Mathematical modelling of the pre-oxidation of a uranium carbide fuel pellet

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ABSTRACT

Uranium carbide is a candidate fuel for future nuclear reactors. However, for it to be implemented in a closed fuel cycle, an outline for its reprocessing is necessary. One proposed method is to oxidise the uranium carbide into uranium oxide which can then be reprocessed using current infrastructure. A mathematical model describing the heat and mass transfer processes involved in such an oxidation has been constructed. The available literature was consulted for reaction coefficients and information on reaction products. A stable and convergent numerical solution has been developed using a combination of finite-difference approximations of the differential equations. Completion times of approximately 3–30 h are predicted given a spherical pellet with a radius of 9.35 mm under varying initial conditions. The transient temperature distribution throughout the system is predicted, with a maximum temperature of 1458 °C observed from an initial temperature of 500 °C at an oxygen concentration of 3.15 mol m^{-3}.

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1. Introduction

Uranium carbide (UC) is a candidate fuel for use in Generation IV nuclear reactors (Legand et al., 2014; Raveu et al., 2014). Its appeal stems from a high thermal conductivity compared to the oxide form (De Coninck et al., 1975; Carbajo et al., 2001) allowing for easier regulation of fuel bed temperatures, and a higher density of heavy metal atoms making it a better plutonium breeder – an invaluable characteristic for fast reactor fuel.

One drawback, however, is that upon dissolution in nitric acid, a step in the PUREX (Plutonium Uranium Redox Extraction) method for oxide fuel reprocessing, organic compounds are formed in solution from the displaced carbon. These organics, in particular carboxylic and mellitic acid (Ferris et al., 1964; Ferris and Bradley, 1965), can then complex the uranium and plutonium ions in the resulting solution making their extraction significantly less effective and consequently wasting valuable fissile material. Therefore, in order for carbide fuels to be reprocessed in the same manner as oxide fuels, and hence be simpler and less expensive to introduce, the problem of organics in solution must be addressed.

The oxidation of uranium carbide to uranium oxide prior to dissolution in nitric acid is one proposed solution, allowing the fuel to then be reprocessed as normal. However, it is not without its own

difficulties. The oxidation in air is known to be highly exothermic (Macleod, 1997; Dell and Wheeler, 1967), especially if the carbide is in powder form (Le Guyadec et al., 2009), resulting in the risk of thermal runaway and the possibility of self-ignition.

The model described in this paper aims to simulate the oxidation of a uranium carbide fuel pellet in air and predict the temperatures reached by the pellet under different initial conditions. Such a model would then be of use in outlining the necessary safety conditions for both general handling of carbides and the oxidation itself.

The oxidation, assumed to be taking place in air, can be written as the following two-step reaction:

$$2UC(s) + 3O_2(g) \rightarrow 2UO_2(s) + 2CO(g) \tag{1}$$

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g) \tag{2}$$

The initial oxidation, Eq. (1), is a heterogeneous reaction taking place at the surface of the carbide pellet and produces carbon monoxide and uranium dioxide. The carbon monoxide is then further oxidised to carbon dioxide by a homogeneous reaction in the bulk gas, Eq. (2).

The oxide product layer is assumed to instantaneously spall off from the carbide pellet surface. It is unclear in the literature whether or not this is the case. Some reports suggest it adheres to the pellet (Mukerjee et al., 1994), which slows the reaction due to diffusion across the oxide layer, whilst Mazaudier et al. (2010) observe that no product layer adheres: perhaps due to the marked

Nomenclature

A	surface area of the uranium carbide pellet (m^2)
C_{CO}	carbon monoxide concentration ($mol\,m^{-3}$)
C_{O_2}	oxygen concentration ($mol\,m^{-3}$)
$C_{O_2}^B$	bulk gas oxygen concentration ($mol\,m^{-3}$)
D	cylindrical pellet diameter (m)
d_e	spherical pellet diameter (m)
E_A	activation energy of the reaction at the carbide surface ($J\,mol^{-1}$)
h	heat transfer coefficient ($W\,m^{-2}\,K^{-1}$)
i	an integer representing the radial increment, $1 \leq i \leq k$
k	an integer representing the maximum value of i; its value at the solid surface
k_C	first order reaction coefficient ($m\,s^{-1}$)
k_{fluid}	thermal conductivity of surrounding fluid ($W\,m^{-2}\,K^{-1}$)
k_g	mass transport coefficient ($m\,s^{-1}$)
k_{UC}	thermal conductivity of uranium carbide ($W\,m^{-2}\,K^{-1}$)
k_1	a constant representing the maximum value of k_C ($m\,s^{-1}$)
L	cylindrical pellet length (m)
n	an integer designating the current time step $n \geq 1$
Nu	Nusselt number
n_{UC}	number of moles of uranium carbide (mol)
p	pressure
Pr	Prandtl number
r	radius within solid (m)
R_C	rate of oxygen consumption at the reaction interface ($mol\,s^{-1}$)
R_C^*	rate of oxygen transfer across the external gas film layer ($mol\,s^{-1}$)
R	gas constant ($J\,mol\,K^{-1}$)
Re	Reynolds number
r_1	radius of the carbide pellet (m)
Sc	Schmidt number
Sh	Sherwood number
t	time passed since oxidation started (s)
T	solid temperature (K)
T^B	bulk gas temperature (K)
u_1, u_2, u_3	solutions at the increment sizes h_1, h_2 and h_3 respectively
u	estimated solution using infinitely small increment sizes
V	total volume of the bulk gas surrounding the oxidising pellet (m^3)

Greek symbol

α	thermal diffusivity ($m^2\,s^{-1}$)
ΔH_R	enthalpy of oxidation at carbide surface ($J\,mol^{-1}$)
Ω	collison integral
ε	emissivity of uranium carbide
μ	fluid dynamic viscosity ($kg\,m^{-1}\,s^{-1}$)
ρ	fluid density ($kg\,m^{-3}$)
σ	Stefan–Boltzmann constant ($W\,m^{-2}\,K^{-1}$)
σ_{O_2-CO}	constant in the Lennard–Jones potential formula (Å)

Eqs. (1) and (2). It is observed by Berthinier et al. (2011, 2009) that further oxidation of the UO_2 occurs under most conditions, producing higher oxides such as U_3O_8 and U_3O_7. However, since the UO_2 produced in the initial surface reaction is assumed to spall off, as suggested by Mazaudier et al. (2010), and hence not be present in this model, these further oxidations are not considered.

The enthalpy of reaction for the overall reaction given in Eqs. (1) and (2) was calculated theoretically to be −1380 kJ/mol, falling within the reported range of −1260 to −1500 kJ/mol (Macleod, 1997). The initial oxidation reaction, Eq. (1), is taken to be first order, and is assumed to occur only at the surface of the carbide with no penetration of the carbide by the oxidising gas. This reaction has an enthalpy calculated to be −1098 kJ/mol. Part of the heat generated at the reaction interface by Eq. (1) is then conducted into the UC pellet, with the remainder transfers to the bulk gas via both convection and radiation.

The density increase from the carbide fuel to the oxide product, plus the fact that gas is formed at the interface between the two materials, is assumed to prevent an oxide layer adhering. The model is therefore a variation, but of a similar form as, the shrinking core model (Smith, 1970).

At the surface of the carbide, i.e. where $r = r_1$, heat transfer between the solid and the bulk oxidising gas is included. The bulk gas can be assumed to be either an infinite medium at a constant temperature, or a finite volume with a variable temperature. In either case, however, there is no oxidant depletion during the reaction, the fluid is assumed to be stagnant and atmospheric pressure is assumed. The assumption of an infinite gaseous oxidant is removed at a later point to examine the effects of the secondary oxidation on the bulk gas composition, but should be assumed to be in place unless stated otherwise.

Oxygen transfers from the bulk gas to the reaction interface by diffusing through a gaseous film layer, assumed to comprise produced carbon monoxide, where it is consumed in the reaction given by Eq. (1). For the system shown in Figs. 1 and 2 are a schematic of the radial oxygen and carbon monoxide profiles through the gaseous film layer depicted in former figure. Additionally, Fig. 3 is a schematic of the radial temperature distribution. In both figures, the initial conditions are shown at time $t = 0$. The profiles are then
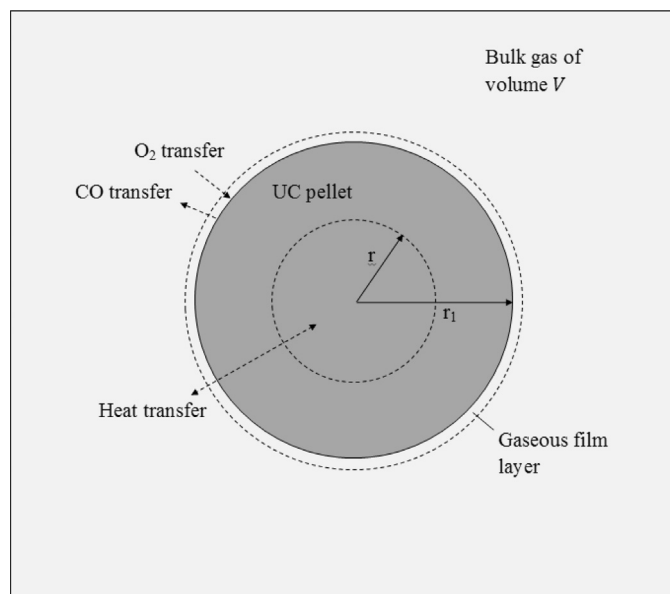

Fig. 1. A one dimensional approximation of a UC pellet as an equivalent volume sphere.

decrease in density from UC (13.6 g/cm³) to UO_2 (11.0 g/cm³), which causes a significant volume expansion of approximately 33%.

This assumption, of an instantaneously spalling oxide product layer, allows the oxidation kinetics to be simply represented by