QUANTITATIVE PROCEDURE TO DETERMINE THE RATE OF U_3O_8 FORMATION ON UO_2

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ABSTRACT

The literature on the rate of U_3O_8 formation on UO_2 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 U_3O_8 formation on the surface of UO_2 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 U_3O_8. 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 UO_2 to form U_3O_7, followed by U_3O_8, is of interest because of the large molar volume change associated with U_3O_8 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 U_3O_8 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 U_3O_8 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 U_3O_8 formation. Also, there is much more kinetic data on oxidation of unirradiated UO_2 than irradiated fuel. It is thus desirable to understand the differences in oxidation kinetics between unirradiated and irradiated UO_2, 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 UO_2 oxidation are based on gravimetric experiments. One serious limitation of this approach is that U_3O_7 formation often interferes with determination of the U_3O_8 formation kinetics. We have thus developed an X-ray diffraction (XRD) procedure to measure directly the formation of U_3O_8 (without interference from U_3O_7) on unirradiated fuel surfaces. Our improved method is described, and then applied to the derivation of an activation energy for the formation of U_3O_8. 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 UO_2 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 U_3O_8 formation. In a recent review (1), we tabulated reported estimates of this activation energy that ranged from 48 to 194 $kJ \cdot mol^{-1}$. 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 U_3O_8 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 $kJ \cdot mol^{-1}$ 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 U_3O_8 formation were based on gravimetric procedures, which are prone to interference from U_3O_7 formation, especially at temperatures below 300°C.

Taking the above concerns into account, we obtained a "best estimate" of the activation energy for U_3O_8 formation on unirradiated UO_2 by averaging the following values:

(a) three independent values, estimated by Boase and Vandergraaf (2), of 170 $kJ \cdot mol^{-1}$ for UO_2 pellets, 163 $kJ \cdot mol^{-1}$ for powder, and 172 $kJ \cdot mol^{-1}$ based on oxide front progression;
(b) estimates of 124 and 139 $kJ \cdot mol^{-1}$ based on semi-quantitative XRD measurements by Taylor et al. (3);
(c) 146 $kJ \cdot mol^{-1}$ for UO_2 powder by Aronson et al. (4);
(d) 160 $kJ \cdot mol^{-1}$ for the advanced stages (post-spallation) of oxidation of unirradiated LWR fuel by White et al. (5);
(e) 143 $kJ \cdot mol^{-1}$ for oxidation of UO_2 pellet fragments by You et al. (6); and

(f) 170.2 kJ·mol^{-1} for oxidation of advanced gas-cooled reactor fuel pellet fragments by Tucker (7).

This "short list" includes only those estimates that both explicitly relate to U_3O_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 U_3O_8 on UO_2 because it uniquely distinguishes between U_3O_8 and intermediate oxidation products of the U_3O_7/U_4O_9 (1) type. As described previously by Choi et al. (8), the fraction $\alpha(t)$ of conversion of the surface (outermost ~1 μm) of a UO_2 specimen to U_3O_8 can be calculated from the integrated intensities of specific XRD peaks associated with U_3O_8 and U_3O_7/U_4O_9, using equation [1].

$$\alpha(t) = \frac{I(U_3O_8)}{\left[I(U_3O_8) + \xi I(U_3O_7)\right]} \qquad [1]$$

where $I(U_3O_8)$ is the integrated intensity of the combined [200] and [130] U_3O_8 peak at $d = 0.34$ nm, $I(U_3O_7)$ is that of the [111] U_3O_7/U_4O_9 peak at $d = 0.31$ nm, and ξ is an empirically determined factor that corrects for the different absolute XRD intensities and mass absorption coefficients of U_3O_8 and U_3O_7. A value of $\xi = 0.450 \pm 0.033$ was determined by measuring the appropriate XRD peak intensities for a series of 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°(2θ)·min^{-1}, but quantitative data for the two selected peaks (see above) were collected at 1°(2θ)·min^{-1}, to minimize background noise in the XRD signal.

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(1) By the time appreciable U_3O_8 has formed, the UO_2 sample surface is covered with a thin film of U_3O_7/U_4O_9.

4. PRINCIPLES OF THE MODEL

The effective XRD sampling depth for UO_2 is small (<1 μm) relative to the dimensions of the individual fuel grains (~10 μm), 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_3O_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

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

where t is the time, and κ is a composite rate constant defined by

$$\kappa = K_G^2 K_N \qquad [3]$$

It is thus possible to determine the reaction kinetics for the formation of U_3O_8 directly by using XRD to determine the fraction, α, 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 κ 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_3O_8 formation (3,8). Specimens were oxidized in a variety of tube furnaces and convection ovens.

The integrated intensity ($I(U_3O_8)$) of the U_3O_8 peak at d = 0.34 nm and the intensity ($I(U_3O_7)$) of the U_3O_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 κ using equation [2]. In cases where several values of $\alpha(t)$ were obtained by sequential oxidation of one specimen, then a value of κ was obtained by a least-squares regression procedure using all the data for that specimen. A summary of the resulting rate constants (κ, 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 κ 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 κ 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:

$$\ln\kappa = \left(-52{,}808 \pm 3{,}442\right)\cdot\frac{1}{T} + 86.165 \qquad [4]$$

which yields a calculated activation energy of 146 ± 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_3O_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, κ, can be calculated from equation [4], and the fraction of the surface oxidized to U_3O_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_3O_8 formation on the surface of a similar sample. Clearly this is a conservative assumption because the rate of U_3O_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_3O_7/U_4O_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_3O_8 formation.

Application of our two-dimensional nucleation-and-growth kinetic data to the rate of U_3O_8 formation in used fuel is also conservative because fission products in solid solution tend to inhibit U_3O_8 formation. For example, Choi et al. (8) examined the rate of U_3O_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 U_3O_8 on irradiated fuel are always lower than they are for unirradiated material.

6. CONCLUSIONS

Critical evaluation of the literature on the rate of U_3O_8 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 U_3O_8 formation kinetics by using XRD to measure the rate of product formation on the surface of unirradiated UO_2 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 U_3O_8 formation on used fuel.

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TABLE 1. EXPERIMENTAL VALUES OF THE RATE CONSTANT, κ, AS A FUNCTION OF TEMPERATURE.

Temperature (°C)	κ, h^{-3}	Temperature (°C)	κ, h^{-3}
300	1.37×10^{-3}	245	2.47×10^{-6}
	2.69×10^{-3}	240	6.60×10^{-8}
	2.61×10^{-3}	230	1.41×10^{-7}
295	5.97×10^{-3}	225	5.10×10^{-10}
288	2.49×10^{-3}		6.05×10^{-11}
275	3.22×10^{-5}		3.09×10^{-9}
	3.85×10^{-5}	210	7.52×10^{-10}
	1.75×10^{-4}		4.09×10^{-9}
	5.51×10^{-5}	200	9.50×10^{-11}
	8.13×10^{-5}		1.64×10^{-12}
265	2.42×10^{-5}	168	1.21×10^{-14}
263	3.14×10^{-5}		1.20×10^{-14}
260	9.30×10^{-7}		7.60×10^{-15}
255	1.86×10^{-6}	Note that different values of κ at the same temperature were obtained in different experiments.	
250	1.66×10^{-7}		
	9.01×10^{-8}		
	1.78×10^{-6}		

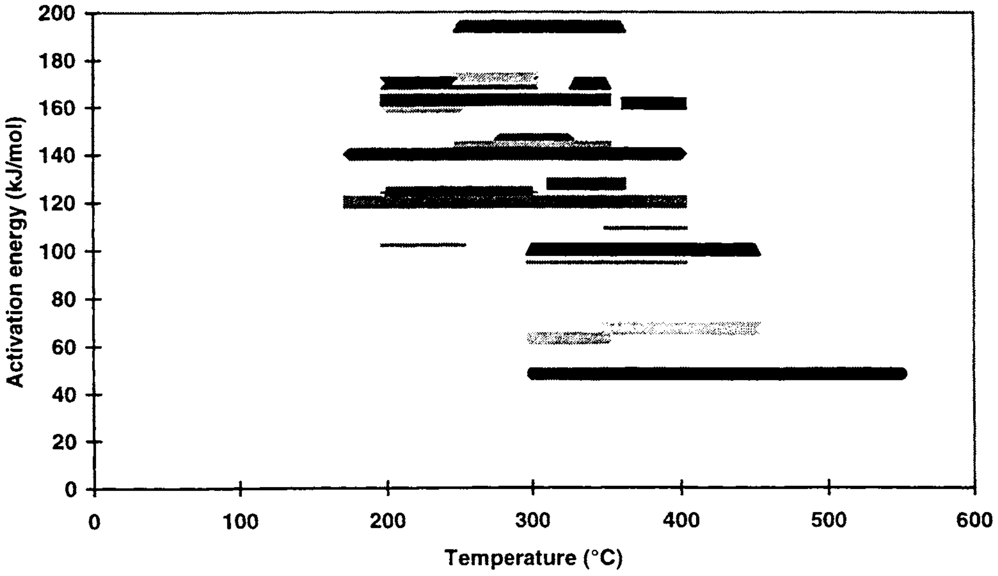

FIGURE 1: REPORTED VALUES OF THE ACTIVATION ENERGY FOR U_3O_8 FORMATION AND THE TEMPERATURE RANGES OVER WHICH THEY APPLY, AS COMPILED BY McEACHERN AND TAYLOR (1).

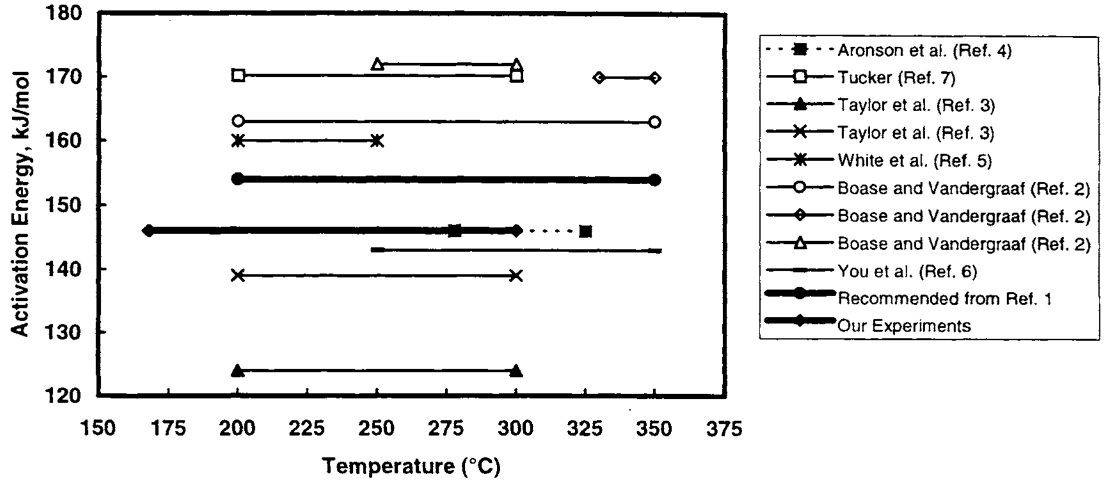

FIGURE 2: SELECTED VALUES OF THE ACTIVATION ENERGY FOR U_3O_8 FORMATION AND THE TEMPERATURE RANGES OVER WHICH THEY APPLY, AS REVIEWED BY McEACHERN AND TAYLOR (1). THIS FIGURE INCLUDES THE EXPERIMENTAL VALUE OBTAINED IN THE PRESENT STUDY.

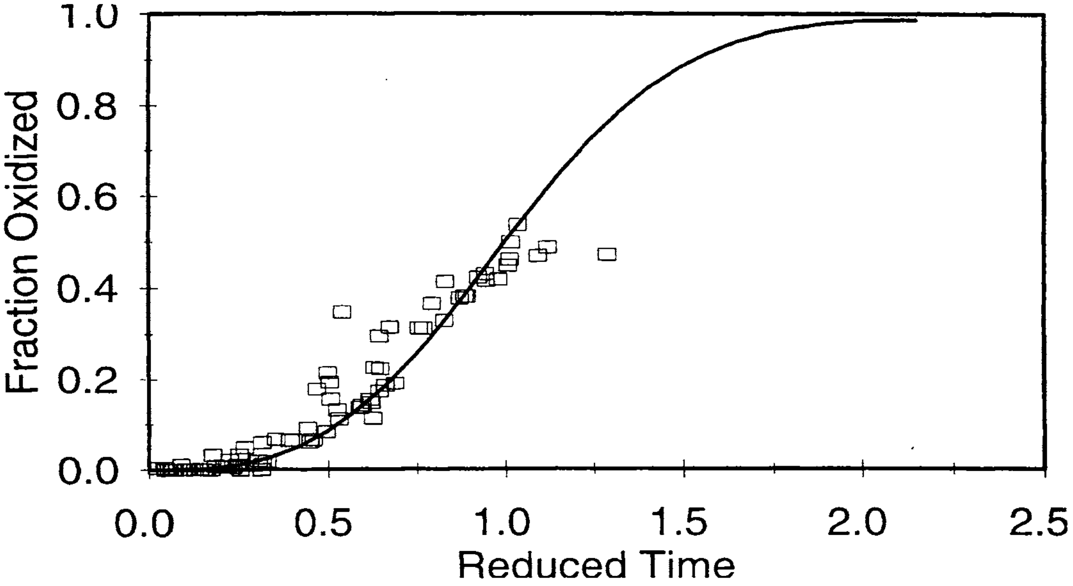

FIGURE 3: EXPERIMENTAL DATA FOR THE FRACTION OF THE SURFACE CONVERTED TO U_3O_8 AS A FUNCTION OF REDUCED TIME (i.e., $t/t_{1/2}$, WHERE $t_{1/2}$ IS THE TIME REQUIRED TO ACHIEVE 50% REACTION.

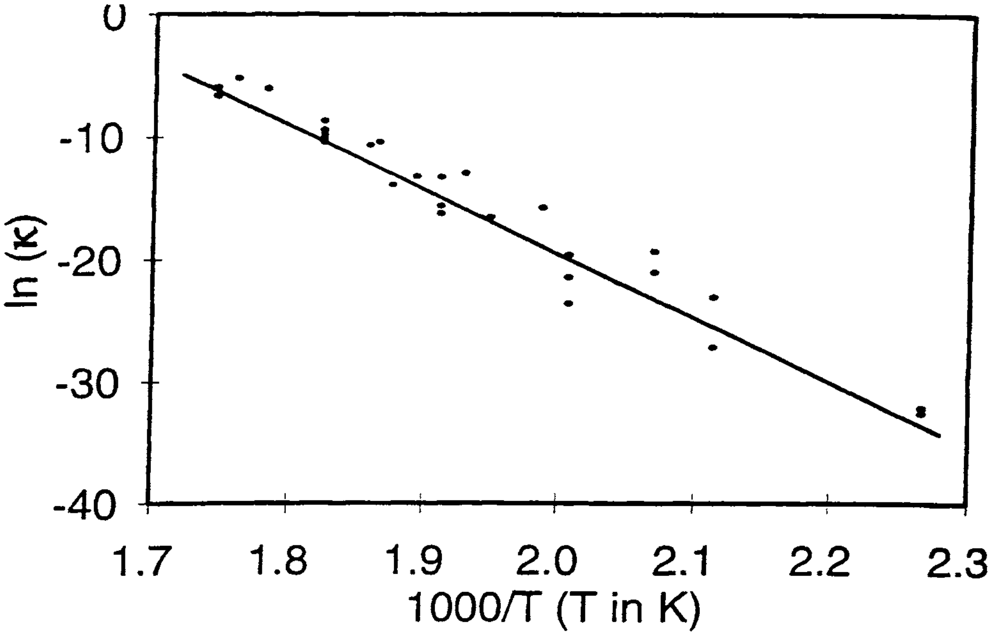

FIGURE 4: ARRHENIUS PLOT FOR THE AVERAGE RATE CONSTANT (κ) FOR THE FORMATION OF U_3O_8 ON UO_2. THE FITTED LINE IS BASED ON A WEIGHTED LINEAR REGRESSION AND YIELDED AN ACTIVATION ENERGY OF 146 ± 10 kJ·mol^{-1}.

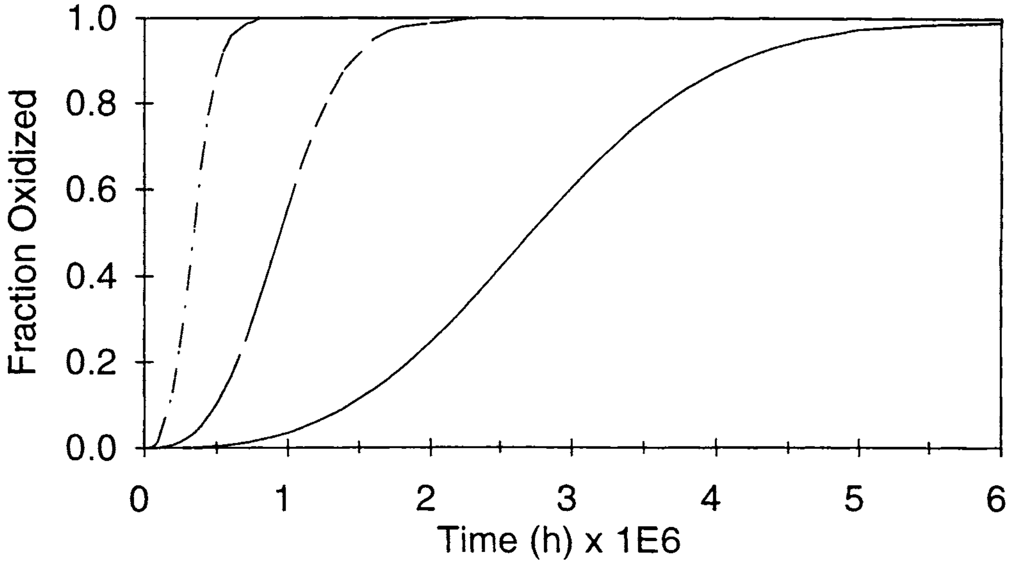

FIGURE 5: CALCULATED EXTENT OF SURFACE OXIDATION (OUTER 1 μm) OF UO_2 TO U_3O_8 AT 130 (——), 140 (— — —), AND 150°C (— ··), BASED ON κ VALUES DETERMINED USING EQUATION [4].