QUANTITATIVE PROCEDURE TO DETERMINE
THE RATE OF U₃O₈ FORMATION ON UO₂

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ABSTRACT

The literature on the rate of U₃O₈ formation on UO₂ has been critically reviewed. Even after inappropriate data have been culled, there remains a large uncertainty in the reported values of the activation energy. We have thus developed an X-ray diffraction technique to measure specifically U₃O₈ formation on the surface of UO₂ pellets, and an appropriate mathematical model to analyse the kinetic data. The resulting Arrhenius expression yields a value of 146 ± 10 kJ mol⁻¹ for the activation energy for the formation of U₃O₈. The kinetic data presented herein can be used to assess the performance of used fuel under dry air storage conditions.

1. INTRODUCTION

The two-step oxidation reaction of UO₂ to form U₃O₇, followed by U₃O₈, is of interest because of the large molar volume change associated with U₃O₈ formation. This can cause swelling and splitting of defective fuel elements, as well as powdering of the oxide fuel, when it is exposed to air at sufficiently high temperatures under dry storage conditions. Therefore, it is important to have a sound understanding of the kinetics of U₃O₈ formation, in order to determine limiting temperatures for air storage or to predict fuel oxidation behaviour in the event that air gains ingress to an inert-gas-filled fuel-storage container.

Nearly all of the available kinetic data for U₃O₈ formation has been obtained at temperatures above 200°C – indeed, much of it above 300°C – whereas dry storage of CANDU® fuel typically involves temperatures well below 200°C. Therefore, prediction of fuel behaviour under storage conditions requires an accurate estimate of the activation energy for U₃O₈ formation. Also, there is much more kinetic data on oxidation of unirradiated UO₂ than irradiated fuel. It is thus desirable to understand the differences in oxidation kinetics between unirradiated and irradiated UO₂, so that data for the oxidation of the former can be used judiciously in predicting the behaviour of the latter material.

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Many of the data on UO₂ oxidation are based on gravimetric experiments. One serious limitation of this approach is that U₃O₇ formation often interferes with determination of the U₃O₈ formation kinetics. We have thus developed an X-ray diffraction (XRD) procedure to measure directly the formation of U₃O₈ (without interference from U₃O₇) on unirradiated fuel surfaces. Our improved method is described, and then applied to the derivation of an activation energy for the formation of U₃O₈. Finally, we discuss the judicious application of the results to prediction of the oxidation of irradiated fuel in air under dry storage conditions.

2. EXISTING ACTIVATION ENERGY ESTIMATES

Although the importance of UO₂ oxidation has long been recognized, and a great deal of effort has been expended internationally on its investigation, the oxidation kinetics are not yet fully understood, and there remains a large range in the reported activation energies for U₃O₈ formation. In a recent review (1), we tabulated reported estimates of this activation energy that ranged from 48 to 194 kJ·mol⁻¹. These estimates, and the temperature ranges over which they were obtained, are depicted in Figure 1. Clearly, the selection of an activation energy for predicting fuel oxidation behaviour under dry storage conditions requires a careful, critical review of these reported values, and preferably also further experimental evaluation.

Several authors have noted a reduction in the apparent activation energy for U₃O₈ formation at temperatures above about 300 to 325°C (Ref. 1, and references therein). This is apparent in Figure 1, which shows that all of the activation energy values below 100 kJ·mol⁻¹ were obtained at temperature ranges extending well above 300°C; therefore, such values can be excluded from consideration for predicting fuel oxidation below 200°C. Moreover, several kinetic studies on U₃O₈ formation were based on gravimetric procedures, which are prone to interference from U₃O₇ formation, especially at temperatures below 300°C.

Taking the above concerns into account, we obtained a "best estimate" of the activation energy for U₃O₈ formation on unirradiated UO₂ by averaging the following values:

(a) three independent values, estimated by Boase and Vandergraaf (2), of 170 kJ·mol⁻¹ for UO₂ pellets, 163 kJ·mol⁻¹ for powder, and 172 kJ·mol⁻¹ based on oxide front progression;
(b) estimates of 124 and 139 kJ·mol⁻¹ based on semi-quantitative XRD measurements by Taylor et al. (3);
(c) 146 kJ·mol⁻¹ for UO₂ powder by Aronson et al. (4);
(d) 160 kJ·mol⁻¹ for the advanced stages (post-spallation) of oxidation of unirradiated LWR fuel by White et al. (5);
(e) 143 kJ·mol⁻¹ for oxidation of UO₂ pellet fragments by You et al. (6); and
This "short list" includes only those estimates that both explicitly relate to \( \text{U}_3\text{O}_8 \) formation (as opposed to overall oxidation rate), and most were obtained at temperatures below 300°C. The resulting average is 154 kJ·mol\(^{-1}\). The above values are depicted in Figure 2, which also includes our experimental value, as described below.

3. X-RAY DIFFRACTION PROCEDURE

Samples used in the present study were disks (~2 mm thick) cut from unirradiated CANDU fuel pellets, and consistently polished to a 400-grit finish. Earlier work (3) had shown that such sample preparation prior to oxidation yields the most reproducible oxidation kinetics. X-ray powder diffraction is a useful tool with which to measure the rate of formation of \( \text{U}_3\text{O}_8 \) on \( \text{UO}_2 \) because it uniquely distinguishes between \( \text{U}_3\text{O}_8 \) and intermediate oxidation products of the \( \text{U}_3\text{O}_7/\text{U}_4\text{O}_9 \)\(^{(1)}\) type. As described previously by Choi et al. (8), the fraction \( \alpha(t) \) of conversion of the surface (outermost ~1 \( \mu \text{m} \)) of a \( \text{UO}_2 \) specimen to \( \text{U}_3\text{O}_8 \) can be calculated from the integrated intensities of specific XRD peaks associated with \( \text{U}_3\text{O}_8 \) and \( \text{U}_3\text{O}_7/\text{U}_4\text{O}_9 \), using equation [1].

\[
\alpha(t) = \frac{I(\text{U}_3\text{O}_8)}{[I(\text{U}_3\text{O}_8) + \xi I(\text{U}_3\text{O}_7) + \xi I(\text{U}_4\text{O}_9) + \xi I(\text{U}_5\text{O}_{11})]}
\]

where \( I(\text{U}_3\text{O}_8) \) is the integrated intensity of the combined [200] and [130] \( \text{U}_3\text{O}_8 \) peak at \( d = 0.34 \text{ nm} \), \( I(\text{U}_3\text{O}_7) \) is that of the [111] \( \text{U}_3\text{O}_7/\text{U}_4\text{O}_9 \) peak at \( d = 0.31 \text{ nm} \), and \( \xi \) is an empirically determined factor that corrects for the different absolute XRD intensities and mass absorption coefficients of \( \text{U}_3\text{O}_8 \) and \( \text{U}_3\text{O}_7 \). A value of \( \xi = 0.450 \pm 0.033 \) was determined by measuring the appropriate XRD peak intensities for a series of \( \text{UO}_2 \) disks (cut from unirradiated CANDU fuel pellets) oxidized at 250°C for various periods of time (8).

In the present study, as in our previous work (8), XRD data were obtained directly from disk surfaces, using a Rigaku Rotaflex diffractometer equipped with a 15-kW rotating-anode X-ray source and a diffracted-beam monochromator. Routine XRD phase identification was performed with a scanning speed of 10°(2\( \theta \))·\( \text{min}^{-1} \), but quantitative data for the two selected peaks (see above) were collected at 1°(2\( \theta \))·\( \text{min}^{-1} \), to minimize background noise in the XRD signal.

\(^{(1)}\) By the time appreciable \( \text{U}_3\text{O}_8 \) has formed, the \( \text{UO}_2 \) sample surface is covered with a thin film of \( \text{U}_3\text{O}_7/\text{U}_4\text{O}_9 \).
4. **PRINCIPLES OF THE MODEL**

The effective XRD sampling depth for UO\(_2\) is small (<1 \(\mu\)m) relative to the dimensions of the individual fuel grains (~10 \(\mu\)m), and it is thus possible to analyse the kinetic data using a two-dimensional nucleation-and-growth model. In this model, it is assumed that the rate of nucleation on the surface is constant (per unit area of unconverted fuel) with a rate constant \(K_N\) (m\(^2\) s\(^{-1}\)). The nuclei subsequently grow isotropically as circular islands of U\(_3\)O\(_8\) with a rate of linear growth \(K_G\) (m s\(^{-1}\)). It has been shown (9) that the fraction, \(\alpha(t)\), of a two-dimensional surface covered by products for such a nucleation-and-growth reaction can be described by

\[
\alpha(t) = 1 - \exp\left(-\frac{\pi\kappa^3}{3} + \frac{\pi^2\kappa^2t^6}{180} - \frac{11\pi^3\kappa^3t^9}{45,360} + \frac{5\pi^4\kappa^4t^{12}}{399,168}\right)
\]  

[2]

where \(t\) is the time, and \(\kappa\) is a composite rate constant defined by

\[
\kappa = K_G^2K_N
\]  

[3]

It is thus possible to determine the reaction kinetics for the formation of U\(_3\)O\(_8\) directly by using XRD to determine the fraction, \(\alpha\), of the surface oxidized as a function of time. The kinetic data can then be analysed by using a least-squares procedure to determine the optimal value of \(\kappa\) according to equation [2].

5. **RESULTS AND DISCUSSION**

Kinetic data were obtained for air oxidation of unirradiated CANDU fuel pellets over a wide temperature range (168 to 300°C) in order to determine accurately the effect of temperature on the rate constants. As in previous studies, specimens were prepared with a 400-grit rough finish that had previously been shown to yield the most reproducible results on U\(_3\)O\(_8\) formation (3,8). Specimens were oxidized in a variety of tube furnaces and convection ovens.

The integrated intensity (I(U\(_3\)O\(_8\))) of the U\(_3\)O\(_8\) peak at \(d = 0.34\) nm and the intensity (I(U\(_3\)O\(_7\))) of the U\(_3\)O\(_7\) peak at \(d = 0.31\) nm were measured from the XRD spectra of each sample after heat treatment. The XRD data were converted to \(\alpha(t)\) values using equation [1]. In cases where a single \(\alpha(t)\) value was obtained from one specimen, this was converted to \(\kappa\) using equation [2]. In cases where several values of \(\alpha(t)\) were obtained by sequential oxidation of one specimen, then a value of \(\kappa\) was obtained by a least-squares regression procedure using all the data for that specimen. A summary of the resulting rate constants (\(\kappa, h^{-3}\)) is provided in Table 1; more detailed data have been provided elsewhere (9).
The validity of equation [2] is illustrated by comparison with experimental data in Figure 3. To facilitate comparison of all experimental data with equation [2], the values of time in Figure 3 have been calculated in terms of the reduced time, i.e., the ratio $t/t_{1/2}$ where $t_{1/2}$ is the time required to achieve 50% reaction. The individual values of the data points in Figure 3 cannot be compared to the curve because the values of $\kappa$ displayed in this figure were calculated by empirical fit to equation [2]. However, there is good agreement between the shape of the curve and the pattern of the data points, which suggests validity of our model (equation [2]).

Values of $\kappa$ were plotted against $1/T(K)$. The resulting Arrhenius plot was linear over the full temperature range (168 to 300°C), as shown in Figure 4. A weighted linear regression of these data yielded the expression:

$$\ln \kappa = (-52,808\pm3,442) \cdot \frac{1}{T} + 86.165$$

[4]

which yields a calculated activation energy of $146 \pm 10$ kJ mol$^{-1}$ (the experimental uncertainty is expressed at the 90% confidence level). This value agrees well with the estimate of $154$ kJ·mol$^{-1}$ that was derived from a critical review of the available literature on UO$_2$ fuel oxidation.

The results of our experiments enable us to extrapolate data on the kinetics of U$_3$O$_8$ formation with reasonable confidence to temperatures (typically below 150°C) that are more representative of the dry storage of used nuclear fuel. For a given temperature, the rate constant, $\kappa$, can be calculated from equation [4], and the fraction of the surface oxidized to U$_3$O$_8$ can be calculated as a function of time using equation [2]. As an illustration, the extent of surface oxidation was calculated as a function of time at 130, 140 and 150°C and the results are presented in Figure 5. One can then assume that the rate of bulk (i.e., three-dimensional) oxidation of a UO$_2$ sample is the same as the rate of U$_3$O$_8$ formation on the surface of a similar sample. Clearly this is a conservative assumption because the rate of U$_3$O$_8$ growth into a UO$_2$ fragment will probably be less than two-dimensional growth along the surface. In particular, this calculation does not take account of the finite time required for the oxidation front (U$_3$O$_7$/U$_4$O$_9$ formation) to penetrate the grain-boundary network of the fuel. This step is important because the associated 2% volume contraction causes intergranular cracking, which exposes the interior of fuel fragments to air ingress and U$_3$O$_8$ formation.

Application of our two-dimensional nucleation-and-growth kinetic data to the rate of U$_3$O$_8$ formation in used fuel is also conservative because fission products in solid solution tend to inhibit U$_3$O$_8$ formation. For example, Choi et al. (8) examined the rate of U$_3$O$_8$ formation on SIMFUEL and reported that the rate of oxidation is slowest for those samples having the highest simulated burnup. These data have recently been supported by similar experiments on unirradiated UO$_2$ doped with a single rare-earth element (Nd) (10). We thus conclude that the results reported herein for unirradiated fuel represent a
conservative case, that is, that the rate constants for the formation of U₃O₈ on irradiated fuel are always lower than they are for unirradiated material.

6. CONCLUSIONS

Critical evaluation of the literature on the rate of U₃O₈ formation has shown that there is a very wide range of reported activation energies. Culling the data of inappropriate results yields a better range of activation energies, and an estimated value of 154 kJ mol⁻¹ for the activation energy.

A novel method has been developed to analyze quantitatively U₃O₈ formation kinetics by using XRD to measure the rate of product formation on the surface of unirradiated UO₂ disks. Rate constants were determined over the temperature range 168 to 300°C. The resulting Arrhenius plot was linear and yields an estimated value for the activation energy of 146 ± 10 kJ mol⁻¹.

It would be most useful to perform an experiment in which the present method was applied to the oxidation of used fuel. Such a test would lead to a significantly improved estimate of the time required for U₃O₈ formation on used fuel.

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REFERENCES


TABLE 1. EXPERIMENTAL VALUES OF THE RATE CONSTANT, $\kappa$, AS A FUNCTION OF TEMPERATURE.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\kappa$, h$^{-3}$</th>
<th>Temperature (°C)</th>
<th>$\kappa$, h$^{-3}$</th>
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Note that different values of $\kappa$ at the same temperature were obtained in different experiments.

FIGURE 1: REPORTED VALUES OF THE ACTIVATION ENERGY FOR $\text{U}_3\text{O}_8$ FORMATION AND THE TEMPERATURE RANGES OVER WHICH THEY APPLY, AS COMPILED BY McEACHERN AND TAYLOR (1).
Figure 2: Selected values of the activation energy for $\text{U}_3\text{O}_8$ formation and the temperature ranges over which they apply, as reviewed by McEachern and Taylor (1). This figure includes the experimental value obtained in the present study.

Figure 3: Experimental data for the fraction of the surface converted to $\text{U}_3\text{O}_8$ as a function of reduced time (i.e., $t/t_{1/2}$, where $t_{1/2}$ is the time required to achieve 50% reaction).
FIGURE 4: ARRHENIUS PLOT FOR THE AVERAGE RATE CONSTANT ($\kappa$) FOR THE FORMATION OF $\mathrm{U_3O_8}$ ON $\mathrm{UO_2}$. THE FITTED LINE IS BASED ON A WEIGHTED LINEAR REGRESSION AND YIELDED AN ACTIVATION ENERGY OF $146 \pm 10 \text{kJ mol}^{-1}$.

FIGURE 5: CALCULATED EXTENT OF SURFACE OXIDATION (OUTER 1 $\mu$m) OF $\mathrm{UO_2}$ TO $\mathrm{U_3O_8}$ AT 130 (—), 140 (— —), AND 150°C (— — ), BASED ON $\kappa$ VALUES DETERMINED USING EQUATION [4].