# MODELLING OF $UO_2$ OXIDATION IN STEAM

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## ABSTRACT

*A computer model has been developed for calculating oxidation of $UO_2$ at high temperatures in steam oxidising conditions. Several methods to calculate the partial pressure of oxygen in the fuel and in the environment surrounding the fuel are available. The various methodologies have been compared and the best models have been compiled into a computer model which will be implemented into fuel thermal/mechanical behaviour codes such as FACTAR 2.0 (LOECI) and ELESIM/ELOCA. Calculations from the computer model have been compared to experimental results. The calculated oxidation reaction kinetics are in good agreement with the experimental data.*

## 1. INTRODUCTION

During CANDU postulated accidents, the reactor fuel is estimated to experience large temperature variations and to be exposed to a variety of environments from highly oxidising to mildly reducing. The exposure of CANDU fuel to these environments and temperatures may affect its stoichiometry and fission product release performance.

One of the possible environments is steam. At elevated temperatures (*i.e.*, in excess of 1000°C), the Zircaloy sheath competes with the $UO_2$ for the available oxygen. Experimental evidence clearly demonstrates[1] that when the Zircaloy sheath has been consumed, the available oxygen in the environment can react with the $UO_2$. Under these conditions, the $UO_2$ can incorporate excess oxygen to form $UO_{2+x}$.[2] Oxidation can cause enhanced fission product releases from the fuel and degradation of the fuel thermal properties. Thus, it is important to model $UO_2$ oxidation reactions as a tool for predicting fuel and fission product behaviour where the sheath is expected to be totally oxidised.[3]

This oxidation model has been jointly developed within the Canadian nuclear industry under the SOURCE 2.0 project.[4] SOURCE 2.0 is a safety analysis code which will model the necessary mechanisms required to calculate fission product release for a variety of accident scenarios, including large break loss of coolant accidents (LOCAs) with or without emergency coolant injection (ECI). In order for the fuel thermal/mechanical behaviour codes to provide appropriate fuel initial and transient conditions to SOURCE 2.0, modelling of the phenomena that modify the fuel stoichiometry is essential. The model for fuel oxidation in steam will be implemented in fuel performance codes such as FACTAR.[5] The computer code FACTAR[6,7] (Fuel And Channel Temperature And Response) models the thermal-mechanical response of a single CANDU fuel channel under loss of coolant conditions. The version 1 code series and FACTAR 2.0 (LOCA) were designed to be applicable for large and transition break LOCA scenarios where emergency coolant injection is assumed available. The next generation of the code, FACTAR 2.0 (LOECI), is being developed for application in scenarios where the ECI system is assumed to be completely or partially unavailable. Loss of emergency coolant injection (LOECI) scenarios result in high fuel and channel temperatures, possibly leading to complete oxidation of the Zircaloy sheath. Therefore, changes to the fuel stoichiometry due to fuel oxidation by steam may occur, resulting in a significant impact on the thermal and mechanical behaviour of the fuel bundle as well as on fission product release.

Rates of $UO_2$ oxidation, reaction product compositions, and morphology of the reaction products are all functions of temperature and the oxygen potential of the gas phase. Several methods for calculating the oxygen partial pressure in the atmosphere and in the fuel exist. This paper presents a comprehensive review of the various methodologies available and gives the models which were chosen for implementation in the fuel thermal/mechanical behaviour codes. The deviation from stoichiometry of the fuel was calculated using the chosen models for various temperature ranges and oxygen partial pressures, and the calculated results are presented here.

## 2. MODEL DESCRIPTION

### 2.1 Steam Oxidation of $UO_2$

The stoichiometry deviation of the fuel will increase as the fuel is exposed to a steam environment.[8] The oxidation process occurs by a series of sub-processes, one or more of which may limit the overall rate of oxidation. Interpretation of experimental data and theoretical models indicates that each different sub-process may dominate the oxidation reaction within definite ranges of oxygen partial pressure, temperature, and gas composition. The fuel oxidation in steam is modelled as an interfacially controlled process (*i.e.*, the overall rate is controlled by the surface-exchange reaction at the solid/gas interface).[4,9]

According to this model,[8,9] the rate of change of the deviation from stoichiometric composition (*i.e.*, x in $UO_{2+x}$) can be expressed:

$$\frac{dx}{dt} = \frac{\alpha S}{V}\left(x^{eq} - x(t)\right)\left(P_{H_2O}\right)^m \tag{1}$$

where: $\alpha$ is the surface exchange coefficient (m/s), S/V is the surface-to-volume ratio of the fuel fragment ($m^{-1}$), $x^{eq}$ is the equilibrium stoichiometry of the fuel, $P_{H2O}$ is the steam partial pressure (atm), and m is the order of the reaction with respect to the steam pressure. This dependence of the fuel oxidation kinetics on the steam pressure was suggested by Abrefah, *et al.*[10] Experiments indicate that at low steam partial pressures (between 0.01 atm and 1 atm) oxidation kinetics follow a square root dependence (*i.e.*, $m = 1/2$).[8]

The surface exchange coefficient, $\alpha$, has been experimentally determined by Cox *et al.*[3,9] and was found to vary with the fuel surface temperature, T (in K) according to the following Arrhenius relationship (derived from data between 1273K and 1873K at 1 atm):

$$\alpha = \alpha_o \exp\left(-\frac{Q_\alpha}{T}\right) = 0.365 \exp\left(-\frac{23500}{T}\right) \tag{2}$$

Above 1673K, a fitting model is complicated by $UO_3$ volatilisation where the weight loss can in fact overcome the oxidation weight gain.[8]

The surface-to-volume ratio is obtained by assuming that the fuel is comprised of two regions: an inner plastic core (bounded by the bridging annulus) and an outer annulus containing a number of radial cracks in which steam can penetrate into the fuel.[11] Thus, the surface-to-volume ratio is equal to the geometrical surface-to-volume ratio of the given region (*i.e.*, the fuel fragments in the outer region, or the inner plastic core). It must be noted that steam is assumed to enter at the external boundaries of the region (*i.e.*, the exposed fuel surface to steam, including the radial cracks).

The stoichiometry deviation as a function of time can be calculated by solving Equation (1) using a first-order Runge-Kutta method.[12] In order to calculate the deviation from stoichiometry of the fuel, the oxygen partial pressure of the atmosphere must be determined, as well as the equilibrium stoichiometry of the fuel.

### 2.2 Calculation of The Environment Oxygen Partial Pressure

The oxidation of the fuel is a function of the oxygen potential of the gas phase (*i.e.*, the environment inside the fuel-to-sheath gap). Two methods for calculating the oxygen partial pressure in the atmosphere (which determines the oxygen potential) are available and are compared for varying temperature and environment composition: the law of mass action[13] and Olander's transcendental equation.[14]

#### 2.2.1 Law of Mass Action

The oxygen partial pressure in the atmosphere can be evaluated at equilibrium at a given temperature T from the law of mass action for the following reaction[13]:

$$2\,H_2O(g) \Leftrightarrow 2\,H_2(g) + O_2(g) \tag{3}$$

Where the equilibrium constant ($K_2$) for water vapour decomposition is given by:

$$K_2 = \frac{p_{O_2}\,p_{H_2}^2}{p_{H_2O}^2} \tag{4}$$

where: $p_{O_2}$ is the partial pressure of oxygen (atm), $p_{H_2}$ is the partial pressure of hydrogen (atm), and $p_{H_2O}$ is the partial pressure of steam (atm). If only steam and hydrogen are initially present, a cubic equation results from Equation (4) and it is given in Section 2.2.1.1. For environment compositions which may include steam, hydrogen, air and inert gases, the solution is given in Section 2.2.1.2

The expression of the equilibrium constant, $K_2$ (Equation (4)) was derived by several authors:[8]

Kubaschewski:[15] $$K_2 = K_{kub}^2 \Rightarrow K_{kub} = \exp\{0.9794\ln(T) - 1.1125 - \frac{28820.0692}{T}\} \tag{5}$$

Olander:[14] $$\log K_2 = -\frac{26200}{T} + 6.032 \tag{6}$$

Wheeler and Jones:[16] $$\log K_2 = -\frac{25026}{T} + 1.958\log T - 0.9659 \tag{7}$$

Ulich:[17] $$\log K_2 = -\frac{25300}{T} + 4.64 + 1.04(0.0007T - 0.2) \tag{8}$$

where: T is the temperature in K.

Figure 1 shows comparisons of these equilibrium constants as a function of temperature. The representation by Ulich deviates significantly from the other representations, therefore it is not chosen. The Wheeler and Jones and Kubaschewski formulations give very similar results which are larger than Olander's equilibrium constant. Because of this characteristic, for implementation in the fuel oxidation model, the Kubaschewski representation was chosen.

### 2.2.1.1 Steam and Hydrogen Gas Mixtures

Assuming that only steam and hydrogen are initially introduced into the system, the laws of mass conservation for hydrogen and oxygen are given by:[8]

$$p_{H_2O} + p_{H_2} = (p_{H_2O})_i + (p_{H_2})_i \tag{9}$$

$$p_{H_2O} + 2p_{O_2} = (p_{H_2O})_i \tag{10}$$

where: i represents the initial values. Equations (4), (9) and (10) lead to a cubic equation for the oxygen partial pressure:

$$4(p_{O_2})^3 + 4[(p_{H_2})_i - K_2]p_{O_2}^2 + [(p_{H_2}^2)_i + 4(p_{H_2O})_i K_2]p_{O_2} - (p_{H_2O}^2)_i K_2 = 0 \tag{11}$$

Simplifications of this cubic equation have been reported by Lewis *et al.*[8] for two asymptotic cases of interest: pure steam case and a case with a large contribution of hydrogen.

### 2.2.1.2 Steam, Oxygen, Hydrogen and Inert Gas Mixtures

When the following gases exist in the system: $H_2O$, $H_2$ (produced due to Zircaloy/steam reaction), $O_2$, and inert (air present in the reactor channels), a more general solution has been developed by Cox[13]. It is assumed that all gases in the system are ideal, therefore:

$$\frac{p_i}{p_{tot}} = \frac{n_i}{\sum_{j=1}^{N} n_j} \tag{12}$$

where: $p_i$ is the partial pressure of component i (atm), $p_{tot}$ is the total pressure of all gases (atm), $n_i$ is the number of moles of component i (moles), and N is the total number of component gases in the system. The equilibrium constant, K, for the reaction $H_2O \Leftrightarrow H_2 + 1/2\ O_2$ (same reaction as given in Equation (3) by dividing the number of moles by 2) can be expressed as:

$$K = \sqrt{K_2} = \frac{p_{H_2}\sqrt{p_{O_2}}}{p_{H_2O}} = \frac{n_{H_2}\sqrt{\dfrac{n_{O_2}\,p_{tot}}{(n_{O_2} + n_{H_2} + n_{H_2O} + n_{inert})}}}{n_{H_2O}} \tag{13}$$

When the input gases are mixed, it is assumed that isobaric gas-phase reactions take place in order for the system to achieve equilibrium. The number of moles of $H_2O$ consumed in this reaction is $\beta$, and the new equilibrium is:

$$K = \frac{(n_{H_2} + \beta)}{(n_{H_2O} - \beta)}\sqrt{\frac{(n_{O_2} + \frac{\beta}{2})p_{tot}}{(n_{O_2} + n_{H_2} + n_{H_2O} + n_{inert} + \frac{\beta}{2})}} \tag{14}$$

Once $\beta$ is determined, knowing the input quantities $n_{H2O}$, $n_{O2}$, $n_{H2}$, and $n_{inert}$, the partial pressures of the individual components are determined as follows:

$$p_{H_2} = \frac{n_{H_2} + \beta}{\sum_{j=1}^{N} n_j + \frac{\beta}{2}}, \quad p_{O_2} = \frac{n_{O_2} + \frac{\beta}{2}}{\sum_{j=1}^{N} n_j + \frac{\beta}{2}}$$

$$p_{H_2O} = \frac{n_{H_2O} - \beta}{\sum_{j=1}^{N} n_j + \frac{\beta}{2}}, \quad p_{inert} = \frac{n_{inert}}{\sum_{j=1}^{N} n_j + \frac{\beta}{2}} \tag{15}$$

### 2.2.2 Transcendental Equation

Another method of solution is to use Olander's transcendental equation.[14] The oxygen partial pressure in the atmosphere ($p_{O2}$ in atm) can be estimated from:

$$K_1 (p_{O_2})^{1/2} \left[ \left( \frac{Q_a}{2} - 1 \right) + \left( \frac{Q_a}{2} + 1 \right) \frac{p_{O_2}}{p_t} \right] = 1 - (Q_a + 1) \left( \frac{p_{O_2}}{p_t} \right) \tag{16}$$

where:

$$K_1 = \exp\left( -\frac{\Delta G^0}{RT} \right), \quad \Delta G^0 = -250800 + 57.8T \text{ J/mol} \tag{17}$$

R is the universal gas constant (8.3145 J/mole.K), and $p_t$ is the total system pressure (atm). The parameter $Q_a$ is the hydrogen-to-oxygen atom ratio of the environment:

$$Q_a \approx 2\left( 1 + \frac{n_{H_2}}{n_{H_2O}} \right) \tag{18}$$

where: $n_{H2}$ is the number of moles of hydrogen in the gas mixture (moles), and $n_{H2O}$ is the number of moles of steam in the gas mixture (moles).

### 2.2.3 Comparison of Models to Calculate the Oxygen Partial Pressure

The previously described methods to calculate the oxygen partial pressure in the gas are compared using the following equilibrium constants: (i) the general form of the law of mass action (Equation (14)) allowing for gas compositions which may include hydrogen, oxygen, steam and inert gases; using the Kubaschewski equilibrium constant (Equation (5)); (ii) Olander's transcendental equation (Equation (16)); and (iii) the law of mass action for gas compositions including steam and hydrogen gas only (Equation (11)), using Olander's equilibrium constant (Equation (6)) (if the Wheeler and Jones equilibrium constant was used, the solutions would give identical results to (i)).

These methods are compared for environment temperatures between 1200 K and 2200 K, and for the following gas compositions: (i) 90% steam and 10% hydrogen gas; (ii) 50% steam and 50% hydrogen gas, and (iii) 20% steam and 80% hydrogen gas. The results are shown in Tables 1 to 3. These results show that the oxygen partial pressure in the environment is higher for the general form of the law of mass action when the oxygen partial pressure becomes more significant (*e.g.*, greater than $10^{-9}$ atm). From these results, the most general form of the law of mass action was chosen for implementation in the fuel oxidation steam model. This solution has the additional advantage of being general enough to calculate the oxygen partial pressure in the environment for gas compositions which may include hydrogen gas, oxygen gas, inert gas and steam. The equilibrium constant to be used with this formulation is the Kubaschewski representation or the Wheeler and Jones representation since they give higher partial pressures than the Olander equilibrium constant.

## 2.3 Calculation Of The Equilibrium Composition

When $UO_2$ is exposed to air, steam or mixtures of air and steam, it will oxidise to a composition which is in equilibrium with the gas phase. It is necessary to calculate the equilibrium composition in order to describe the oxidation process. The equilibrium composition can be calculated from thermodynamic data, as a function of temperature and the oxygen potential of the gas. In steam dominated environments, the equilibrium composition is hyper-stoichiometric $UO_2$ (*i.e.*, $UO_{2+x}$, $x > 0$).

To calculate the equilibrium deviation from stoichiometry of the fuel, $x^{eq}$, the partial pressure of oxygen in the environment is equated to the partial pressure of oxygen in the fuel. Two methods to calculate the fuel equilibrium stoichiometry are examined in this paper: the Blackburn thermomechanical model[18] and the solid solution representation of Lindemer and Besmann[19].

### 2.3.1 Blackburn Thermomechanical Model

The partial pressure of oxygen of the fuel, as given by the Blackburn thermomechanical model,[18] is:

$$\ln(p_{O_2}) = 2\ln(x) - 2\ln(1 - x) + 2\ln(2 + x) + 108x^2 - \frac{32700}{T} + 9.92 \qquad (19)$$

where: $p_{O_2}$ is the partial pressure of oxygen in the fuel (atm), x is the deviation from stoichiometry of the fuel, and T is the fuel temperature (K).

### 2.3.2 Lindemer and Besmann Solid Solution

The partial pressure of oxygen in equilibrium with the fuel, as given by the solid solution representation of Lindemer and Besmann,[19] is:

$$\ln(p_{O_2}) = -\frac{360000}{RT} + \frac{214}{R} + 4\ln\left[\frac{2x(1-2x)}{(1-4x)^2}\right], \quad \text{for } p_{O_2} \le (p_{O_2})_B \qquad (20)$$

$$\ln(p_{O_2}) = -\frac{312800}{RT} + \frac{126}{R} + 2\ln\left[\frac{x(1-2x)^2}{(1-3x)^3}\right], \quad \text{for } p_{O_2} > (p_{O_2})_B \qquad (21)$$

where: T is the fuel temperature (K), R is the universal gas constant (8.3145 J/mole.K), and $(p_{O_2})_B$ is the limiting oxygen partial pressure (atm) between Equation (20) and Equation (21), given by:

$$(p_{O_2})_B = \exp\left[-\frac{266700}{RT} + \frac{16.5}{R}\right] \qquad (22)$$

### 2.3.3 Comparison of Models to Calculate the Equilibrium Composition

The Blackburn thermomechanical model is a physically-based model, whereas the solid-solution representation by Lindemer and Besmann is an experimentally-based correlation. Lindemer and Besmann[19] have shown that the Blackburn thermomechanical model agrees very well with the experimental data for oxygen partial pressure higher than the pressure boundary between the two Lindemer and Besmann solutions (Equation (22)), though it over-predicts experimental data for oxygen partial pressures lower than the pressure boundary between the two Lindemer and Besmann solutions (Equation (22)). However, it must be noted that the Lindemer and Besmann correlation can be used with confidence only up to the limit of experimental data (approximately 1773K). For temperatures higher than this limit, any extrapolations to a correlation should be avoided until further experimental information is obtained. Therefore, the Blackburn model should be used for temperatures above the experimental data limit, because the extrapolation of a physical model lends more confidence to the solution than the extrapolation of a correlation. The Lindemer and Besmann model for low oxygen partial pressures should be used for temperatures lower than the limit of the experimental information and for pressures lower than $(p_{O2})_B$.

To determine which model should be used for temperatures less than 1773K and for high oxygen partial pressures (higher than $(p_{O2})_B$), the two solution methods are compared for fuel temperatures between 1200K and 2200K in pure steam as shown in Table 4. Note that for these calculations, the oxygen partial pressure in the environment was calculated using the general form of the law of mass action with the Kubaschewski equilibrium constant. The pure steam case was chosen because it results in partial pressures which are always higher than the boundary limit (*i.e.*, $(p_{O2})_B$) for the temperature range prescribed, thus providing information in the range which must be determined. At temperatures lower than 1773K, the Lindemer and Besmann model predicts higher fuel equilibrium stoichiometry than Blackburn. The lower limit of the Lindemer and Besmann solution (*i.e.*, Equation (20)) is used for $p_{O2} \leq (p_{O2})_B$, and for $p_{O2} > (p_{O2})_B$, the higher limit of the Lindemer and Besmann solution (*i.e.*, Equation (21)) is used.

The experimental measurements published by Abrefah *et al.*[10] for temperatures between 1273K and 1623K fall between the values calculated using the Blackburn thermomechanical model and the Lindemer and Besmann solid solution.

At temperatures higher than 1773K the Blackburn model predicts higher equilibrium stoichiometry values than the Lindemer and Besmann model. In order to maximise oxidation of the fuel, and to attain confidence in the extrapolation of models, for temperatures higher than 1773 K, the Blackburn thermomechanical model should be used (*i.e.*, Equation (19)).

## 3. COMPARISON TO EXPERIMENTAL DATA

The amount of published kinetic data for $UO_2$ oxidation in steam is very limited. Experiments have been performed at Chalk River Laboratories at constant temperature and environment conditions.[9] There are no experimental data available for transient temperature and environmental compositions.

Comparisons between experimental data and calculations using the model described in this paper are presented in Figures 2 to 6, at fuel-environment equilibrium temperatures of 1273K, 1473K, 1623K, 1773K and 1873K. In all cases, the calculated kinetics is in good agreement with the experimental data. For the 1273K case, the scattering of the data arises from the difficulty of holding constant temperatures and environment conditions during the experiments for long periods of time. It should be noted that the values used for the surface-to-volume ratio are the samples' geometric values. Experimental data for transient conditions in high temperature steam are needed to fully validate this oxidation model.

## 4. SUMMARY

A fuel oxidation in steam model has been developed under the SOURCE 2.0 development program to be implemented in fuel accident behaviour codes (*e.g.*, FACTAR 2.0 (LOECI)). The model predictions for the oxidation of the fuel under high temperature steam oxidising conditions are in excellent agreement with the available experimental data on fuel oxidation kinetics. Several methodologies to calculate the oxygen partial pressure in the environment and in the fuel have been examined and compared. The model chosen for the calculation of the oxygen partial pressure in the environment was the general form of the law of mass action using the Kubaschewski equilibrium constant. For the calculation of the fuel equilibrium stoichiometry, the Blackburn thermomechanical model was chosen for temperatures higher than 1773K. For temperatures lower than 1773K, the Lindemer and Besmann model was selected. The fuel oxidation kinetics is controlled by the surface-exchange reaction at the solid/gas interface using the model by Cox *et al.*[9]

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## 6. REFERENCES

(1) D.S. COX, Z. LIU, R.S. DICKSON and P.H. ELDER, "Fission Product Releases During Post-Irradiation Annealing of High Burnup Fuel," Proceedings of 3rd International Conference on CANDU Fuel, Pembroke, Ontario, 1992.

(2) D.S. COX, C.E.L. HUNT, Z. LIU, F.C. IGLESIAS, N.A. KELLER, R.D. BARRAND, R.F. O'CONNOR, "A Model for the Release of Low-Volatility Fission Products in Oxidizing Conditions," presented at the 12th Annual Conference of the Canadian Nuclear Society, Saskatoon, Saskatchewan, Canada, June 9-12, 1991.

(3) D.S. COX, F.C. IGLESIAS, C.E.L. HUNT, R.F. O'CONNOR and R.D. BARRAND, "High Temperature Oxidation Behaviour of $UO_2$ in Air and Steam," Proceedings of the International Symposium on High Temperature Oxidation and Sulphidation Processes, Hamilton, Ontario, Canada, August 26-30, 1990, Pergammon Press, ISBN 0-18-040415-4, AECL report, AECL-10442.

(4) A.C. BRITO, F.C. IGLESIAS, Y. LIU, M.A. PETRILLI, M.J. RICHARDS, R.A. GIBB and P.J. REID, "SOURCE 2.0: A Computer Program to Calculate Fission Product Release From Multiple Fuel Elements for Accident Scenarios," presented at the 4th International Conference on CANDU Fuel, Pembroke, Ontario, October 1-4, 1995.

(5) C.J. WESTBYE, J.C. MACKINNON, B.W. GU, J.D. BALLYK, A.C. BRITO, D. EVENS, and R.C.K. ROCK, "The Fuel and Channel Thermal/Mechanical Behaviour Code FACTAR 2.0 (LOCA)," Presented at the 17th Annual Conference of the Canadian Nuclear Society, Fredericton, New Brunswick, Canada, June 9-12, 1996.

(6) C.J. WESTBYE, A.C. BRITO, J.C. MACKINNON, H.E. SILLS and V.J. LANGMAN, "Development, Verification and Validation of the Fuel Channel Behaviour Code *FACTAR*," Presented at the 16th Annual Conference of the Canadian Nuclear Society, Saskatoon, Saskatchewan, Canada, June 4-7, 1995.

(7) C.J. WESTBYE, A.C. BRITO, J.C. MACKINNON, H.E. SILLS and V.J. LANGMAN, "Fuel Thermal/Mechanical Behaviour Under Loss of Coolant Accident Conditions as Predicted by the *FACTAR* Code," Presented at the 4th International Conference on CANDU Fuel, Pembroke, Ontario, Canada, October 1-4, 1995.

(8) B.J. LEWIS, B. ANDRE, B. MOREL, P. DEHAUDT, D. MARO, P.L. PURDY, D.S. COX, F.C. IGLESIAS, M.F. OSBORNE and R.A. LORENZ, "Modelling the Release Behaviour of Cesium During Severe Fuel Degradation," *J. Nucl. Mater.*, **227** (1995) 83.

(9) D.S. COX, F.C. IGLESIAS, C.E.L. HUNT, N.A. KELLER, R.D. BARRAND, J.R. MITCHELL, and R.F. O'CONNOR, "Oxidation of $UO_2$ in Air and Steam with Relevance to Fission Product Releases," Proceedings of the Symposium on Chemical Phenomena Associated with Radioactivity Release During Severe Nuclear Plant Accidents, Anaheim, California, U.S.A., September 9-12, 1986. Report NUREG/CP-0078.

(10) J. ABREFAH, A. DE AGUIAR BRAID, W. WANG, Y. KHALIL and D.R. OLANDER, "High Temperature Oxidation of $UO_2$ in Steam/Hydrogen Mixtures," *J. Nucl. Mater.* **208** (1994) 98.

(11) B.J. LEWIS, F.C. IGLESIAS, D.S. COX and E. GHEORGHIU, "A Model for Fission Gas Release and Fuel Oxidation Behaviour for Defected $UO_2$ Fuel Elements," *Nucl. Technol.* **92** (1990) 353.

(12) G.H. GOLUB and J.M. ORTEGA, Scientific Computing and Differential Equations - An Introduction to Numerical Methods, Academic Press, Inc., San Diego, California, 1992.

(13) D.S. COX, "FOXSIM Version 2: Fuel Oxidation Simulation for $UO_2$ in Air and Steam," Atomic Energy of Canada Report RC-402, February 1990.

(14) D.R. OLANDER, "Oxidation of $UO_2$ by High-Pressure Steam," *Nucl. Technol.* **74** (1986) 215.

(15) O. KUBASCHEWSKI and C.B. ALCOCK, Metallurgical Thermochemistry, 5th Edition, Pergammon Press, New York, 1979.

(16) V.J. WHEELER and I.G. JONES, "Thermodynamic and Composition Changes in $UO_{2\pm x}$ ($x < 0.005$) at 1950 K," *J. Nucl. Mater.* **42** (1972) 117.

(17) B. MOREL, N. SEROSE, S. GAMAURY, and P. DEHAUDT, "Cinitique d'Oxydation du Combustible par la Vapeur d'Eau; Influence du S/V," Comissariat à l'Energie Atomique, Report NT / DTP / SECC no. DR94-55 (June 1994).

(18) P.E. BLACKBURN, "Oxygen Pressures over Fast Breeder Reactor Fuel, (i) A Model for $UO_{2\pm x}$," *J. Nucl. Mater.* **46** (1973) 244.

(19) T.B. LINDEMER and T.M. BESMANN, "Chemical Thermodynamic Representation of $<UO_{2\pm x}>$,' *J. Nucl. Mater.* **130** (1985) 473.

## TABLE 1
## COMPARISON OF MODELS TO CALCULATE THE ENVIRONMENT OXYGEN PARTIAL PRESSURE FOR 10% HYDROGEN GAS AND 90% STEAM

| Temperature (K) | Oxygen Partial Pressure (atm)[*] | | |
|---|---|---|---|
| | Transcendental | General | Hydrogen/Steam Only |
| 1200 | 1.30E-14 | 1.30E-14 | 1.28E-14 |
| 1300 | 6.20E-13 | 6.11E-13 | 6.12E-13 |
| 1400 | 1.71E-11 | 1.68E-11 | 1.68E-11 |
| 1500 | 3.02E-10 | 2.99E-10 | 2.98E-10 |
| 1600 | 3.73E-09 | 3.74E-09 | 3.68E-09 |
| 1700 | 3.43E-08 | 3.51E-08 | 3.38E-08 |
| 1800 | 2.46E-07 | 2.58E-07 | 2.43E-07 |
| 1900 | 1.44E-06 | 1.55E-06 | 1.42E-06 |
| 2000 | 7.02E-06 | 7.80E-06 | 6.92E-06 |
| 2100 | 2.95E-05 | 3.38E-05 | 2.91E-05 |
| 2200 | 1.09E-04 | 1.28E-04 | 1.07E-04 |

## TABLE 2
## COMPARISON OF MODELS TO CALCULATE THE ENVIRONMENT OXYGEN PARTIAL PRESSURE FOR 50% HYDROGEN GAS AND 50% STEAM

| Temperature (K) | Oxygen Partial Pressure (atm)[*] | | |
|---|---|---|---|
| | Transcendental | General | Hydrogen/Steam Only |
| 1200 | 1.60E-16 | 1.60E-16 | 1.57E-16 |
| 1300 | 7.66E-15 | 7.54E-15 | 7.61E-15 |
| 1400 | 2.11E-13 | 2.07E-13 | 2.08E-13 |
| 1500 | 3.73E-12 | 3.69E-12 | 3.68E-12 |
| 1600 | 4.60E-11 | 4.62E-11 | 4.54E-11 |
| 1700 | 4.23E-10 | 4.33E-10 | 4.17E-10 |
| 1800 | 3.04E-09 | 3.19E-09 | 3.00E-09 |
| 1900 | 1.77E-08 | 1.91E-08 | 1.75E-08 |
| 2000 | 8.67E-08 | 9.63E-08 | 8.55E-08 |
| 2100 | 3.65E-07 | 4.18E-07 | 3.60E-07 |
| 2200 | 1.35E-06 | 1.59E-06 | 1.33E-06 |

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[*] *Transcendental* represents Olander's transcendental equation (Equation (16)). *General* represents the general form of the law of mass action (Equation (14)), and *Hydrogen/Steam Only* represents the law of mass action for gas compositions including steam and hydrogen gas only (Equation (11)).

## TABLE 3
## COMPARISON OF MODELS TO CALCULATE THE ENVIRONMENT OXYGEN PARTIAL PRESSURE FOR 80% HYDROGEN GAS AND 20% STEAM

| Temperature (K) | Oxygen Partial Pressure (atm)* | | |
|---|---|---|---|
| | Transcendental | General | Hydrogen/Steam Only |
| 1200 | 1.00E-17 | 1.00E-17 | 3.33E-17 |
| 1300 | 4.79E-16 | 4.72E-16 | 5.70E-16 |
| 1400 | 1.32E-14 | 1.29E-14 | 1.30E-14 |
| 1500 | 2.33E-13 | 2.31E-13 | 2.30E-13 |
| 1600 | 2.88E-12 | 2.89E-12 | 2.84E-12 |
| 1700 | 2.64E-11 | 2.71E-11 | 2.61E-11 |
| 1800 | 1.90E-10 | 1.99E-10 | 1.87E-10 |
| 1900 | 1.11E-09 | 1.19E-09 | 1.09E-09 |
| 2000 | 5.42E-09 | 6.02E-09 | 5.34E-09 |
| 2100 | 2.28E-08 | 2.61E-08 | 2.25E-08 |
| 2200 | 8.41E-08 | 9.97E-08 | 8.29E-08 |

## TABLE 4
## COMPARISON OF MODELS TO CALCULATE THE EQUILIBRIUM STOICHIOMETRY OF THE FUEL IN PURE STEAM

| Temperature (K) | $p_{O_2}$ (atm) | $(p_{O_2})_B$ (atm) | Equilibrium Stoichiometry** | |
|---|---|---|---|---|
| | | | Blackburn | Lindemer & Besmann |
| 1200.0 | 3.42E-06 | 1.79E-11 | 2.2275 | 2.6667 |
| 1300.0 | 1.24E-05 | 1.40E-10 | 2.2140 | 2.2454 |
| 1400.0 | 3.73E-05 | 8.15E-10 | 2.2020 | 2.2280 |
| 1500.0 | 9.73E-05 | 3.76E-09 | 2.1914 | 2.2105 |
| 1600.0 | 2.26E-04 | 1.43E-08 | 2.1818 | 2.1934 |
| 1700.0 | 4.76E-04 | 4.65E-08 | 2.1732 | 2.1768 |
| 1773.0 | 7.79E-04 | 1.01E-07 | 2.1674 | 2.1654 |
| 1800.0 | 9.25E-04 | 1.33E-07 | 2.1654 | 2.1613 |
| 1900.0 | 1.68E-03 | 3.39E-07 | 2.1583 | 2.1468 |
| 2000.0 | 2.87E-03 | 7.88E-07 | 2.1517 | 2.1336 |
| 2100.0 | 4.67E-03 | 1.69E-06 | 2.1457 | 2.1216 |
| 2200.0 | 7.25E-03 | 3.39E-06 | 2.1402 | 2.1107 |

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* *Transcendental* represents Olander's transcendental equation (Equation (16)). *General* represents the general form of the law of mass action (Equation (14)), and *Hydrogen/Steam Only* represents the law of mass action for gas compositions including steam and hydrogen gas only (Equation (11)).

** *Blackburn* represents the Blackburn Thermomechanical model given by Equation (19), and *Lindemer & Besmann* represents the Lindemer and Besmann solid solution given by Equations (20) and (21).

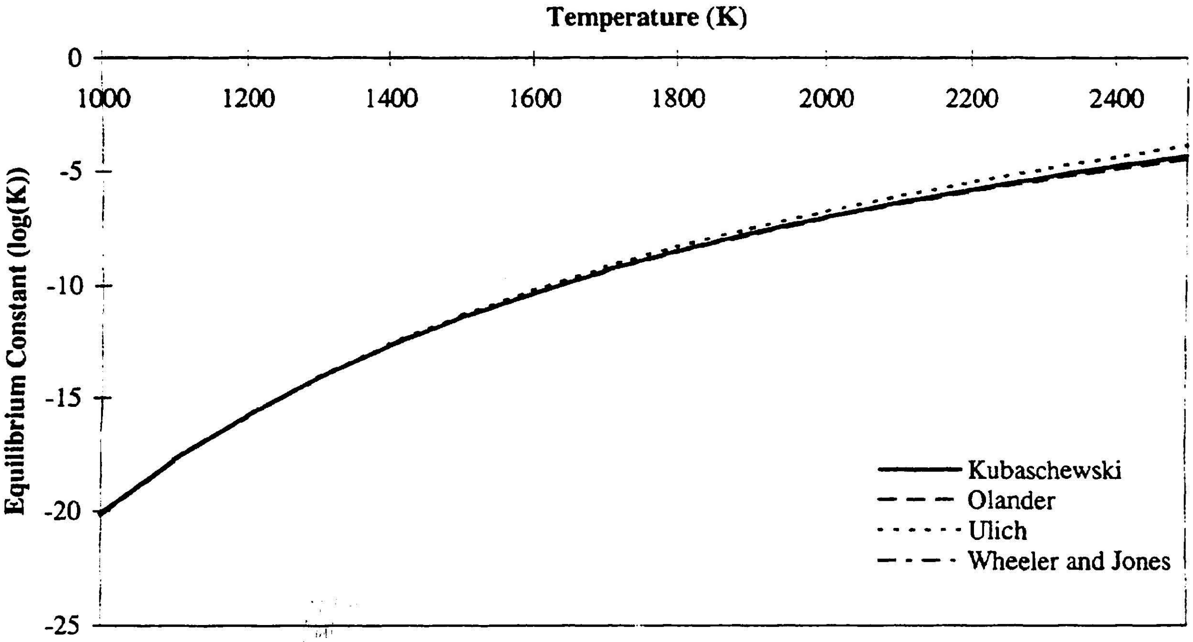

FIGURE 1
COMPARISON OF THE EQUILIBRIUM CONSTANT FOR WATER VAPOUR DECOMPOSITION AS A FUNCTION OF TEMPERATURE

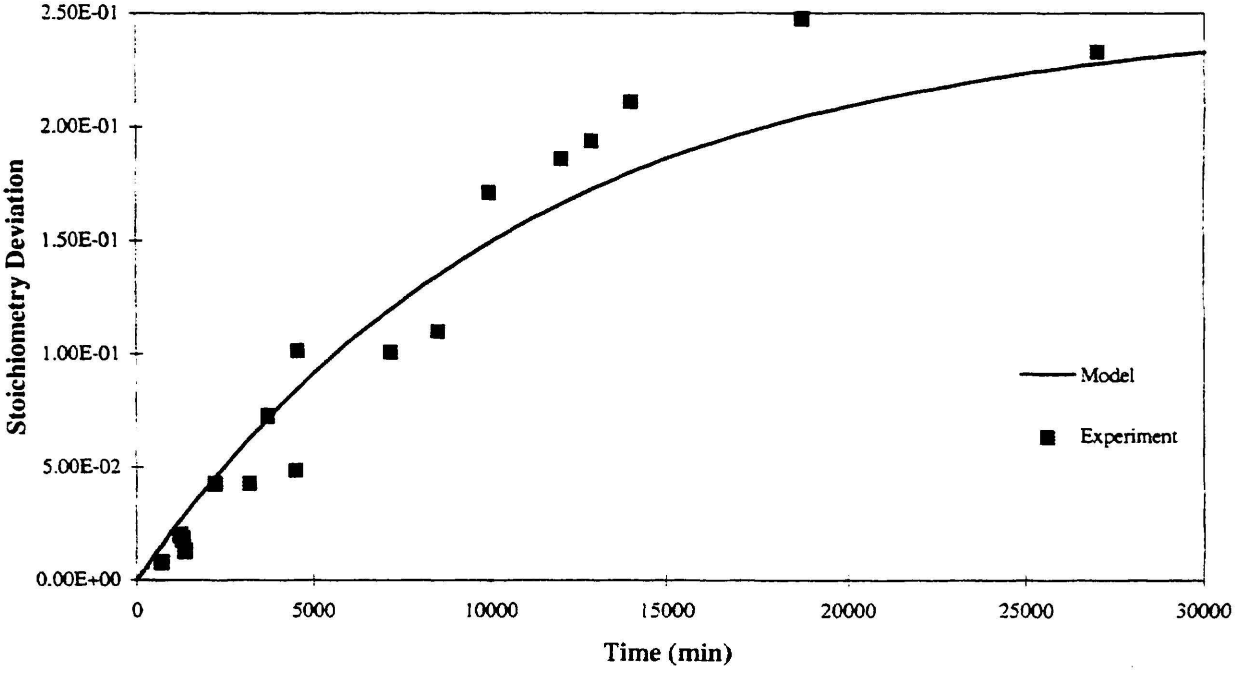

FIGURE 2
COMPARISON OF CALCULATIONS AND EXPERIMENTAL DATA FOR STEAM OXIDATION OF FUEL FRAGMENTS AT 1273K (90% STEAM, 10% INERT)

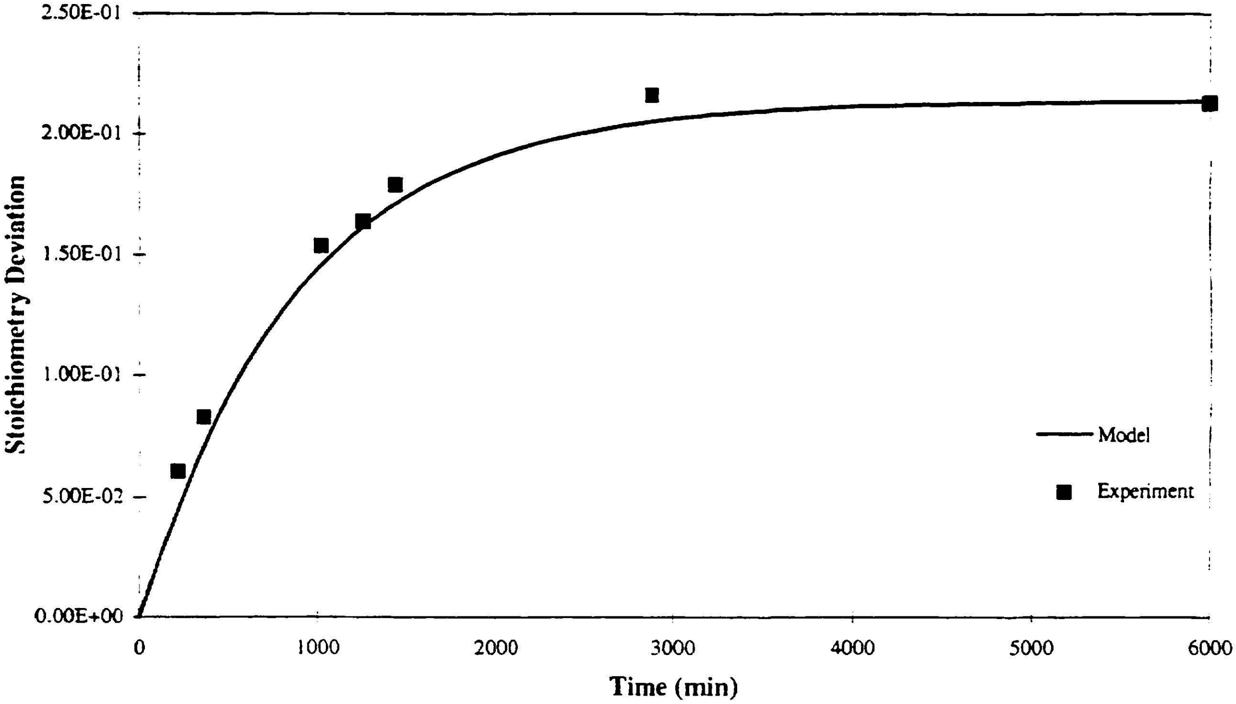

FIGURE 3
COMPARISON OF CALCULATIONS AND EXPERIMENTAL DATA FOR STEAM OXIDATION OF FUEL FRAGMENTS AT 1473K (90% STEAM, 10% INERT)

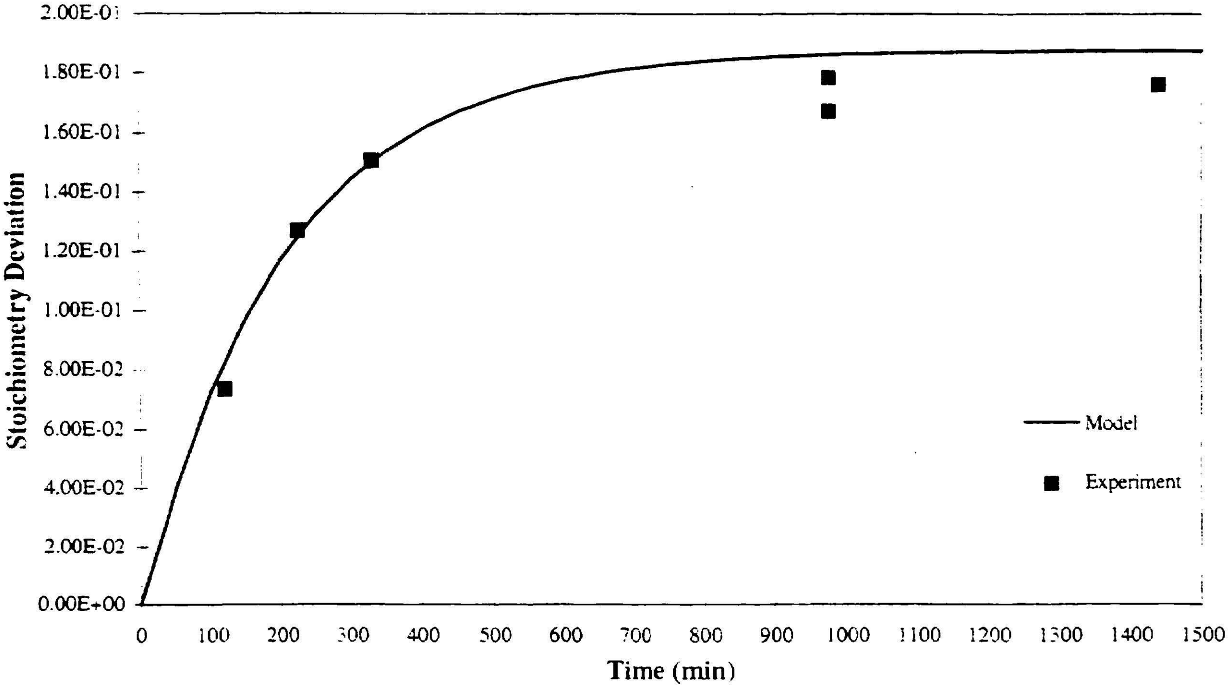

FIGURE 4
COMPARISON OF CALCULATIONS AND EXPERIMENTAL DATA FOR STEAM OXIDATION OF FUEL FRAGMENTS AT 1623K (90% STEAM, 10% INERT)

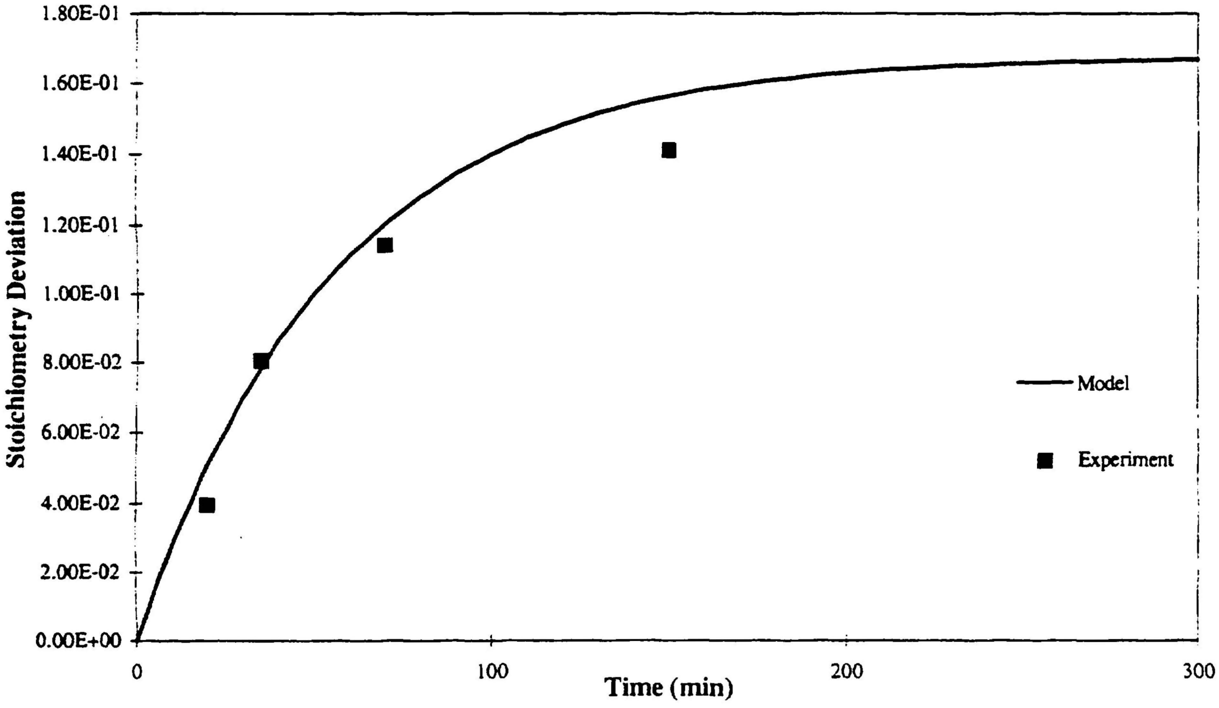

FIGURE 5
COMPARISON OF CALCULATIONS AND EXPERIMENTAL DATA FOR STEAM OXIDATION OF FUEL FRAGMENTS AT 1773K (90% STEAM, 10% INERT)

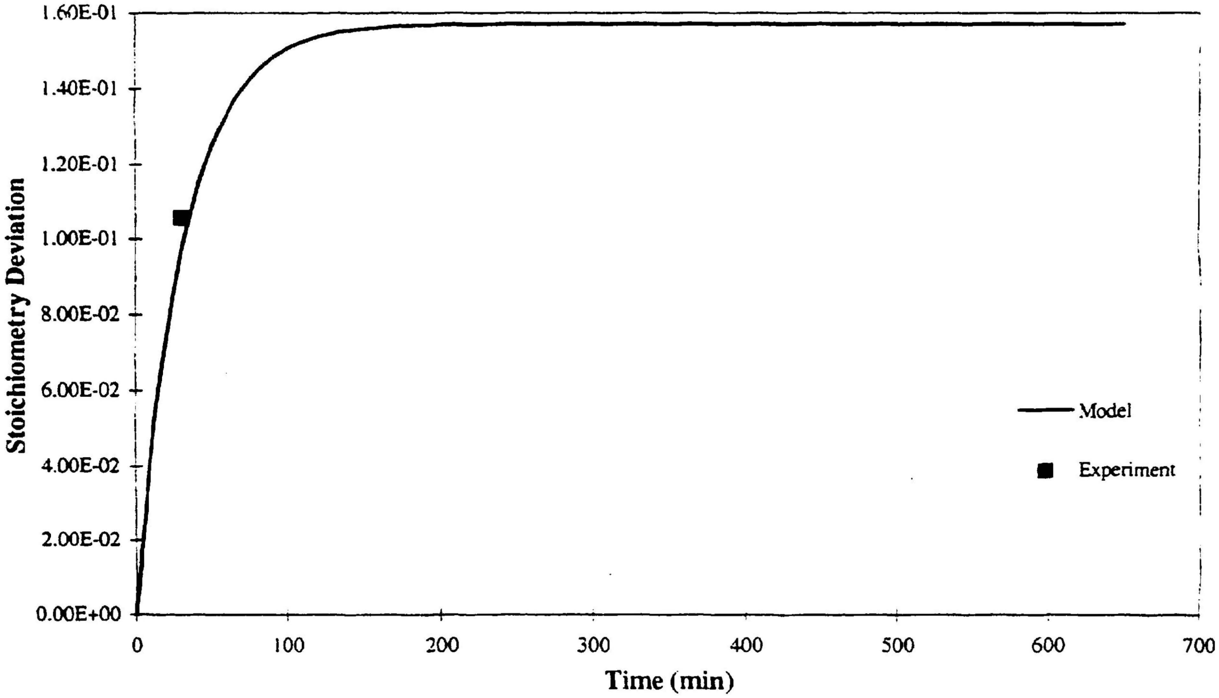

FIGURE 6
COMPARISON OF CALCULATIONS AND EXPERIMENTAL DATA FOR STEAM OXIDATION OF FUEL FRAGMENTS AT 1873K (80% STEAM, 20% INERT)