

# KINETIC MODELING STUDY OF A VOLOXIDATION FOR THE PRODUCTION OF $U_3O_8$ POWDER FROM A $UO_2$ PELLET

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A kinetic model for the oxidation of a  $UO_2$  pellet to  $U_3O_8$  powder has been suggested by considering the mass transfer and the diffusion of oxygen molecules. The kinetic parameters were estimated by a fitting of the experimental data. The activation energies for the chemical reaction and the product layer diffusion were calculated from the kinetic model. The oxidation conversion of a  $UO_2$  pellet was simulated at various operating conditions. The suggested model explains the oxidation behavior of  $UO_2$  well.

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**KEYWORDS** : Voloxidation,  $U_3O_8$  Powder,  $UO_2$  Pellet, Nucleation and Growth, Kinetics, Activation energy, Diffusion

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## 1. INTRODUCTION

Pyroprocessing technology based on a molten salt electrolysis has been focused on for treating and recycling metallic or oxide spent fuels in the past several years because of its benefits, such as its inherent proliferation resistance, compactness of the process equipment, and lower cost [1-9]. The pyroprocessing of spent oxide fuel involves the reduction of a spent oxide to a metal by an electrolytic reduction process and the recovery of the fuel components by means of an electro-refining process [10].

The Korea Atomic Energy Research Institute (KAERI) is currently developing the Advanced Spent Fuel Conditioning Process (ACP) based on pyroprocessing with the aim of a reduction of the volume, the radio-toxicity, and the heat load of the spent fuels discharged from the commercial pressurized water reactors. The final product forms of the ACP are a metallic ingot for disposal and a pellet form of a waste salt [11]. The ACP consists of several steps: slitting, voloxidation, electrolytic reduction, smelting and so on. Fig. 1 shows the process stream of the ACP. In the ACP concept (Fig. 1), the pellet form of the oxide spent fuel is changed to a powder form of  $U_3O_8$  by an oxidation, which is called a voloxidation. A unique phenomenon at the voloxidation step is pulverizing and oxidizing the  $UO_2$  pellet at the same time. The voloxidized uranium oxide ( $U_3O_8$ ) powder is converted to metallic uranium by means of electrolysis in the following electrolytic reduction step.

A powder form is much more favorable than a dense pellet form in terms of the cell efficiency, the rate of the electrochemical reaction, and the reduction conversion in this step.

Therefore, a kinetics study of the voloxidation of a  $UO_2$  pellet is important to interpret the reaction behavior and to predict the reaction extent during the voloxidation step as a head-end process for a pyrometallurgical process as well as to develop whole integrated processes successfully. The oxidation of  $UO_2$  has been extensively studied to understand its degradation mechanism during a long-term storage of spent nuclear fuel which consists mainly of  $UO_2$  [12-15]. Much attention has been paid to the oxidation of  $UO_2$  because of its importance to a long-term disposal of spent nuclear fuel. Although a number of investigations have been carried out to determine the oxidation behavior of  $UO_2$ , the kinetics and mechanism of this reaction are still unclear. It has been generally accepted that the oxidation of  $UO_2$  occurs in two successive steps from  $UO_2$  to  $U_3O_7$  and from  $U_3O_7$  to  $U_3O_8$ . On the other hand, some investigators have observed on the basis of a differential thermal analysis that a direct oxidation from  $UO_2$  to  $U_3O_8$  in a single step has occurred [12]. After a complete oxidation, about a 36 % net volume expansion occurs because of the structural changes of  $UO_2$  to  $U_3O_8$ .

In general, the kinetics for the oxidation of  $UO_2$  to  $U_3O_8$  powder have been expressed according to the Johnson-Mehl equation for nucleation and growth as the following

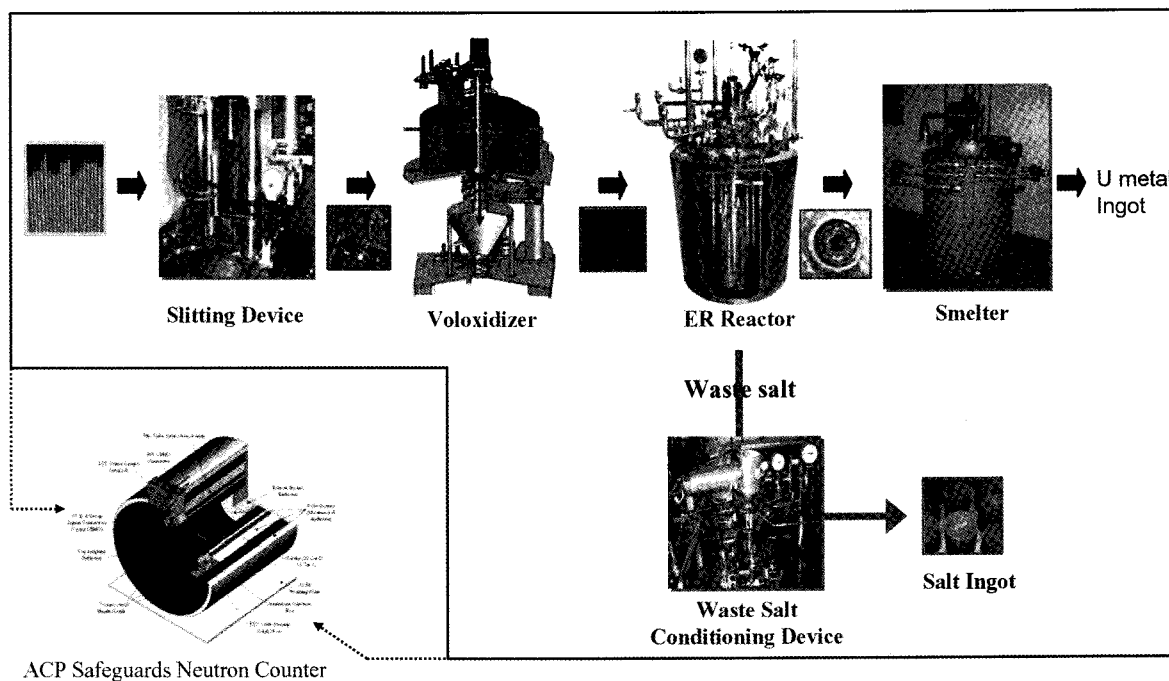


Fig. 1. Process Stream of the Advanced Spent Fuel Conditioning Process

equation [13].

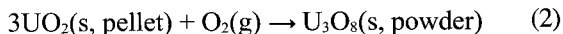
$$x = 1 - \exp[-(kt)^n], \tag{1}$$

where  $t$  is the reaction time,  $k$  is the rate constant of the intrinsic reaction,  $x$  is the degree of reaction, and  $n$  is the time exponent which is assumed to be independent of  $x$ . However, this model can not explain the mass transfer through the gas film and the diffusion through the product layer in a general gas-solid reaction. Harrison et al. [16] reported that a rate curve for this reaction is a hybrid of diffusion and nucleation/growth forms. Park and Seo [17] suggested a practical model for describing the oxidation behavior of UO<sub>2</sub> for the voloxidation process.

In the present work, we have suggested a kinetic model for the oxidation of a UO<sub>2</sub> pellet by considering the diffusion of the oxygen molecules and fitted it to the experimental data. Also, the effects of the reaction temperature, the O<sub>2</sub> concentration and the pellet size have been investigated by predicting the oxidation conversion through a suggested model.

## 2. KINETIC MODEL

An overall reaction for the oxidation of UO<sub>2</sub> can be represented as follows:



Jeong et al. [18] suggested a kinetic model for the oxidation of a UO<sub>2</sub> pellet by considering the mass transfer and the diffusion of oxygen molecules. They proposed the following eqn. (3) by replacing the term for the chemical reaction resistance of the shrinking unreacted core model for cylindrical pellets to the Johnson-Mehl equation.

$$t = \frac{\rho_s r}{2bk_g C_{Ag}} x + \frac{\rho_s r^2}{4bD_e C_{Ag}} [x + (1-x)\ln(1-x)] + \frac{\rho_s r}{bk_s C_{Ag}} [-\ln(1-x)]^{1/n} \tag{3}$$

where,  $t$  is the reaction time,  $\rho_s$  is the molar density of a solid reactant,  $r$  is the pellet radius,  $b$  is a stoichiometric coefficient,  $C_{Ag}$  is the molar concentration of a gaseous reactant in the gas phase,  $x$  is the degree of reaction,  $k_g$  is the mass transfer coefficient of the gas phase,  $D_e$  is the effective diffusivity of the product layer and  $k_s$  is the rate constant of the intrinsic reaction.

The first term on the right of eqn. (3) represents the resistance associated with the mass transfer through the gas film. The second term represents the product layer diffusion resistance, and the final term describes the chemical reaction resistance. Eqn. (3) can be numerically solved to estimate the three parameters,  $k_g$ ,  $D_e$ , and  $k_s$ .

### 3. RESULTS AND DISCUSSION

Most studies have been conducted with UO<sub>2</sub> powder with surface areas > 1 m<sup>2</sup>/g in a non-isothermal condition up to 400 °C [15, 19]. In this work, the experimental data reported by a previous publication [14] was used to fit eqn. (3) and to evaluate the parameters by assuming an isokinetic reaction, where the value of *n* is constant regardless of the reaction temperature. They investigated the oxidation of an un-irradiated UO<sub>2</sub> pellet (14.28 mm dia. × 20.12 mm length, 10.42 g/cm<sup>3</sup> density) in an isothermal condition under an air atmosphere. They used a thermobalance fabricated from a Mettler H-35 laboratory balance for the oxidation of UO<sub>2</sub> pellet. They observed that the kinetic curves during the oxidation of UO<sub>2</sub> are sigmoidal, with no evidence of the formation of an intermediate product

such as U<sub>3</sub>O<sub>7</sub>. Also, they reported that no other phases were detected except for U<sub>3</sub>O<sub>8</sub> in the powder product, confirmed by an X-ray diffraction analysis.

The mass transfer coefficient *k<sub>g</sub>*, the effective diffusivity *D<sub>e</sub>*, and the rate constant of the intrinsic reaction *k<sub>s</sub>* were estimated for each temperature by fitting the model calculation to the experimental data. The data in a previous publication was fitted to the Johnson-Mehl equation of eqn. (1) and the values for the time exponent, *n*, varied from 1.13 to 3.4 over the temperature range [14]. This means that the reactions are not isokinetic and that the relative rates of the nucleation and growth change with the temperature. In this work, however, it is assumed that the time exponent is constant regardless of the reaction temperature by the isokinetic condition. The model equation exhibits the best fit in the condition of *n* = 4 and the results are listed in Table 1. Fig. 2 shows the oxidation conversion

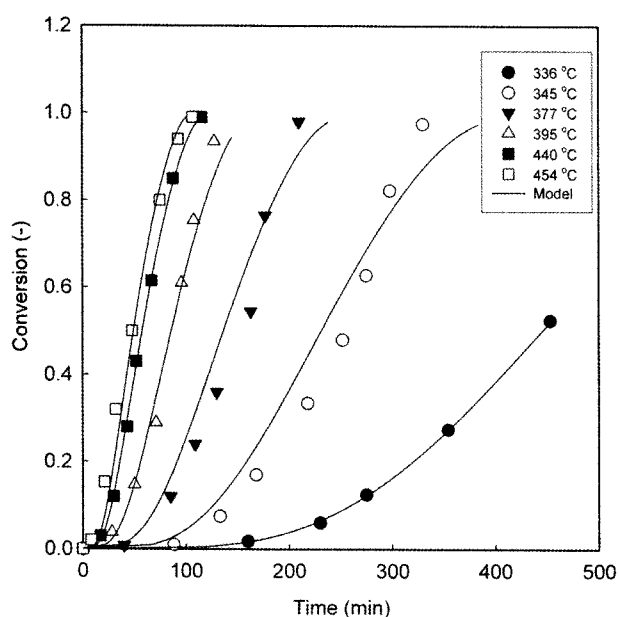


Fig. 2. Oxidation Conversion as a Function of the Reaction Time with a Variation of Temperature. Symbols are the Experimental Data Obtained by a Previous Publication[14]

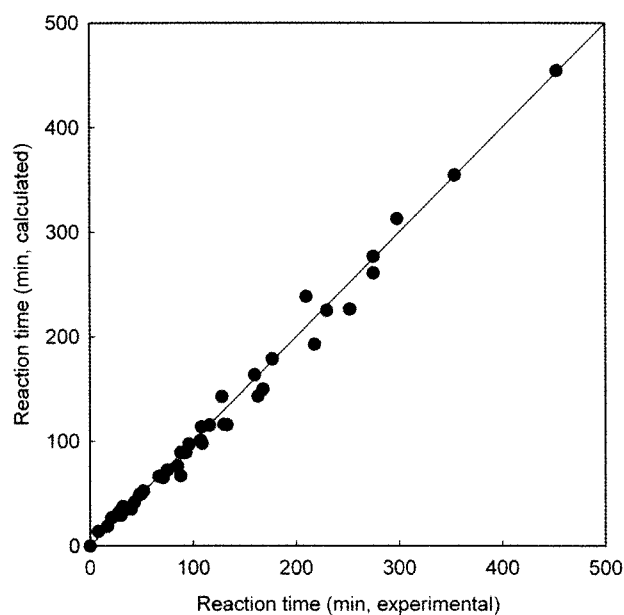


Fig. 3. Comparison of Reaction Time Obtained by the Experimental Data and the Model Prediction

Table 1. Predicted Model Parameters

Temperature (°C)	<i>k<sub>g</sub></i> (cm/min)	<i>D<sub>e</sub></i> (cm <sup>2</sup> /min)	<i>k<sub>s</sub></i> (cm/min)
336	1.466	1.481	0.494
345	1.492	1.491	1.048
377	2.096	1.515	1.874
395	3.034	1.535	3.125
440	3.802	1.5504	5.076
454	4.398	1.565	6.080

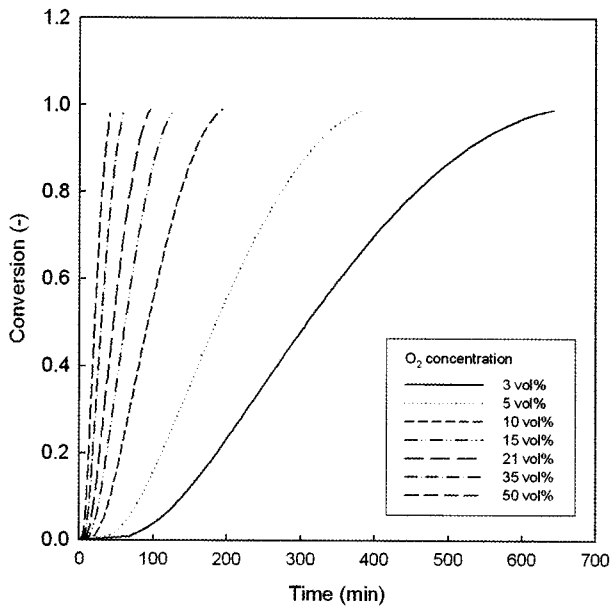


Fig. 4. Oxidation Conversion Predicted by a Model with a Variation of the O<sub>2</sub> Concentration in the UO<sub>2</sub> Oxidation

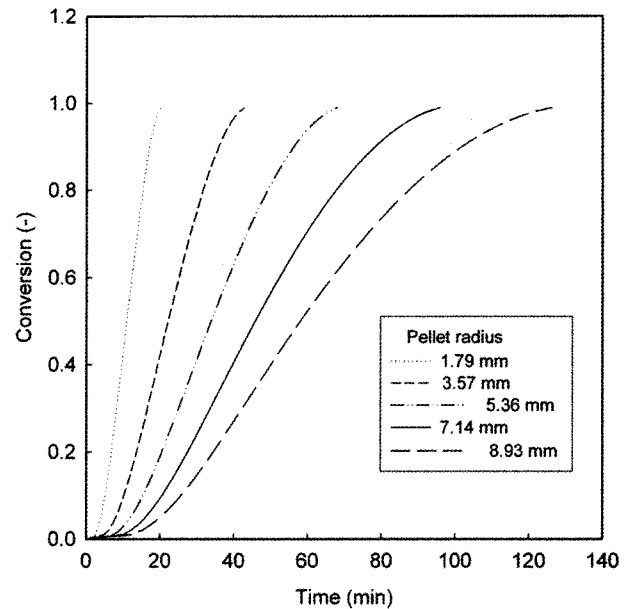


Fig. 5. Oxidation Conversion Predicted by a Model with a Variation of the Pellet Size in the UO<sub>2</sub> Oxidation

of UO<sub>2</sub> as a function of the reaction time with a variation of the reaction temperature. As can be seen, the kinetic curves exhibit S-shapes indicating the typical characteristics of nucleation and growth. The reaction rate increases sharply with increasing the reaction temperature.

Fig. 3 shows the comparison of the experimental and the calculated values with respect to the reaction time. As can be seen, the calculated values are in good agreement with the experimental ones obtained in a thermobalance reactor. This model makes the prediction of a conversion with the reaction time, temperature, pellet size, and O<sub>2</sub> concentration in a gas phase during the oxidation of a UO<sub>2</sub> pellet to U<sub>3</sub>O<sub>8</sub> powder possible.

Fig. 4 shows the predicted conversion as a function of time with variation of the oxygen concentration in the gas phase. The conversion was predicted at the condition of 454 °C of a reaction temperature and a UO<sub>2</sub> pellet of 14.28 mm in diameter. The reaction time needed for a complete conversion of the UO<sub>2</sub> pellet increases with decreasing oxygen concentration. Also, the reaction rate increases sharply with an increase in the oxygen concentration. The result indicates that the oxygen concentration strongly affects the oxidation rate of the UO<sub>2</sub> pellet. This is because the chemical reaction in the oxidation of UO<sub>2</sub> is dependent on the oxygen partial pressure. Also, the diffusion rates of O<sub>2</sub> through the gas film and the product layer increase with increasing O<sub>2</sub> partial pressure, resulting in a positive effect on the oxidation rate.

The effect of the pellet size on the oxidation of UO<sub>2</sub> at 454 °C under an air atmosphere is shown in Fig. 5. As

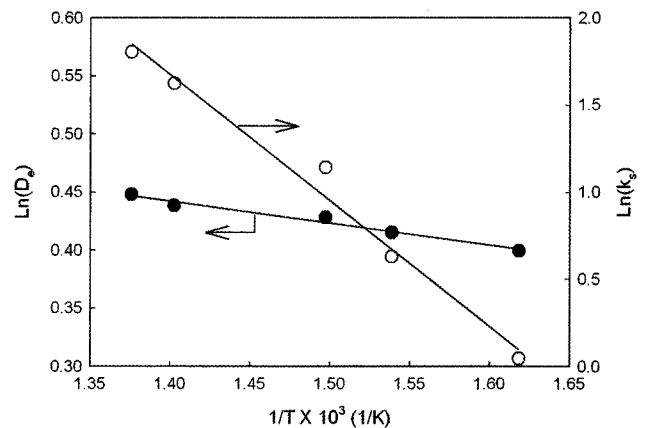


Fig. 6. Arrhenius Plot of  $\ln D_e$  and  $\ln k_s$  vs.  $1/T$  for the Oxidation of UO<sub>2</sub> to U<sub>3</sub>O<sub>8</sub>

can be seen, the model predicts that the oxidation rate decreases with an increase in the pellet radius because not only the large pellets have a larger diffusion resistance of oxygen through the gas film and the product layer, but also the larger pellet has a smaller surface to volume ratio.

Also, the activation energies for a chemical reaction and the product layer diffusion can be estimated by Arrhenius plots, as shown in Fig. 6. The reaction activation energy was found to be 60.0 kJ/mol, which is a similar value to the result (66.5 kJ/mol) in a previous publication

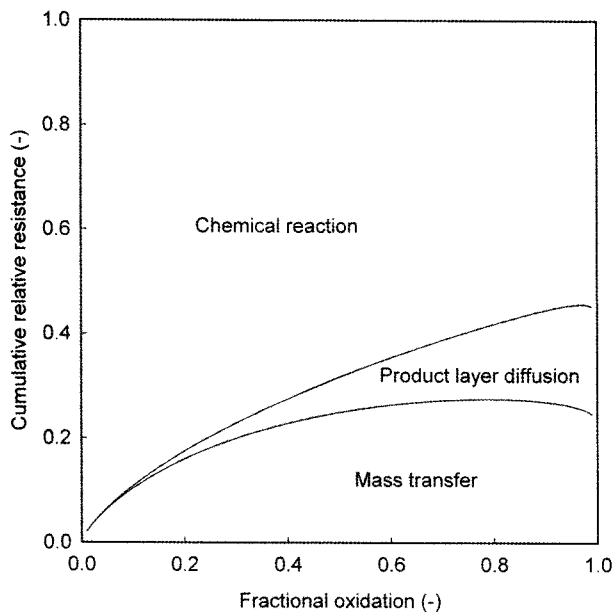


Fig. 7. Variation of the Relative Resistances from the Mass Transfer, the Product Layer Diffusion and the Chemical Reaction with the Degree of Reaction. This Figure has been Reported in Our Previous Publication [18]

[14]. The diffusion activation energy was calculated as 1.6 kJ/mol. Low diffusion activation energy may be due to the physical change from a pellet to a fine powder during oxidation. That is, a fine  $U_3O_8$  powder produced in the oxidation is separated from the unreacted  $UO_2$  pellet and as a result, a porous product outside the unreacted core is more than likely maintained as a thin layer. This phenomenon leads to a low resistance of the product layer diffusion. This result suggests that the chemical reaction step including nucleation and growth is strongly influenced by the reaction temperature and it controls the overall reaction.

Fig. 7 shows the relative importance of each of the three resistances in eqn. (3) at 440 °C as a function of the degree of oxidation. It was found that most of the total initial resistance is due to the chemical reaction resistance. This result implies that a chemical reaction including nucleation and growth proceeds much slower than the mass transfer through the external gas film, which plays a dominating role in the initial stage of a general gas-solid reaction. However, the relative chemical reaction resistance decreases gradually up to about 38 % of the total resistance during the final stage of an oxidation. Initially no product layer exists, and the unreacted core model requires that the pore diffusion resistance must be zero. As a product layer of  $U_3O_8$  is formed, the product layer diffusion resistance increases with the degree of oxidation up to about 40 %. Nevertheless, the relative resistance caused by the product layer is much smaller than the value reported by Jothimurugesan and Harrison [20], indicating

a physical change of the pulverization of a pellet during oxidation. This finding means that the resistances from the mass transfer and the pore diffusion are negligible, and the overall reaction is controlled by the chemical reaction at the initial stage of the oxidation. However, these resistances become more important with an increase in the reaction time.

#### 4. CONCLUSIONS

A kinetic model has been suggested to explain the mass transfer and the diffusion effects during the oxidation of a  $UO_2$  pellet. The results calculated by the model equation are in good agreement with the experimental data. The kinetic parameters were estimated by a fitting of the experimental data. The activation energies for the chemical reaction and diffusion were found to be 60.0 and 1.6 kJ/mol by an Arrhenius plot, respectively. The reaction rate increased sharply with increasing oxygen concentration, indicating that the oxygen concentration strongly affected the oxidation rate of the  $UO_2$  pellet. Also, the oxidation rate decreased with increasing pellet radius because small radius pellets have a smaller diffusion resistance of oxygen through the gas film and the product layer. The resistances from the mass transfer and the pore diffusion increased with an increase of the fractional oxidation. The oxidation characteristics of the  $UO_2$  were interpreted by the suggested kinetic model.

#### NOMENCLATURE

$b$	stoichiometric coefficient [-]
$C_{Ag}$	molar concentration of gaseous reactant [mol/cm <sup>3</sup> ]
$D_e$	effective diffusivity of product layer [cm <sup>2</sup> /min]
$k$	rate constant in Johnson-Mehl equation [cm/min]
$k_g$	mass transfer coefficient of the gas phase [cm/min]
$n$	time exponent [-]
$r$	pellet radius [cm]
$t$	reaction time [min]
$T$	reaction temperature [K]
$x$	degree of reaction [-]

#### Greek Symbol

$\rho_s$	molar density of solid reactant [mol/cm <sup>3</sup> ]
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