

## Leaching Mechanism and Modelling of $UO_2$ Pellets

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### $UO_2$ Pellet 의 침출거동 및 Modelling

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#### Abstract

A rate equation for  $UO_2$  pellet leaching has been derived and compared with some experimental results. The leach rate model comprises the processes of oxygen penetration into  $UO_2$  pellets and the dissolution and transport of oxidized  $UO_2$  depending on the penetration depth of oxygen. The model may be analyzed with two regions of transient and steady state behaviors, which should depend on the initial oxidation state of pellets. Also this model can be utilized in the analyses of general leach processes if the oxidation reaction of  $UO_2$  is replaced with similar mechanism of those processes.

#### 요 약

$UO_2$  Pellet 의 침출도식을 유도하고 실험자료와 비교검토 하였다. 침출속도 모델은 산소의 Pellet 내부로의 침투로 인한  $UO_2$ 의 산화과정과 침투 깊이에 따른 산화  $UO_2$ 의 용해 및 이동과정을 고려하여 얻어졌다. 이 모델에 의하면 침출속도는 전이상태와 정상상태의 두 영역으로 나뉘어질 수 있으며 변화하는 양상은 초기의 산화상태에 따라 달라진다. 또한 이 모델식은  $UO_2$ 의 산화반응을 유사한 다른 침출구조에 적용할 수 있어서 일반적인 침출현상의 해석에 사용될 수 있다.

#### 1. Introduction

Concerning the radioactive waste disposal and spent nuclear fuel storage, many researches on their leachability have been undertaken over the past several years[1-7]. The leaching is in concept a process of extraction of a soluble component from a mixture with an insoluble component, by

percolation of the mixture with a solvent, resulting in the solution, and thus can have direct effects on the environmental release of radioactive materials.

The leaching process can have very complex aspects of behavior since it depends much on the physical structure, composition and chemical interactions with environment. There have been developed some leach rate models based on the transport theory of dissolution and film diffusion[7]

or pore diffusion [7,8,9] depending on what the rate determining process is. Particularly, the leach mechanism of spent nuclear fuels can vary with the composition of fission products and physical structure of the matrix, and there have been some discussions with experimental results concerning this problem. Katayama[5] said that the leach rate would not be significantly influenced by burn up within the accuracy of the structural difference of materials and the method of analysis. Eklund and Forsyth[6], on the other hand, had a different result that the leach rate would increase with burn up. However, considering the change in the structure and composition of fission products, the leach rate can be predicted to change with burn up.

In the leach mechanism of  $\text{UO}_2$  pellets, the oxidation state has been thought to be a major factor to affect the uranium solubility and escaping tendency from the matrix[12]. Furthermore, possible formation of hydrogen peroxide at the interface of pellets and water by the radiolysis of water has been suggested[10], and in the presence of hydrogen peroxide the leach rate has been reported to promote more than hundred times faster than at the same concentration of oxygen. Most of the models which have been developed by this time can not give us the complete solution for those problems, especially in consideration of pertinent chemical reactions.

Wang and Katayama[12], through their single crystal experiments, explained the leaching mechanism in several steps, which includes oxidation, dissolution, transportation and crystal formation by hydrolysis. We propose in this article a simplified leach rate model based on the penetration of oxygen into the matrix, dissolution and transportation through the matrix, which are fundamentally from the mechanism of Wang and Katayama, and the results are compared with the experimental data of Katayama *et al*[1]. Also we present the general utilization of this model as an analytical tool for the cases of similar mechanisms of leaching and as a useful empirical rate equa-

tion.

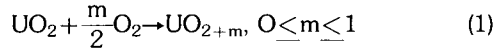
## 2. Mechanism

It is well known that the leach rate of  $\text{UO}_2$  pellets can be dominated by the leachant acidity, oxidation states of the pellets, and temperature[3]. They may increase the solubility of uranium species and can thus promote dissolution rate. Wang and Katayama[12], explaining the leach mechanism of single crystal  $\text{UO}_2$  in different range of acidity (pH), put the oxidation step prior to the other reactions. For the penetration of oxygen, a diffusion process should be considered in the first. By the experimental result of Wang[14] in air atmosphere the oxygen penetration is known about 20 angstroms of depth, mostly in the hydrated form of  $\text{UO}_2$  on pellet surfaces. Though the experimental result in water atmosphere is not shown precisely, the penetration depth might be greater than that of air atmosphere by the effect of leach out.

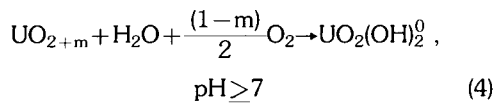
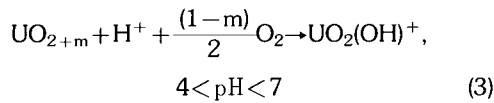
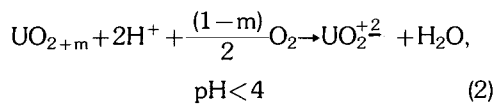
The next step would be the dissolution of oxidized  $\text{UO}_2$  and transportation of dissolved uranium through pores and surface film to the bulk region of aqueous phase. Wang and Katayama gave an explanation for the effect of hydrogen ion in this oxidation-dissolution step. For the transportation of hydrogen ion involved in the reaction, we must refer to the porosity of the sintered  $\text{UO}_2$  pellets, which can be almost negligible when it is not oxidized. However, as oxidation propagates, the porosity increases and the dissolved species in water can move into the pores. Therefore, we may assume that the rate determining step is still the oxygen penetration. They also noticed the hydrolysis reaction of dissolved uranium producing hydrate ( $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ ) and crystal form  $\text{UO}_2(\text{OH})_2$  on crystal surfaces. For the application of the single crystal leaching process to the case of sintered  $\text{UO}_2$  pellets, it is plausible to consider the whole processes of oxygen penetration, dissolution, and transportation involved in the pores.

The leaching mechanism of Wang and Katayama can be presented as follows.

(1) surface Oxidation

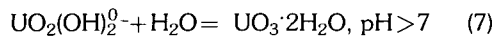
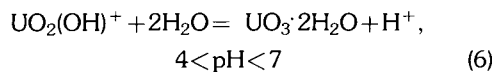
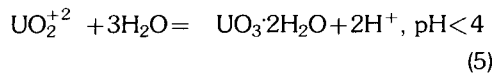


(2) Oxidation-Dissolution

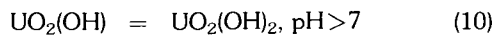
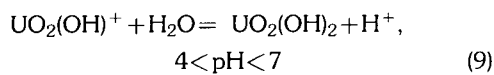
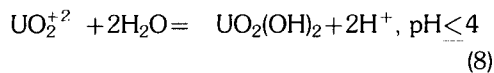


(3) Transport

(4) Hydrolysis-Film Formation (25-75°C)



(5) Hydrolysis-Crystal Growth (150°C)



### 3. Modelling of Leach Rate

Among the reaction steps of the mechanism above mentioned, the fourth and fifth of hydrolysis reactions, forming film and crystal, which can be considered to happen as a result of chemical equilibrium and thermodynamic stability in aqueous phase, may be largely dependent on temperature and acidity. However, since these steps can be thought of as the later steps of leaching, we are not including these steps in for-

mulating leach rate model of UO<sub>2</sub> pellets.

**Oxygen Penetration:** For the mathematical simulation of leach process of UO<sub>2</sub> pellets, the first step of leaching can be considered as the surface oxidation and propagation of oxidation into the pellets. Therefore, the overall penetration rate can be determined by solid diffusion rate, and in this case the system can be usually expressed as a differential equation for oxygen concentration change in homogeneous solid. Furthermore, since we consider that all the oxygen penetrated into the pellets are involved in the oxidation reaction of UO<sub>2</sub> with the form of UO<sub>2+c</sub>, a homogeneous solid diffusion model can be formulated with the form of partial differential equation as

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (11)$$

For this equation, the initial and boundary conditions are defined as

$$\begin{aligned} c(x, 0) &= c_0(x, \tau_0) \\ c(0, t) &= c_s \end{aligned} \quad (12)$$

$$\frac{\partial c}{\partial x}(L, t) = 0$$

Where *c* is the oxidized UO<sub>2</sub> concentration in the pellet, and *c*<sub>0</sub> is the initial concentration profile depending on the initial penetration depth  $\tau_0$ , *D* is representing effective diffusivity, *c*<sub>s</sub>, the surface oxygen concentration of fixed value, and *L*, the feasible depth of penetration.

Even though the exact solution of equation(11) for fixed value of *c*<sub>s</sub> is already known[15], the equation may undergo transformation into the integral formulation of simple type,

$$\frac{d}{dt} \int_0^L c \, dx = -D \frac{\partial c}{\partial x} \Big|_{x=0} \quad (13)$$

Now we introduce the concept of penetration depth  $\tau(t)$  as shown in Figure 1, which is always less than *L*. Meanwhile the boundary condition on the other surface at  $x = \tau$  is not valid. Instead we

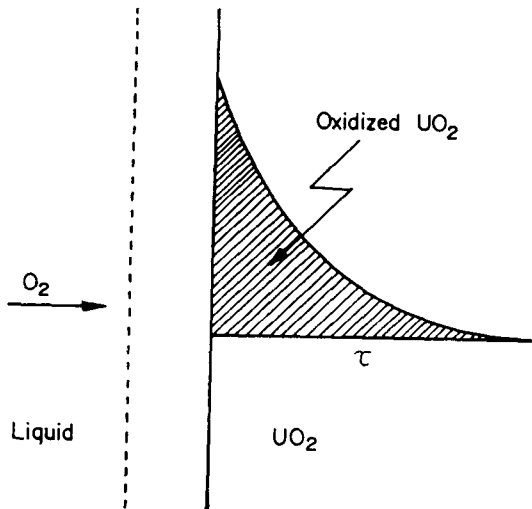


Fig. 1. Penetration of Oxygen into Pellet.

assumed zero mass flux across the plane surface at the penetration depth,  $\partial c / \partial x(\tau, t) = 0$ . Applying the boundary condition we suggest an approximate solution of parabolic profile as generally used in the approximation of diffusional problems[17].

$$c = \frac{c_s}{\tau^2} (\tau - x)^2 \quad (14)$$

Then by putting (14) into (13), we obtain the differential equation for  $\tau$ .

$$\left. \frac{d\tau}{dt} \right|_{\text{Oxid}} = \frac{6D}{\tau} \quad (15)$$

This equation tells how the penetration depth varies with time, typically proportional to the square root of time lapse, so that we put the subscript Oxid representing the oxidation step of  $\text{UO}_2$  pellets.

**Dissolution and transport:** The next step of oxygen penetration for leaching could be the dissolution and transport process of oxidized  $\text{UO}_2$ . The dissolution is thought to occur mostly at the surface of the pellet. However, as the oxidation propagates, the porosity may increase and thus the dissolved species in water which may affect the dissolution reaction can penetrate through the

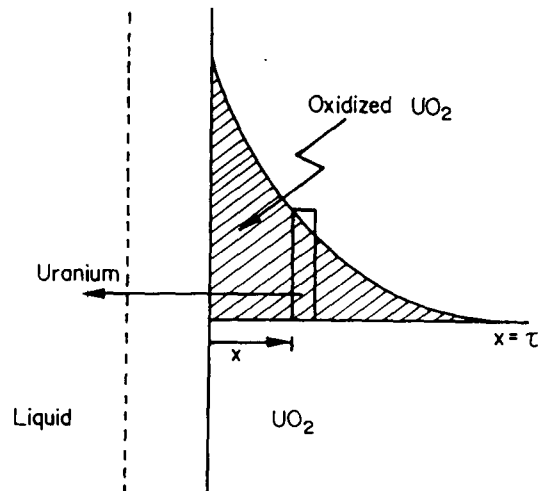


Fig. 2. Dissolution and Transport of Oxidized  $\text{UO}_2$ .

very shallow depth of the pellet interior. Regarding this problem, we restrict ourselves to the reaction (4), and in the presence of hydrogen ion we may need to put this effect in the dissolution rate constant at least. Then the dissolution rate, which is dependent on the oxidation state of  $\text{UO}_2$ , can be expressed as the first order reaction model of the concentration of oxidized  $\text{UO}_2$  in the pellet.

$$-\frac{dc(x)}{dt} = k_d' c(x) \quad (16)$$

Since thus dissolved uranium should transport to the bulk region of aqueous phase through the pore and aqueous film, this process will have influence to the overall leach rate. We take into consideration of this effect in the form of mass transfer resistances by the aqueous film and the pore diffusion as  $(1/k' + x/D)$ . Then, the dissolution rate constant can be replaced as

$$k_d' = \frac{k_d}{(1 + k'x/D)} \quad (17)$$

where  $k_d$  is the modified dissolution rate constant and somewhat dependent on  $k'$ . Meanwhile the overall concentration change in the pellet can be thought as the leach rate and expressed in the integral form within the feasible range of  $0 < x < \tau$

$$N = -\frac{d}{dt} \int_0^\tau c(x) dx = \int_0^\tau \frac{k_d c(x)}{1 + k'x/D} dx \quad (18)$$

For the simplicity, letting

$$a = \frac{D'}{k'}$$

and solving equation(18) by putting(14), we have

$$N = \frac{a k_d c_s}{\tau^2} \left[ (\tau^2 + 2 a \tau + a^2) \ln \frac{\tau + a}{\left(\frac{3}{2} \tau^2 + a \tau\right)} \right] \quad (19)$$

Here, we expanding the logarithmic term in series for a>0 and τ+a>0 and neglecting the third or higher order terms,

$$\ln(\tau + a) = \ln a + \frac{2\tau}{\tau + 2a} + \frac{2}{3} \left(\frac{\tau}{\tau + 2a}\right)^3 + \dots \quad (20)$$

the leach rate equation reduces to the following simpler form

$$N = \frac{a k_d c_s \tau}{2(\tau + 2a)} \quad (21)$$

Also from (18) and (21) we obtain the equation of penetration depth change by dissolution,

$$\frac{d\tau}{dt} \Big|_{Diss} = -\frac{3a k_d \tau}{2(\tau + 2a)} \quad (22)$$

and we put subscript Diss on this process.

**Penetration Depth Change:**The net rate of penetration depth change thus can be expressed as the sum of two rate equation of (15) and (22),

$$\begin{aligned} \frac{d\tau}{dt} &= \frac{d\tau}{dt} \Big|_{Oxid} + \frac{d\tau}{dt} \Big|_{diss} \\ &= \frac{6D}{\tau} - \frac{3a k_d \tau}{2(\tau + 2a)} \end{aligned} \quad (23)$$

This equation explains how the two different tendencies at a same state can appear in the net change of penetration depth. The time variant solution for τ can be obtained by direct integration of (23) from initial depth τ<sub>0</sub>.

$$(\tau - \tau_0) + p \ln\left(\frac{\tau - \tau_1}{\tau_0 - \tau_1}\right) + q \ln\left(\frac{\tau - \tau_2}{\tau_0 - \tau_2}\right)$$

$$= -\frac{3}{2} a k_d t \quad (24)$$

The coefficients are denoted as follows.

$$\begin{aligned} b &= \frac{d}{a k_d} \\ p &= \frac{2[(a+2b)\tau_1 + 4ab]}{\tau_1 - \tau_2} \\ q &= -\frac{2[(a+2b)\tau_2 + 4ab]}{\tau_1 - \tau_2} \end{aligned} \quad (25)$$

$$\begin{aligned} \tau_1 &= 2(b + \sqrt{b^2 + 2ab}) \\ \tau_2 &= 2(b - \sqrt{b^2 + 2ab}) \end{aligned}$$

These all have the same dimension of distance like τ. The τ<sub>1</sub> and τ<sub>2</sub> are the algebraic solutions when the derivative term of (23) dies away, for which we may call the feasible τ<sub>1</sub> as the penetration depth at steady state. At this state, the dissolution rate of oxidized UO<sub>2</sub>, becomes equivalent to the penetration and oxidation rate of the pellets, so that the penetration depth does not vary with time and the leach rate becomes constant. Therefore, if τ<sub>0</sub> is greater than τ<sub>1</sub>, the leach rate will be decreasing with time to reach the steady state, and if τ<sub>0</sub> is less than τ<sub>1</sub>, the leach rate will be increasing with time to reach the steady state. Hence the leach rate at steady state can be expressed with equation (21) as

$$N = \frac{a k_d c_s \tau_1}{2(\tau_1 + 2a)} \quad (26)$$

The transient leach rate can be determined from (21) with explicit solution of (24), τ=f(t), which however can not be obtained analytically. The logarithmic terms of equation (24) can be expanded in series for τ<sub>0</sub>>τ<sub>1</sub>.

$$\ln \frac{\tau - \tau_1}{\tau_0 - \tau_1} = \frac{\tau - \tau_0}{\tau_0 - \tau_1} - \frac{1}{2} \left(\frac{\tau - \tau_0}{\tau_0 - \tau_1}\right)^2 + \dots \quad (27)$$

$$\ln \frac{\tau - \tau_2}{\tau_0 - \tau_2} = \frac{\tau - \tau_0}{\tau_0 - \tau_2} - \frac{1}{2} \left(\frac{\tau - \tau_0}{\tau_0 - \tau_2}\right)^2 + \dots \quad (28)$$

Here, neglecting the second and higher order

terms, equation (24) reduces to

$$\tau = \tau_0 - \frac{3a k_d t}{2(1 + \frac{p}{\tau_0 - \tau_1} + \frac{q}{\tau_0 - \tau_2})} \quad (29)$$

This relation indicates the linear dependency of  $\tau$  on time, and will not be exact for profound lapse of time including steady state. Therefore this may not be used to put directly into (21). Now consider equation (21) with different form

$$N = \frac{a k_d c_s}{2} - \frac{a^2 k_d c_s}{\tau + 2a} \quad (30)$$

and put (29) into the second term of (30). Then by replacing the first term of (30) with (26), the steady state leach rate can be adjusted. Hence the leach rate is expressed as

$$N = A + \frac{B}{t - C} \quad (31)$$

The coefficients are as follow.

$$\begin{aligned} A &= \frac{a k_d c_s \tau_1}{2(\tau_1 + 2a)} \\ B &= \frac{2}{3} a c_s \left(1 + \frac{p}{\tau_1 - \tau_1} + \frac{q}{\tau_0 - \tau_2}\right) \\ C &= \frac{2(\tau_0 + 2a)}{3 a k_d} \left(1 + \frac{p}{\tau_1 - \tau_1} + \frac{q}{\tau_0 - \tau_2}\right) \end{aligned} \quad (32)$$

One thing to note is that this equation can be valid only for  $t > C$  and the solution becomes exact as the leach rate approaches to a steady state. For the case of  $t < C$ , the solution may depend on numerical computation of equation (24). Also, for the case of  $\tau_0 < \tau_1$ , the approximation of (28) may cause greater error and thus (29) is not credible anymore. However considering the increasing tendency of penetration depth, we may possibly expect a form with negative values of B and C in (31). The accumulation of leachate can be obtained by integration of (31),

$$S = S_0 + A(t - t_0) + B \ln\left(\frac{t - C}{t_0 - C}\right) \quad (33)$$

where  $t_0$  and  $S_0$  are given as initial values for the

range  $t > C$  as noted above.

**Film effect on oxygen penetration:** Previously we treated the leaching process of constant surface concentration of  $UO_2$  pellet. We now need to consider the effect of film diffusion on the leach rate. Instead of the boundary condition  $c(o, t) = c_s$  of (12), we apply the following condition,

$$-D \frac{\partial c}{\partial x}(o, t) = k C_o \quad (34)$$

where  $k$  is the mass transfer coefficient of oxygen brought about by the concentration difference between the bulk and the pellet surface which is neglected. If we take the same procedure as before, the solution profile may be suggested as

$$c = \frac{k C_o}{2D} (\tau - x)^2 \quad (35)$$

and from this we obtain the leach rate equation,

$$N = \frac{a k k_d C_o \tau^2}{4D(\tau + 2a)} \quad (36)$$

also the net rate of penetration depth change becomes

$$\frac{d\tau}{dt} = \frac{3D}{\tau} - \frac{3 a k_d \tau}{4(\tau + 2a)} \quad (37)$$

This equation represents very similar dynamical behavior with (23), and especially the penetration depth at steady state will be same as  $\tau$  of (25). Therefore considering the difference between two leach rate equations (21) and (36), we can deduce the following relation.

$$\frac{k C_o \tau}{2D} = c_s \quad (38)$$

Since it is very reasonable in a sense of chemical characteristics of  $UO_2$  that the surface oxidation state  $c_s$  is assumed constant, the mass transfer rate of oxygen, expressed as  $k C_o$ , may be thought to be dependent on the penetration depth  $\tau$ . When the oxidation propagated much,  $\tau_0 > \tau_1$ , we can esteem that the mass transfer rate of oxygen be-

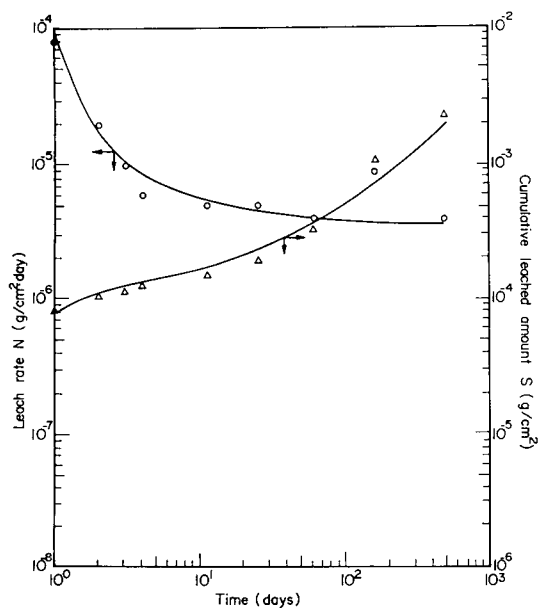


Fig. 3. Leach Rate and Cumulative Amount of Uranium Leached in Demi-water at 25°C ( $A=4.0 \times 10^{-6}$ ,  $B=1.44 \times 10^{-5}$ ,  $C=0.85$ ).

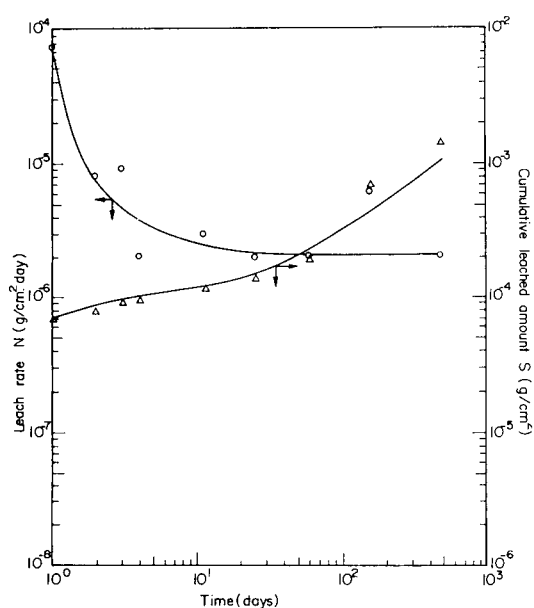


Fig. 4. Leach Rate and Cumulative Amount of Uranium Leached in NaCl Solution at 25°C ( $A=1.99 \times 10^{-6}$ ,  $B=5.3 \times 10^{-6}$ ,  $C=0.94$ ).

tween bulk and pellet surface will be low. On the other hand, when the oxidation state is insignificant,  $\tau_0 < \tau_1$ , mass transfer rate will be fast as much as oxidation rate. Though this sort of approach may not give us rigorous solution, it would be enough for us to understand the relations between the surface oxidation state and oxygen concentration in the aqueous phase. For a more exact analysis of mass transfer effect of oxygen, the concentration distribution through the film should be considered further in detail. However, we are not dealing with this problem any more.

#### 4. Discussion

We have shown above how the leach rate equation was derived from the mechanism of Wang and Katayama concerning the penetration of oxygen, oxidation of UO<sub>2</sub>, dissolution and transport processes. Though it was inevitable to adopt an approximation scheme in the mathema-

tical handling, we can deduce from the result that an initial oxidation state of UO<sub>2</sub> pellet may be an important factor to predict the transient behavior of leaching and after some time the rate will have a constant value of steady state.

In the figure 3 to 5, the leaching experimental results of Katayama *et al* [1] are shown with those of our rate equation model in terms of leach rate and cumulative amount of uranium leached. The leach rates in various leachants of demineralized water, NaCl and CaCl<sub>2</sub> solutions all appear high in the beginning of leaching and gradually come to steady states. From these, we can predict that the initial penetration depth  $\tau_0$  is greater than  $\tau_1$  and that the pellet surface had been oxidized to some degree before leaching. Here we may expect that there might be the fourth and fifth step reaction of the mechanism previously noted. However since the experiments were performed at room temperature and at this temperature those reactions are known to occur scarcely, we may neglect these effects.

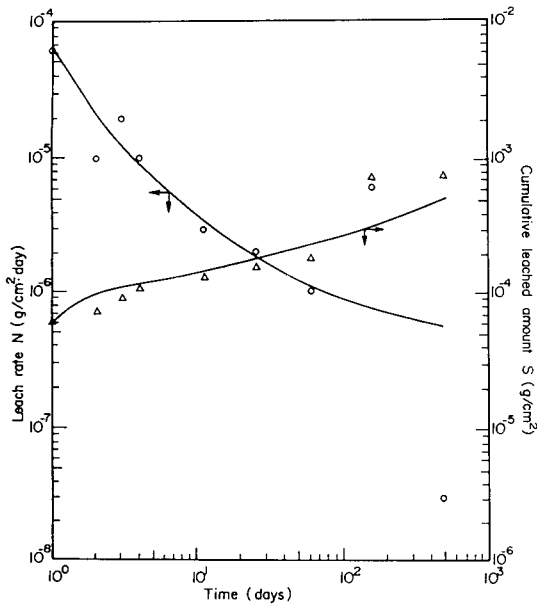


Fig. 5. Leach Rate and Cumulative Amount of Uranium Leached in  $\text{CaCl}_2$  Solution at  $25^\circ\text{C}$  (A =  $5.35 \times 10^{-7}$ , B =  $3.0 \times 10^{-5}$ , C = 0.56).

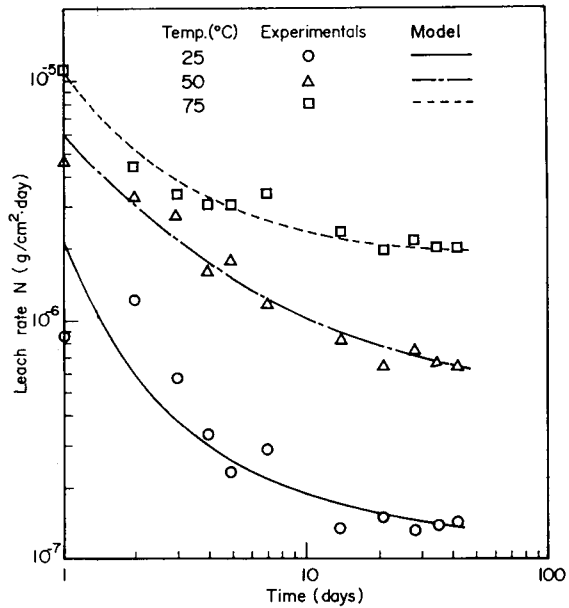


Fig. 6. Leach Rate of Uranium in Demi-Water. (o : A =  $1.23 \times 10^{-7}$ , B =  $5.85 \times 10^{-7}$ , C = -0.72,  $\Delta$  : A =  $5.23 \times 10^{-7}$ , B =  $4.68 \times 10^{-6}$ , C = -0.18,  $\square$  : A =  $1.91 \times 10^{-6}$ , B =  $3.38 \times 10^{-6}$ , C = -0.459).

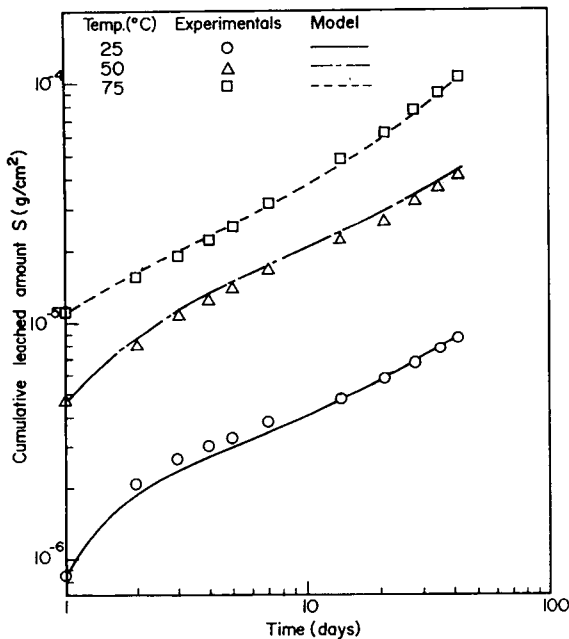


Fig. 7. Cumulative Amount of Uranium Leached in Demi-Water.

Figure 6 and 7 exhibit the results of our leaching experiments of unirradiated  $\text{UO}_2$  pellets in demineralized water at various

temperatures[16]. The experimental methods are just the same as those of Katayama *et al* [1] except using unirradiated intact fuels. Hence we do not give further explanation. Though the temperature effect on leach rate is not considered in the subject, the diffusion rate is expected to increase with temperature and thus will influence the leach rate, too. However, it is uncertain how the fourth step of hydrolysis reaction affects on the overall leach rate at high temperature ( $75^\circ\text{C}$ ). At least judging from the figures, we can not notice any effect hydrolysis reaction. One thing to note is that the leach rates of unirradiated  $\text{UO}_2$  pellets are relatively lower than those of irradiated ones of Katayama *et al*. There might have been some burn up effects.

In the figures 8 and 9, we have shown the experimental results of Ru and Cs leaching from Katayama *et al* in comparison with our model. though their reaction mechanisms are not exactly same as  $\text{UO}_2$ , they are esteemed to be similar rather physically than in the reaction mechanism



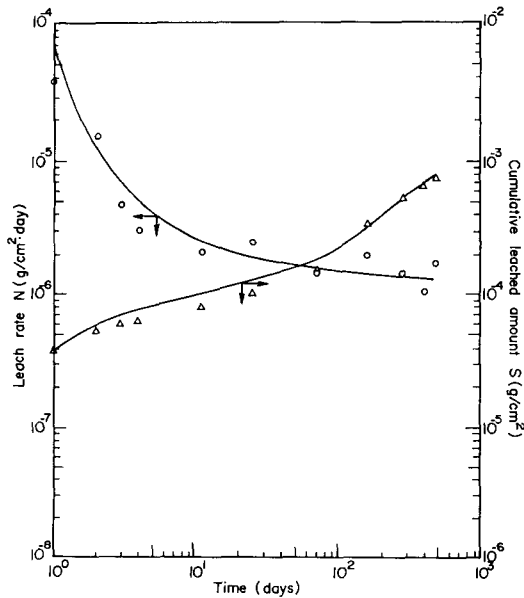


Fig. 8. Leach Rate and Cumulative Amount of Ru Leached in Demi-Water at 25°C (A=1.49×10<sup>-6</sup>, B=1.215×10<sup>-5</sup>, C=0.798).

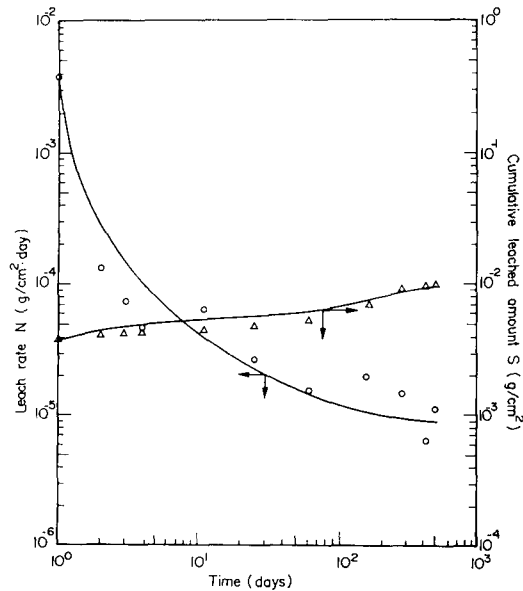


Fig. 9. Leach Rate and Cumulative Amount of <sup>137</sup>Cs Leached in Demi-Water at 25°C (A=1.01×10<sup>-5</sup>, B=2.965×10<sup>-4</sup>, C=0.92).

with pellet surface oxidation. Considering these similar aspects of leaching, the leach rates can be determined mostly by the UO<sub>2</sub> oxidation and permeation of leachant water into the pellets.

From the above results, our leach rate model can be adequately used for the explanation of leaching process with cases  $\tau_0$  greater than  $\tau_1$ . Also we see a possibility that this model can be used as an empirical equation for the cases of increasing tendency of leach rate, i.e., the cases  $\tau_0 < \tau_1$  even though the steady state analysis of leach rate model we can predict overall and long term leachability of spent nuclear fuel depending on various factors.

### 5. Conclusion

We have derived a leach rate model of UO<sub>2</sub> pellet based on the reaction mechanism suggested by Wang and Katayama[12]. This model implicates a penetration process of oxygen or oxidizing

species, and dissolution and transport phenomena. The aspects of leaching behavior can be analyzed in two regions of transient and steady state, whose types are much influenced by the initial oxidation states. Also this model suggest a possible utilization in the analyses of general leaching processes of similar mechanism.

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### Nomenclature

A: See Equation (32)

a:  $D'/k'$   
 B: See Equation (32)  
 b:  $D/(a \cdot d_d)$   
 c: See Equation (32)  
 C<sub>o</sub>: Concentration of oxygen in the solution  
 c: concentration of oxidized  $UO_2$   
 c<sub>o</sub>: Initial concentration profile  
 c<sub>s</sub>: Surface concentration of oxidized  $UO_2$   
 D, D': Effective diffusivities of oxygen and uranium  
 k, k': Mass transfer coefficients of oxygen and uranium  
 k<sub>d</sub>, d<sub>d</sub>: Dissolution rate constats  
 L: Feasible depth of penetration  
 N: Leach rate per unit surface area  
 p: See Equation (25)  
 q: See Equation (25)  
 S, S<sub>o</sub>: Accumulated leached amount and initial value  
 t, t<sub>o</sub>: Time and initial value  
 x: distance from solid surface

### Greek Letters

$\tau, \tau_o$ : Penetration depth and initial value  
 $\tau_1$ : Steady state penetration depth, See Equation (25)  
 $\tau_2$ : See Equation (25)