ln K = 31.9618 - 13284/T \text{ (}\mu\text{g (wt gain)/cm}^2\text{/hr)}, \quad (36)$$

which converts to:

$$\log K = 13.8808 - 5769.69/T \text{ (mg (wt gain)/cm}^2\text{/hr)} \quad (37)$$

This rate equation is valid for a temperature range of 40-100 °C and is independent of humidity in the range RH = 11 to 75%.

Similarly, Ritchie derives the following equations below: are derived from Ritchie (1981), converting the reported rate constant units from mg U/cm²/hr to mg wt gain/cm²/hr assuming production of uranium dioxide.

(units are mg wt gain/cm²/hr and temperature in °K)

1. Dry Air

For (313 < T < 673 573),

the reported rate constant = $6.9 \times 10^8 \text{ Exp } (-18300/RT) \text{ mg Uranium/cm}^2\text{/hr}$

Where R = 1.987 cal/g mole/K.

Therefore, $K = [6.9 \times 10^8 \text{ Exp } (-9210/T)] (32/238 \text{ mg wt gain/mg Uranium})$ or

$$\log K = 7.968 - 4000/T \quad (39)$$

2. Water Vapor (oxyfree)

For ($293 < T < 373$ K 100% RH),
 the reported rate constant = $3.2 \times 10^8 \text{ Exp } (-13800/RT)$ mg Uranium/cm²/hr.
 Therefore, $\text{Log } K = 7.633 \text{ } 7.634 - 3016/T$ (40)

3. Water Vapor-Oxygen

For ($298 < T < 373$ K 100% RH),
 the reported rate constant = $4.6 \times 10^8 \text{ Exp } (-17800/RT)$ mg Uranium/cm²/hr.
 Therefore, $\text{Log } K = 8.791 - 3891/T$ (41)

From Equation (37),
 For ($273 < T < 373$ K 11-75% RH)
 $\text{Log } K = 13.8808 - 5769.9/T$ (42)

5.1.1 Conclusions

Ritchie predicts the corrosion of uranium metal in dry air, moist air, and in moist inert gas environments. Ritchie's results are considered accurate over the experimental conditions reported. Ritchie's temperature ranges are not as wide as those considered by Pearce, although within commonly shared temperature ranges, the results of both Pearce and Ritchie are comparable. For this reason, Pearce's results are taken as the base case, and Ritchie's equations are only used in those few cases where Pearce's results do not cover a particular humidity range.

If the characterization program shows that the activation energy for N-fuel has changed significantly from the Pearce data, it may be necessary to use a calibratable model such as Ritchie, to develop an N-fuel corrosion model.

5.2 MCGILLIVRAY MODEL

The McGillivray model is based on conditions where there is a relatively low relative humidity and temperatures ranging from 115 to 250 °C with data available for temperatures as high as 350 °C. In the McGillivray model, as with the Ritchie model, it is assumed that oxygen exists at a concentration of at least 1000 ppm. The McGillivray model predicts an observed corrosion rate constant of:

$$K = k_1 * P / (1 + k_2 * P) + D \quad (43)$$

Values of k_1 and k_2 and D are obtained from a series of curve fits to actual uranium corrosion data, as a function of water vapor pressure, where the corrosion data is obtained at

specific temperatures ranging from 115 to 250 °C. Corrosion data is available at temperatures up to 350 °C and that data does appear to show close correlation with the McGillivray formula (42).

McGillivray, like Ritchie, employs the simple Langmuir adsorption model to model the corrosion process in uranium. In contrast to Ritchie, McGillivray employs the Langmuir model as it is presented in most engineering or science text books (Hougen 1954 or Barrow 1961).

Defining $\bar{\theta}$ = fraction of surface covered and ignoring the change in heats of adsorption as a function of $\bar{\theta}$, the rate of evaporation of the adsorbed specie is proportional to $\bar{\theta}$; therefore, the rate of evaporation of the adsorbed species = $k_a \bar{\theta}$.

Similarly, the rate of condensation is proportional to the pressure of the adsorbing gas and the fraction of the surface that is not covered:

$$\text{so the rate of condensation} = k_b P(1 - \bar{\theta})$$

At equilibrium, these two rates are equal and:

$$k_a \bar{\theta} = k_b P(1 - \bar{\theta}) \quad (44)$$

Solving for $\bar{\theta}$

$$\bar{\theta} = k_b P / (k_a + k_b P) \quad (45)$$

by introducing $\alpha = k_a/k_b$, this result can be written

$$\bar{\theta} = P / (\alpha + P) \quad (46)$$

where α is the ratio of the adsorption coefficient/desorption coefficient.

Now McGillivray assumed that the reaction rate was proportional to the fraction of surface that was covered by the adsorbed gas (water in this case).

Reaction rate

$$= k_a \bar{\theta} = k_a (P / (\alpha + P)) \quad (47)$$

now by dividing through by α

and letting

$$k_1 = k_a / \alpha \text{ and } k_2 = 1/\alpha$$

Rate

$$= k_1 P / (1 + k_2 P) \quad (48)$$

Experimental results can be compared to Langmuirian theory most easily if θ is defined as the ratio of the gas adsorbed (Y) to the maximum amount of gas needed to form a monolayer (Y_m).

then

$$(Y/Y_m) = P/(a + P) \quad (49)$$

rearranging

$$P/Y = a/Y_m + P/Y_m \quad (50)$$

a plot of P/Y vs P will give a straight line for Langmuirian kinetics.

at low vapor pressures $k_2 P \ll 1$

and at high vapor pressures $k_2 P \gg 1$, and

the condition where $k_2 P \gg 1$ the rate is defined as $\text{Rate}(\text{max})$ and the max rate constant $k_{(\text{max})}$ is defined as k_1/k_2 .

To determine the values of k_1 and k_2 data, Tables 5-2 through 5-5 and Figures 5-2 through 5-7 are used.

Table 5-2. Rate of Corrosion as a Function of Water Vapor Pressure at Various Temperatures.

Water vapor pressure kPa	Rate of Gain (mg/cm ² min) ^a					
	115°C ^b	150°C	200°C	250°C	300°C	350°C
0.0000				0.0060	0.0320	0.1250
					0.0340	
0.4270	0.0004					
0.6130				0.0081	0.0580	
0.8660	0.0005					
1.2300	0.0006			0.0090	0.0690	0.3670
				0.0095		
1.6900	0.0007					
2.1200	0.0007					
2.3300			0.0134		0.1070	
2.4900	0.0008	0.0025				
2.8100		0.0027				
3.1700	0.0008			0.0186	0.1170	0.6700
				0.0217	0.1260	0.6600
4.2400		0.0030	0.0153		0.1500	
7.3700		0.0039	0.0228	0.0390	0.2430	
12.3300		0.0039	0.0318	0.0850	0.3250	
19.9200			0.0448	0.1460	0.6280	
31.1600			0.0577			
47.3400			0.0706			

a. Assumes uniform reaction over coupon surface

b. Baker (unpublished data)

Figure 5-2. Reaction Rate vs Pressure 115 °C.

Figure 5-3. Reaction Rate vs Pressure 150 °C.

Figure 5-4. Reaction Rate vs Pressure 200 °C.

Figure 5-5. Reaction Rate vs Pressure 250 °C.

Figure 5-6. Reaction Rate vs Pressure 300 °C.

Figure 5-7. Reaction Rate vs Pressure 350 °C.

Table 5-3. Polynomial Curve Fits to Oxidation Rate Constant Data as a Function of Water Vapor Pressure at Designated Temperatures (°C).

T (°C)	Rate Constant (mg/cm ² /min)
115	$3.21 * 10^{-4} + 2.66 * 10^{-4}P - 3.56 * 10^{-5}P^2$
150	$1.33 * 10^{-3} + 5.33 * 10^{-4}P - 2.63 * 10^{-5}P^2$
200	$7.49 * 10^{-3} + 2.20 * 10^{-3}P - 1.84 * 10^{-5}P^2$
250	$-2.57 * 10^{-4} + 7.04 * 10^{-3}P$
300	$3.16 * 10^{-2} + 2.83 * 10^{-2}P$
350	$0.1388 + 1.68 * 10^{-1}P$

The constant k_i is defined as the initial slope of rate constant versus water vapor pressure curve. Taking the first derivative of the polynomial curve fit expressions listed in Table 3 and evaluating at $P = 0$, yields the values for k_i . Referring to Table 5-3, it can be noted that the rate constant expressions for temperatures 115, 150 and 200 °C are polynomial while those for temperatures 250, 300 and 350 °C are first order. Since the initial rates yield values for k_i , it was noted that at lower temperatures the plots of rate constant vs water vapor pressure reached a maximum as water vapor pressure increased. In the temperature range 250 to 350 °C, the initial part of the curve is linear and either remains linear or increases rapidly at higher water vapor pressures. For those data where the rate curve did not reach a maximum value, the initial part of the curve was fitted with a first order expression. Values for the initial slopes, (k_i) are listed in Table 5-4.

Table 5-4. Initial Slope as a Function of Temperature.

T (°C)	Initial Slope (k_i)
115	$2.66 * 10^{-4}$
150	$5.33 * 10^{-4}$
200	$2.20 * 10^{-3}$
250	$7.04 * 10^{-3}$
300	$2.84 * 10^{-2}$
350	0.167

Figure 5-8 is a plot of initial rate constant as a function of temperature.

Figure 5-8. Initial Rate Constants.

Assuming that the rate constant/temperature dependence can be expressed by an Arrhenius relation, Figure 5-9 is a plot of $\ln k_1$ versus $1/T(^{\circ}\text{K})$.

The regression equation for the Arrhenius plot is:

$$\ln k_1 = 7.917 - 6482.82/T \quad (51)$$

Figure 5-9. Arrhenius Plot for Initial Rate Constants.

Since the initial rate-constant is determined with $P_{\text{water vap}} \sim 0$, k_1 should be a function of temperature only and indeed follows an Arrhenius dependence.

To determine the rate constant for the maximum rate of corrosion in the absence of air oxidation, reference is again made to Figures 5-2 through 5-7. The first derivative of the curve

fit expression, evaluated at $P = 0$, yields k_1 . Evaluation of the curve fit expression at $P = 0$ yields the dry air oxidation rate, D . Then the rate constant for the observed corrosion, k , as determined from the curve fit expression, minus the constant term in the curve fit expression, $(k - D)$, yields a number $k_{\max}$, where $k_{\max}$ is the maximum water-induced corrosion rate. Assuming a Langmuir adsorption analogy, a plot of $P/(k-D)$ versus P is made and in fact, yields a straight line with slope $1/(k-D)$. The reciprocal of the slope yields the value for $k_{\max}$, k_1/k_2 . Knowledge of the initial rate constant, k_1 , and the rate constant for the max rate, k_1/k_2 , allows for the calculation of k_2 .

Table 5-5 lists the dry air oxidation rates as determined for the curve fits in Figures 5-2 through 5-7. Table 5-6 lists the regression equations for the Langmuir plots.

Table 5-5. Dry Air Oxidation Rates.
(as determined from Figures 5-2 through 5-7)

T (°C)	Dry air rate constant (mg/cm ² min)
115	3.211×10^4
150	1.33×10^{-3}
200	7.49×10^{-3}
250	4.44×10^{-3}
300	3.04×10^{-2}
350	0.139

Table 5-6. Regression Equations for Langmuir Plots.

T (°C)	Regression Equation
115	$4550.47 - 601.18P + 392.86P^2$
150	$1907.25 + 53.724P + 12.592P^2$
200	$467.65 + 1.1230P + 0.1104P^2$
250	$155.29 - 0.33015P + 0.002072P^2$
300	$35.1418 + 0.00476P - 2.928E-5P^2$
350	$5.9533 - 2.282E-5P + 1.4278E-7P^2$

5.2.1 Sample Calculation

Description: This calculation simulates a condition where the rate of corrosion of a uranium metal surface is desired. The results of this calculation could be used to predict the rate of hydrogen gas production and/or the rate of uranium oxide formation. The initial conditions chosen are a temperature of 150 °C and a water vapor pressure of 10 kPa. Liquid water is assumed not to be present.

Initial conditions:

Temperature - 150 °C.

P_{H_2O} - 10 kPa

$T = 150\text{ °C} = 423\text{ °K}$

$1/T = 0.00236$

From the log rate expression

$$\begin{aligned}\ln k_1 &= 27.3732 - 25637.24/T + 4.5936 \times 10^6/T^2 \\ &= -7.5586\end{aligned}\tag{52}$$

$$k_1 = 0.000522\text{ mg/cm}^2/\text{min.}$$

From the Table 5-6 regression values:

$$1/(k-D) = 370.37$$

$$k-D = k_{\max} = 0.0027$$

$$\begin{aligned}k_2 &= k_1/k_{\max} = 0.000522/0.0027 \\ &= 0.19333\end{aligned}\tag{53}$$

Then the rate constant for the observed rate will be:

$$\begin{aligned}&= (k_1 * P / (1 + k_2 P)) + D \\ &= (5.22E-4 * 10 / (1 + 0.1933 * 10)) + 1.33E-5 \\ &= 0.00311\text{ mg/cm}^2/\text{min}\end{aligned}\tag{54}$$

The measured rate of oxidative corrosion rate constant reported in the literature, considering both water-induced corrosion and dry air oxidation, is $0.0039 \text{ mg/cm}^2 \text{ min}$.

5.2.2 McGillivray Conclusions

The McGillivray model predicts corrosion rates at temperatures from 115 to 350 °C and low water vapor pressures (0 to 60 kPa). When one compares McGillivray's model results to the results of other investigators and even to an equation derived from regressing McGillivray's own raw data, it is evident that more accuracy can be achieved by reducing the temperature range over which the model is exercised. In conclusion, one may state that McGillivray's model is a unique approach to understanding the mechanisms controlling uranium corrosion in water vapor; however, it gives only approximately correct results when exercised over a wide temperature range (115 - 350 °C). For this reason, the equations derived by Pearce are to be preferred for uncorroded, unirradiated uranium metal. McGillivray's model has potential for calibrating the reactivity of corroded, irradiated uranium metal over the temperature range of 115 - 200 °C.

5.3 CONDON MODEL

Condon derived a perfusion-precipitation model that can be calibrated to specific reaction conditions (Condon 1983). Hydrogen dissolves into uranium metal until the metal is saturated and uranium hydride begins precipitating. Since the density of uranium hydride is approximately half that of uranium metal, the precipitation process occurring within the metal must necessarily swell the metal. The low solubility of hydrogen in uranium metal prevents the formation of hydride deep within the metal except in void spaces. Formation of hydride along deep intergranular surfaces is not observed. Instead, uranium hydride is found at or within the first micron of metal. Near the surface, the forces are sufficient to swell the metal enough to accommodate the lower density hydride.

Starting from basic concepts involving hydrogen solubility and diffusibility resulting in the formation of uranium hydride, Condon presents the following rate formula:

$$V_s = (-K C_o / \ln[U_s]) * \text{Sqrt}[D/aKU] \quad (55)$$

where:

$$V_s = \text{linear corrosion rate Meters/Sec.}$$

$$K_{\text{hydriding}} = 10.4 * \text{Exp}[1592/T] \quad (56)$$

$$K_{\text{dehydriding}} = 4.2E4 * \text{Exp}[-8700/T] \quad (57)$$

$$C_o = [H_2]^{0.5} * (4.18E-6 * \text{Exp}[-894/T]) \quad (58)$$

$$D = \text{Effective Hydrogen Diffusivity} = 1.9\text{E-}06 * \text{Exp}[-5820/T] \quad (59)$$

$$a = \# \text{ of hydrogens on Hydride} = 3 \quad (60)$$

$$U_s = \text{mole fraction of U metal on surface side of reaction front} = 0.97 \quad (61)$$

$$U = \text{mole fraction of U metal on metal side of reaction front} = 1 \quad (62)$$

5.3.1 Oxygenated Reactions

The Condon model can be used by entering a known hydrogen pressure directly into equation 58. If hydroxide ion from water is the reactant, hydrogen is generated in-situ by its reaction with uranium metal. In any case, the hydrogen pressure in contact with the metal must be known or calculable. Since the water reaction is known to be slow when poisoned by the presence of oxygen, let us assume the hydrogen pressure is determined by the uranium hydride equilibria, in which case the pressure can be calculated by:

$$\text{Ln}[P_{H_2}] = 69.32 - (14.64\text{E}3/T) - 5.65 \text{Ln}[T] \quad (63)$$

Using these parameters, the results of the Condon model are compared in Figure 5-10 with the Ritchie (1981) results for the 100% RH, oxygen-poisoned case.

Figure 5-10. Comparison of Rate Constants (Condon vs Ritchie; Oxygenated).

A comparison of these two plots leads one to suspect that the hydrogen activity in the metal is indeed controlled by the hydride equilibria for the oxygenated case at 100% RH. The Condon model could theoretically be applied to determine the oxygen poisoned water corrosion rate for relative humidities less than 100% RH. However, at this time, it is not known how to calculate the hydrogen pressure.

5.3.2 Anoxic Reactions

In the case where the uranium water reaction is not oxygen poisoned, there is no reason to believe that the hydrogen concentration is in thermodynamic equilibrium with uranium hydride. The hydrogen activity in this case is determined in some complicated way by the water pressure. The saturation pressure of water may be calculated by:

$$P_{H_2O} = 1.165E11 * \text{Exp}[-5205/T] \quad (64)$$

We do not know, a priori, how the hydrogen concentration varies with water pressure; however, it is possible to calibrate the Condon model against corrosion rates from Ritchie (1981) and develop the ratio of hydrogen vs water pressures as a function of temperature.

The hydrogen pressure resulting from U metal reaction with this water is:

$$\begin{aligned} P_{H_2} = P_{H_2O} * ((2.76011E-13) + (3.73511E-11)*T + \\ (3.07134E-9) * T^2 - (2.12709E-11)*T^3 + \\ (2.24093) * T^4 + (8.24567E-17)*T^5 - \\ (8.72323E-20) * T^6) \end{aligned} \quad (65)$$

Since Condon's model is directly calibrated to fit the Ritchie data at 100% RH, it has no more direct value than the Ritchie data; however, once this fit is obtained at 100% RH, it becomes a simple matter to calculate reaction rates at water vapor pressures < 100% RH using Condon's model. Figure 5-11 compares the reaction rates at 20 torr water when calculated by Condon and by Pearce equations.

Figure 5-11. Rate Constants for Uranium-Water Reaction at 20 Torr H_2O .

Figure 5-11 shows the close correlation between the predicted uranium metal reactivity for the Condon and Pearce models. This demonstrates that with specific metals and under specific reaction conditions, Condon's model can be calibrated to yield accurate results for a particular metal and at variable water vapor pressures.

6.0 CONCLUSIONS

A review of the available data and models for uncorroded, unirradiated uranium metal corrosion in water and air shows that Pearce has derived the most useful and robust equations based upon regressing the available data over wide temperature and water partial pressure ranges.

The results of Richie and Condon also give accurate corrosion rates; however, since they apply to smaller temperature ranges than Pearce, they will not be used except in those few cases where the Pearce model does not cover the required humidity range.

McGillivray's model gives approximate results that can be improved by regressing the data over smaller temperature ranges than that used by McGillivray.

Pearce's equations may be applied directly to unirradiated, uncorroded uranium metal. However, for highly swollen or corroded fuel, the Pearce equations must be adjusted by the ratio of the true surface area to the geometric area. There is no evidence for highly swollen N-fuel; however, exposed portions are highly corroded. The reactivity of the highly corroded fuel must be determined through the fuel characterization program and enough specific data must be gathered to determine if a simple multiplier can be used for the Pearce model, or if an entirely new model must be created. Until such data is received, a multiplication factor of 10 will be used to adjust the Pearce model for calculations involving N-fuel reactivity.

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APPENDIX

URANIUM CORROSION CHEMISTRY

Uranium metal is a powerful reductant. The reduction potential is given by:

The reaction with water is:

The reaction with oxygen is:

Both reactions are strongly exothermic, with the most energy obtained from the reaction with oxygen. When both oxidants are mixed, the following net reaction is observed:

Water does not appear to be a reactant, since its mass is balanced on both sides of the equation; however, it can be shown that the corrosion rate is functionally dependent upon the water concentration, and isotopic experiments confirm that the oxygen in UO_2 is obtained from the water. As long as the oxygen activity is above 0.001 (1000 ppm), the total water activity does not decrease, and oxygen is steadily depleted. When the oxygen activity sinks below 1000 ppm, water is depleted and the hydrogen appears as either uranium hydride or hydrogen gas. For the anoxic reaction, a typical split for hydrogen between uranium hydride and hydrogen gas is 10% to 90% respectively.

The above observations may be explained mechanistically by:

and

Water is reacting as a catalyst and its net effect is to increase the reaction rate of oxygen with uranium. In the absence of oxygen, the reaction is no longer catalytic, and hydrogen radicals can combine to make hydrogen molecules or with uranium to make UH_3 .

Reaction rates for uranium with oxygen and/or water are typically calculated from gravimetric experiments wherein a coupon of metal is exposed to a specific atmosphere at a specific temperature.

Since reaction of the oxidants can only occur at the metal surface, a simple correlation between the weight gain and the surface area is obtained:

$$W^n = K \cdot A \cdot t \quad (\text{A9})$$

where:

$n = 3, 2, \text{ or } 1$

W = weight gain

K = reaction rate constant

A = reactive area

t = reaction time

High initial rate constants are observed for bare metal and for thin oxide films wherein cubic ($n=3$), or quadratic ($n=2$) rate behavior is observed. When an equilibrium oxide thickness is reached, i.e., the rate of oxide spalling equals the rate of oxide formation, linear ($n=1$) rate constants are typically observed. It is these linear rate constants that are typically reported in the literature.

Typical reaction sequences are described in the following sections.

Water Reaction

Evidence for the mechanistic reaction of water vapor with uranium metal is developed in the following references, Colmenares (1984), Winer (1987), McGillivray (1994), and Condon (1983).

Water vapor adsorbs upon the outer oxide surface. Dissociation of the water occurs to give hydroxide ions and hydrogen cations. The fluorite structure of the uranium oxide lattice contains defect vacancies and the migration of hydroxide ions through the oxide lattice to the metal surface is comparatively rapid and characterized by an activation energy. At the metal surface, these anions react with the uranium metal to produce UO_{2+x} (* = 0.0 to 0.1), monatomic hydrogen, and free electrons.

Monatomic hydrogen, and free electrons migrate, countercurrent to the anion flow, and react at the outer oxide surface. Monatomic hydrogen, can react with available oxygen to yield water, recombine in the absence of oxygen to give hydrogen gas, or can dissolve into the uranium metal. The absorption rate for monatomic hydrogen into the metal is proportional to the square root of the hydrogen pressure. Monatomic hydrogen is very mobile and penetrates throughout the bulk of the metal (although in very low concentration). When supersaturated with monatomic hydrogen, uranium hydride begins precipitating, not within the bulk phase, but within the first micron of the uranium surface.

The density of UH_3 (10.95 g/cc) is less than the metal density (19.05 g/cc) and the associated swelling breaks up the surface, thereby increasing the diffusivity of hydrogen within that volume element. This swelling and breaking of the surface is the overall rate controlling factor for corrosion over the temperature range in which hydride is stable.

In summary then, the factors affecting the reaction rate constants are:

- The temperature,
- The fraction of the oxide surface that is covered by water,
- The transport rate of water through the oxide scale, and
- The porosity of the metal.

All of these above factors affect and control:

- The hydrogen concentration and diffusivity within the metal, which ultimately controls the water corrosion rate in a manner explained more completely in the Condon model.

Oxygen Reaction

Oxygen adsorbs upon the outer oxide surface. Oxygen is dissociated on the surface and combines with electrons from the interior reactions to form oxide ions. The penetration of these oxide ions through the oxide scale is characterized by an activation energy and occurs in a manner similar to the penetration of hydroxide ions. Upon reaching the metal surface, these oxide ions dissolve, releasing free electrons. These free electrons migrate back to the oxide surface to continue the cycle. Monatomic oxygen does not penetrate uranium metal nearly as well as monatomic hydrogen, and a sharp oxygen gradient is found near the metal surface. Monatomic oxygen can react with uranium hydride:

or can react directly with the metal:

Uranium can exist in 3 oxidation states +4, +5, and +6,

It can therefore form the theoretical oxides

During the air oxidation of uranium, the compounds formed may be best described as UO_{2+x} where x varies continuously from 0 to 1. In this case, a continuum of oxidation states ranging from 4 to 6 are being formed. Due to crystal habit stability characteristics, certain values of x seem to be favored and values of x seem to cluster around 0, 0.25, 0.66, and 1.0, which correspond to the formation of compounds possessing empirical formulas UO_2 , U_4O_9 , U_3O_8 , and UO_3 .

Low temperature air oxidation gives uranium-oxygen compounds wherein x varies from 0.2 to 0.4. Calcination at 600-800 °C in air typically yields x values approximating 0.66 for the compound U_3O_8 .

The presence of free molecular oxygen in excess of 100-1000 ppm (depending on the purity of the uranium metal) drastically reduces reactivity of water with the uranium metal. This is explained by the competition of oxygen and water for the same adsorption sites on the oxide surfaces, and the solution of oxygen into the uranium metal surface, thereby reducing the solubility of monatomic hydrogen in the oxygen poisoned region of the metal. Both factors reduce the reaction rate of water vapor with the uranium metal.

Carbon Dioxide Reaction

Carbon dioxide adsorbs on the outer oxide surface. The carbon dioxide is dissociated on the surface to form carbon monoxide and monatomic oxygen.

(A11)

The monatomic oxygen combines with electrons from interior reactions to form oxide ions. The oxide ions migrate through the oxide scale and react in a manner similar to the oxygen reaction.

Since the activation energy is higher for the carbon dioxide reaction than for the oxygen reaction, the reaction rates for the carbon dioxide reaction are smaller than for reaction in air at or near ambient temperatures, but are quite large above 700 °C.

Nitrogen Reaction

Reaction of dry nitrogen with bulk uranium metal is difficult to detect at ambient temperature, since the rate constants are 3 to 4 orders of magnitude lower than for the dry air reaction.

In a moist nitrogen atmosphere, water is the primary reactant with uranium, forming uranium hydrides as a product. These hydrides greatly extend the available surface area. Even though the uranium hydride-nitrogen rate constants are small, appreciable reactions may occur in the presence of hydrides, because of the large hydride surface area. This phenomena is especially observed when reaction times are long as in storage. As hydrogen is displaced by the nitrogen, the hydrogen simply forms more hydride and therefore acts as a catalyst for the nitrogen reaction.

If uranium nitride is subsequently exposed to the atmosphere, its reactivity toward oxygen, carbon dioxide, or water vapor is about the same as the reactivity of uranium hydride.

Reactions of nitrogen with bulk metal are readily detected above 500 °C (Pearce 1989). The nitride composition is UN_x where x ranges from 1.5 at 500 °C to 1.7-2 at 800 °C. At this temperature a coarse easily spalled powder forms after only 1 hour of reaction. Reactions over liquid uranium show the formation of compact, adherent mono-nitride (UN) layers. There is a marked increase in the reaction rate at 750 °C in a manner similar to the observed increase for carbon dioxide.

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