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A Two-Dimensional, Finite-Difference Model of the Oxidation of a Uranium Carbide Fuel Pellet

James Shepherd, Michael Fairweather, Bruce C. Hanson, and Peter J. Heggs

School of Chemical and Process Engineering, University of Leeds, Leeds, LS2 9JT, UK

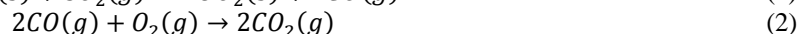
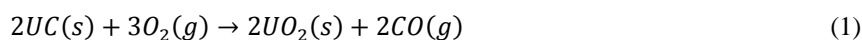
Abstract. The oxidation of spent uranium carbide fuel, a candidate fuel for Generation IV nuclear reactors, is an important process in its potential reprocessing cycle. However, the oxidation of uranium carbide in air is highly exothermic. A model has therefore been developed to predict the temperature rise, as well as other useful information such as reaction completion times, under different reaction conditions in order to help in deriving safe oxidation conditions. Finite difference-methods are used to model the heat and mass transfer processes occurring during the reaction in two dimensions and are coupled to kinetics found in the literature.

INTRODUCTION

Uranium carbide is a proposed fuel for Generation IV reactors on account of its higher thermal conductivity and metal atom density than the oxide fuel counterpart; the current fuel of choice in most reactors. Like any prospective nuclear fuel, a reprocessing route must be produced before the fuel can be implemented so that waste is minimised. Ideally, carbides would be oxidised in a similar manner to oxide fuels so that current infrastructure and methods could be used. To this end, pre-oxidation of spent carbide fuel to produce the oxide has been suggested.

The aim of this work is to produce a model that simulates such an oxidation. Due to the highly exothermic nature of the oxidation [1], it is important that the model is able to predict safe operating conditions. The model has been designed, therefore, to calculate the transient temperature distribution throughout the pellet over the course of the reaction, as well as the reaction rate and completion times given a set of initial oxidation conditions. This is achieved by assembling a variety of partial and ordinary differential equations that describe the various effects occurring, and using finite-difference approximations to solve them numerically.

The oxidation reaction is taken to be occurring only at the surface of the pellet, requiring the assumption of a non-porous pellet, and proceeds according to the reactions described in Eqs. (1) and (2) that are roughly similar to those observed by Naito *et al.* [1]:



In reality, a number of higher oxides are formed as a result of further oxidation of the uranium dioxide produced such as U_3O_8 and U_3O_7 [2]. However, these reactions are not considered due to the assumption that the UO_2 product layer produced by the reaction instantaneously spalls off and hence is not present in the system being modelled, as has been suggested by Mazaudier *et al.* [3], although this effect was in fact observed on a porous pellet.

The model considers the initial oxidation, represented by Eq. (1), to occur on the surface of the pellet and the second oxidation, Eq. (2), to occur in the gas phase surrounding the pellet. Both reactions have a calculated enthalpy that contributes to changes in the pellet and gas temperatures.

The two-dimensional approximation of the pellet used in the model is illustrated in Fig. 1. The fuel pellet is assumed to be axisymmetric, allowing a plane, or a 'slice', that is rotationally symmetrical about the central length axis of the cylinder to be the domain under consideration. Furthermore, because this plane is also symmetrical across the radius and length, only a quarter of it needs to be considered, as shown in Fig. 1.

Mass transfer of oxygen to the pellet surface from the bulk gas, as well as carbon monoxide in the opposite direction, is considered across a gaseous film layer surrounding the pellet. Heat transfer is considered between the bulk gas and the pellet and through the pellet itself.

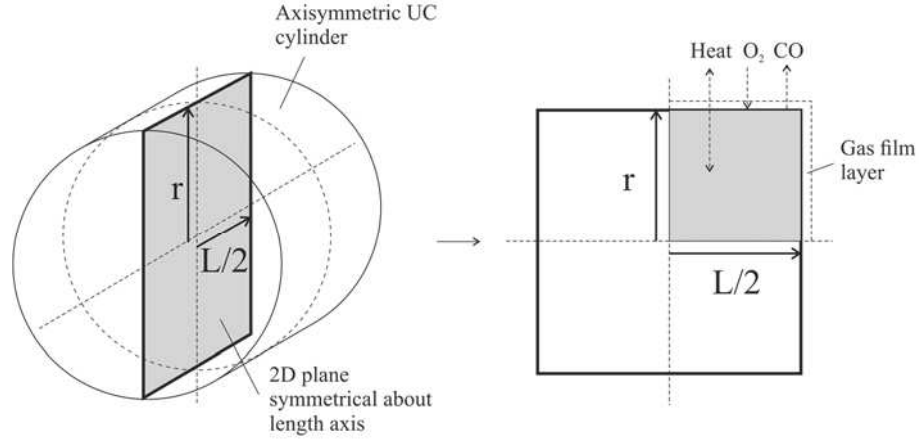


FIGURE 1. The two-dimensional representation of the pellet as a ‘slice’ through an axisymmetric cylinder, and the quarter considered as the domain by the model.

MATHEMATICAL REPRESENTATION

The reaction kinetics for the oxidation occurring at the pellet surface, represented by Eq. (1), are taken from work published by Scott [4] and are presented below in Eq. (3):

$$R_C = k_1 \exp(-E_A/RT|_s) A C_{O_2}|_s \quad (3)$$

where R_C is the rate of oxygen consumed by the surface reaction, k_1 is a constant, E_A the activation energy, R the gas constant, A the surface area of the sphere and $T|_s$ and $C_{O_2}|_s$ are the temperature and oxygen concentration at the surface of the pellet.

The reaction kinetics for the homogeneous oxidation of carbon monoxide in the gas phase are provided by Howard *et al.* [5] and given in Eq. (4):

$$-\frac{dC_{CO}^B}{dt} = 1.3 \times 10^{14} C_{CO}^B (C_{O_2}^B)^{0.5} (C_{H_2O}^B)^{0.5} \exp\left(\frac{-30}{RT^B}\right) \quad (4)$$

where T^B is the temperature of the bulk gas and C^B represents the concentration of the relevant species in the bulk gas.

The heat transfer in the system is modelling using the two-dimensional, cylindrical form of the Fourier equation for heat conduction:

$$\frac{\partial T}{\partial t} = \alpha \left(\frac{\partial^2 T}{\partial x^2} + \frac{1}{r} \cdot \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} \right) \quad (5)$$

where α is the thermal diffusivity of uranium carbide and r and x are the radius and length of the cylinder, respectively.

The boundary conditions applied to Eq. (5) are then used to complete the heat transfer description. At the centre of the plane illustrated in Fig. 1, the symmetry of the system means an adiabatic boundary condition is in place. At the pellet surface, the boundary condition includes heat exchange with the bulk gas via convection and radiation and also the heat generated by reaction in Eq. (1).

In order to calculate a value for the reaction rate presented in Eq. (1), it is necessary to know the surface oxygen concentration as well as the surface temperature. This is calculated by considering the mass transfer of oxygen from the bulk gas across the gaseous film layer surrounding the pellet as follows:

$$R_C^* = k_g A (C_{O_2}^B - C_{O_2}|_s) \quad (6)$$

where R_C^* is the rate of oxygen transfer across the film layer and k_g the mass transfer coefficient.

Eqs. (3)-(6) give a brief overview of the equations used in modelling the reaction kinetics and the resulting heat transfer through the pellet. These equations, in conjunction with the stoichiometry of Eq. (1), can be used to

then provide the decrease in the size of the carbide, both radially and along its length, and hence predict a reaction rate and completion time.

NUMERICAL SOLUTION

To solve the array of partial and ordinary differential equations that represent the model, finite-difference methods are used. For the solution of the Fourier equation given in Eq. (5) in two dimensions, the fully implicit backward method [6] coupled with the alternating directions method [6] is used. An example of the general approximation of Eq. (5) through the carbide plane is given in Eq. (7):

$$\frac{T_{i,j}^{n+1} - T_{i,j}^n}{\Delta t} = \frac{\alpha}{(\Delta x^2)} \left((T_{i+1,j}^{n+1} - 2T_{i,j}^{n+1} + T_{i-1,j}^{n+1}) \right) + \frac{\alpha}{(\Delta r^2)} \left(\left(1 + \frac{1}{2j}\right) T_{i,j+1}^n - 2T_{i,j}^n + \left(1 - \frac{1}{2j}\right) T_{i,j-1}^n \right) \quad (7)$$

where i and j represent discrete positions along the length and radius of the pellet respectively, and Δx and Δr are the increment sizes between them.

The alternating directions method requires the solution to be solved in one direction, for example the length of the pellet, across the time step from n to $n + 1$. Across a second time step, $n + 1$ to $n + 2$, the solution would be found in the alternate direction, in this case the radius. Eq. (7) is solving in the x-direction as those are the unknown values occurring at $n + 1$.

To solve the boundary conditions, a backward difference approximation is taken and a central difference is used for the equations describing the changing dimensions.

The non-linearity of the boundary condition at the reaction surface, due to the dependence of the calculation of the heat flux on temperature, is exacerbated by the decreasing size of the pellet affecting the heat and mass transfer constants. Therefore, to ensure the stability of the numerical solution, iterative techniques are used where the solution is solved multiple times at each time step. The stability of the time step size is maintained through use of the Courants-Friedrichs-Lewy condition [6], where the time step is determined according to the radial and length increment sizes and also the factor α affecting the Fourier equation.

RESULTS AND DISCUSSION

The resulting model is capable of calculating the transient temperature distribution through the solid during the reaction, as displayed in Fig. 2, allowing for maximum temperatures to be predicted. In Fig. 2, a pellet initially at 25°C and of a diameter and length of 1.87cm was oxidised in a bulk gas at 500°C and 1atm with an oxygen concentration of 3.15mol m⁻³ (corresponding to 20% oxygen in air).

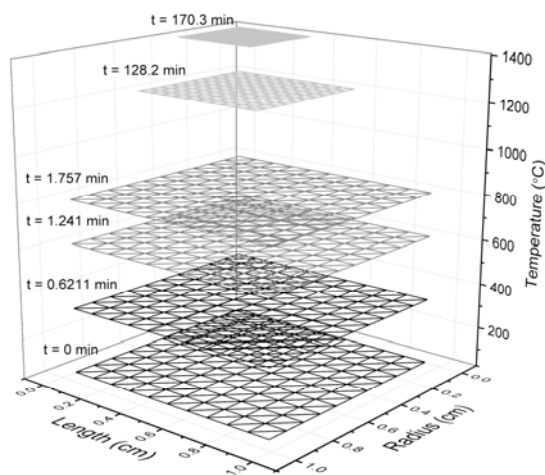


FIGURE 2. The two dimensional temperature distribution across the plane that represents the cylinder during the reaction.

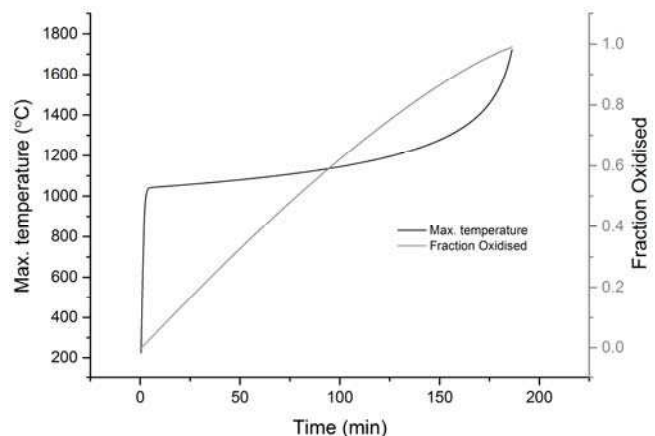


FIGURE 3. The maximum temperature in the pellet and the fraction of carbide oxidised as a function of time.

Figure 2 illustrates the temperature uniformity through the pellet due to the high conductivity of UC. There is a small thermal gradient through the pellet after the initial exposure to the hotter gas, but as the temperature changes at the boundaries become more incremental, the carbide pellet becomes essentially isothermal.

Figure 3 is a plot of the maximum temperature in the pellet over time. This maximum occurs at the outer corner of the plane due to the greater heat flux there, but is only marginally hotter than the rest of the pellet. The pellet initially experiences a steep temperature rise due to exposure to the bulk gas and the reaction beginning. This is followed by a plateau in temperature as the radiative and convective heat losses roughly equal the heat generated by the reaction. As the reaction approaches completion, thermal runaway begins to occur due to the depleted carbide providing less of a heat sink to the reaction enthalpy.

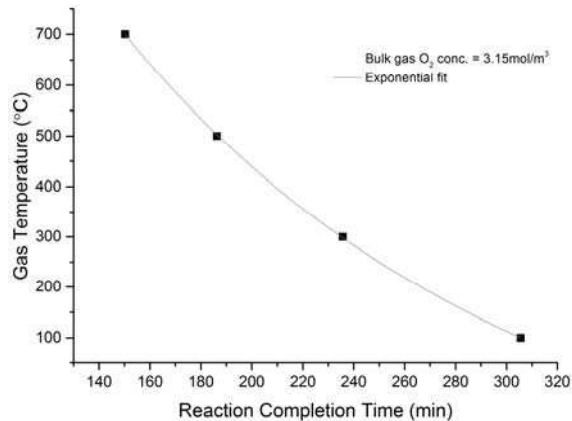


FIGURE 4. The effect of varying the bulk gas temperature on the reaction time.

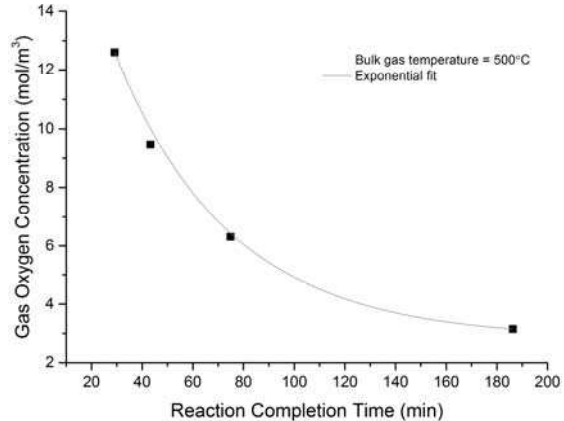


FIGURE 5. The effect of varying the bulk gas oxygen concentration over time.

Figures 4 and 5 are examples of sensitivity studies carried out by varying the oxidation parameters. Figure 4 is a plot of oxidations carried out at different bulk gas temperatures, and Fig. 5 at different bulk gas oxygen concentrations. Increasing both the initial temperature and oxygen concentration of the bulk gas increases the reaction rate exponentially. The reaction completion time for a pellet of this size has been shown to be between 30 and 300mins under the conditions considered.

CONCLUSIONS

A two-dimensional model of the oxidation of a uranium carbide fuel pellet in air has been completed using finite-difference methods. The model is capable of predicting the oxidation completion time and the temperatures reached given a set of initial conditions, of value in the specification safe oxidation conditions..

Further work will consider the scenario where the oxide product adheres to the carbide pellet and presents an obstacle for the mass transfer of oxygen to the interface. Further oxidation of this oxide layer will also be considered and the effect it has on temperature and reaction rate. More advanced modelling techniques will also be employed to investigate the effects of fluid flow and batch oxidation, and also to consider the interactions at the interface between the carbide and oxide product at a molecular scale.

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