

The Leaching Behavior of Unirradiated UO₂ Pellets in Wet Storage and Disposal Conditions

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Abstract

The leaching behavior of uranium from unirradiated CANDU UO₂ fuel pellets in the spent fuel wet storage and disposal conditions has been investigated. A modified IAEA leach test method was used, and then the extent of leaching was monitored by analysis for uranium in the leachant. The leach test has been performed in various leachants(demineralized water and boric acid solution at pH=6, synthetic granite groundwater) for a long-term period of 5.4 years, and the effect of temperature on the leach rate of uranium has been analyzed. The leach rates of uranium at 25°C were dependent on the leachants. Over initial 100 days of leach periods, the leach rate in groundwater was the highest in three leachants and no significant differences of leach rates were observed in the demineralized water and boric acid solution. But these leach rates in three leachants around 2,000 days at 25°C appeared to be reached the steady rates in the range of $1\sim5\times10^{-8}\text{g/cm}^2\cdot\text{day}$. The leach rate of uranium in groundwater showed to be independent of the temperature, but those in both demineralized water and boric acid solution increased with temperature. These results show that the leaching behavior of uranium from UO₂ fuel in both the demineralized water and boric acid may be controlled by the surface oxidative-dissolution reaction of UO₂ and the leach rate of uranium in groundwater at room temperature could mainly be controlled by the complex reaction of dissolved uranyl ions with carbonate ions and no variation of leach rate of UO₂ in groundwater with temperature may be due to the local deposition of passivating uranyl phases on the surface.

1. Introduction

The environmental and safety assessment of a radioactive waste and spent fuel storage and disposal would require the accurate predictions of the rates at which radionuclides will be released from the spent UO₂ fuel and radioactive waste. Regarding 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 release mechanism of radionuclides from spent fuel into the pool water or groundwater under storage or disposal conditions may generally be summarized as follows : When spent fuel contacts with pool water or groundwater after container defect resulting from material corrosion, the fission products(I, Cs) from the fuel/sheath gap and fuel grain boundaries are released relatively fast. This is followed by a slow, con-

gruent release of the fission products and actinides contained within the UO_2 grains, which is controlled by the dissolution of UO_2 . 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 behavior since it depends much on the physical structure, composition and chemical interactions with environment. 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[8].

In Johnson's leaching experiment[9], the leach rate of Cs-137 has been observed to remain higher than the release rates of the other radionuclides even after eight-year exposure to solution. The surface analyses suggest that this is due to the release of Cs-137 from the grain boundaries. Based on this result, the mechanism for the release of fission products such as Cs-137 and I-129 has been presented to take place in the following three ways. (1) The release from the fuel/sheath gap takes a few days. (2) The release from the grain boundaries may continue several years depending on the irradiation history of the fuel. (3) The fission products in the UO_2 grains are released at a rate controlled by the dissolution of UO_2 matrix.

In spent fuel disposal conditions, the leach rate of uranium from UO_2 pellet is limited by the solubility of UO_2 since the groundwater flow is very slow. The solubility of UO_2 depends on the geochemical conditions, the chemical stability of UO_2 and the leaching mechanism of UO_2 under the disposal conditions[11, 12]. For example, under oxidizing conditions UO_2 is not the stable uranium solid. Furthermore, possible formation of hydrogen peroxide at the interface of pellet and water by the radiolysis of water has been suggested to produce the oxidizing conditions[5,13,

14], 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. Wang and Katayama[10], through their single crystal experiments, explained the leaching mechanism in several steps, which includes oxidation, dissolution, transportation and crystal formation by hydrolysis.

Since more than 90% of the radionuclides inventory is contained within the UO_2 grains, the major factor controlling the long term release of radionuclides from spent fuel may be the leach rate of UO_2 matrix to the pool water and groundwater under the storage and disposal conditions.

The aim of this study is to provide the fundamental information for use in predicting the leaching behaviors and rates of spent UO_2 fuel under the long-term storage and disposal conditions. The effects of the nature of leachant, temperature on the leach rate of uranium from unirradiated UO_2 pellets leached for a long-term period of 5.4 years are discussed and qualitatively analyzed for the relationship between the leach rates and surface oxidation states of UO_2 pellets.

2. Experimental

(1) Material

The material used was the sintered UO_2 pellets taken from unirradiated CANDU fuel bundles. The geometric density was 10.53g/cm^3 and have $\sim 97\%$ of theoretical density. The average surface area of each sample was 8.4cm^2 .

(2) Leachant

For UO_2 leaching experiments with unirradiated CANDU UO_2 fuel pellet, three leaching solutions were used through this experiment: demineralized water($\text{pH}=6$) as a reference leachant and boric acid solution ($112\text{ppm H}_3\text{BO}_3$, $\text{pH}=6$), synthetic granite groundwater ($\text{pH}=6.8$) shown in Table 1[15].

(3) Experimental Procedure

Leaching experiments were carried out using the leachant replenishment method called a modified IAEA method[16].

The unpolished UO₂ pellet was placed in a polypropylene jar as shown in Fig. 1 in order to increase contact surface area of UO₂ with leachant, filled with 70ml of leachant, which was placed in constant temperature water bath controlled at fixed temperature (25°C, 50°C, 75°C, respectively). The oxygen content in the leachants was assumed to be air-saturated condition and the amount of uranium in leachants was initially zero. Over the fixed period, the pellet was removed from the leachant and transferred to new polypropylene jar with fresh leachant. The leachant in the jar, from which the pellet was removed, was acidified with 1 ml of 68% nitric acid, evaporated and dried. Then 70ml aliquots of 5M HNO₃ + 0.05M HF solution was added to the dried jar to remove the adsorbed uranium on the leachant container wall. The acidified leachant was left for one week to desorb the adsorbed uranium from the container walls and then uranium concentration in this leachant was measured.

(4) Uranium Concentration Analysis

The analyses of uranium in the leachants after leaching experiment were performed using Jarrell-Ash

Fluorimetric instrument in addition with low background α/β counter. The detection limit of solid fluorimetric method is $\sim 0.01 \mu\text{g/ml}$. After leaching experiment for 5.4 years, UO₂ pellet surface was analyzed by X-ray powder diffractometry (XRD) to produce basic data for analysis of UO₂ surface oxidation state which may affect the leach rate of uranium.

3. Results and Discussion

(1) Calculation of leach rates

The average uranium leach rate (R) is calculated as [16, 17]:

$$R (\text{g} \cdot \text{cm}^{-2} \cdot \text{day}^{-1}) = \frac{C_u (\text{g/ml}) \cdot V (\text{ml})}{S (\text{cm}^2) \cdot T (\text{day})} \quad (1)$$

where C_u : Concentration of uranium in leachant

V : Volume of leachant

S : Geometric surface area of UO₂ pellet

T : Duration of the leach period

Thus, R corresponds to the mass of uranium leached per unit surface area per unit time. This ap-

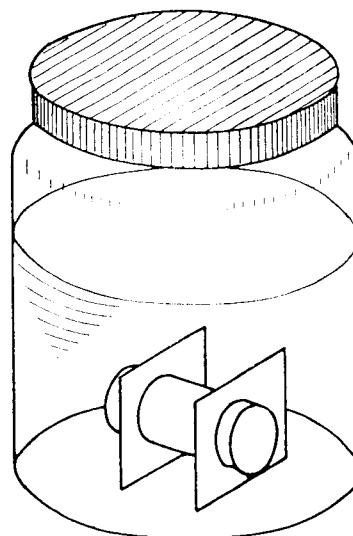


Fig. 1. Leaching Test Apparatus.

Table 1. Groundwater Compositions Used in the Leaching Experiment.

| Species | mg/L | mol/L |
|------------------|------|-----------------------|
| Ca | 13 | 3.24×10^{-4} |
| Mg | 3.9 | 1.60×10^{-4} |
| Na | 8.3 | 3.61×10^{-4} |
| K | 3.5 | 8.95×10^{-5} |
| Cl | 5 | 1.41×10^{-4} |
| SO ₄ | 8.6 | 8.95×10^{-5} |
| HCO ₃ | 61.6 | 1.01×10^{-3} |
| F | 0.19 | 1.00×10^{-5} |
| NO ₃ | 0.62 | 1.00×10^{-5} |

proach to the calculation of the leach rate of uranium is based on the following assumptions: (1) The leach rate is first order with respect to the surface area of the pellet. The geometric surface area of UO_2 pellet is 2~3 times less than true surface area, and inclusion of this roughness factor would result in smaller leach rates. (2) The volume of leachant and leach duration are such that the concentrations of dissolved uranium species in leachant are below their saturation values, so that equilibrium will not be established nor will reprecipitation occur. Since the uranium concentrations measured over the whole leach periods were considerably below saturation value, the formation of secondary products such as UO_3 hydrate on the UO_2 surface was not found. Therefore, the leach rates reported here are unlikely to be influenced by the secondary product formation.

(2) Effect of leaching solution on leach rate

Leachants contacted with UO_2 pellet were removed at intervals and submitted for analysis. The leach rates of uranium from the total amount of uranium leached into each leachant were calculated by Eq.(1). Fig. 2 show the variation of leach rates in three leachants as a function of leaching time over the initial leach period at 25°C. The leach rates of uranium showed some variations depending on leachant. Although there are considerable scattering data in the results after 50 days, the leach rates in all leachants sharply decreased over the 10 days of initial leaching period and clearly leach rates tended to be slowly decreased after initial high leach rates. Over initial 100 days of leach periods, the leach rate in groundwater was the highest in all leachants. Although the leach rate in boric acid at pH=6 is slightly greater than that in demineralized water, no significant differences were observed between leach behavior in demineralized water and boric acid solution (pH=6). But these leach rates in all the leachants around 2,000 days at 25°C have a similar values with $1\sim5\times10^{-8}$ g/cm². day. Fig. 3 displays the cum-

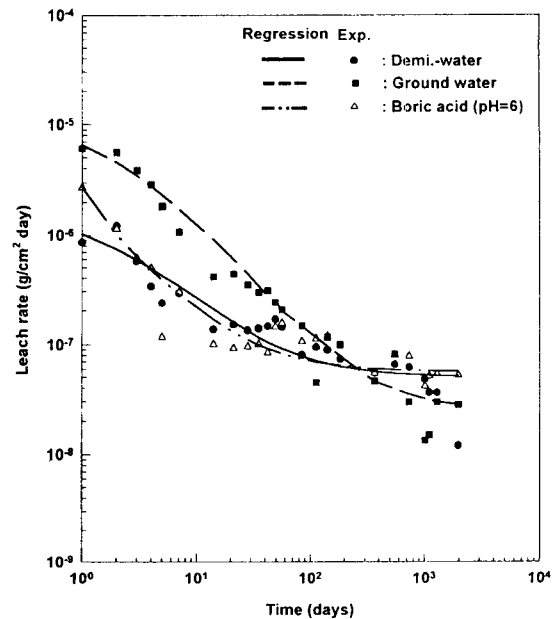


Fig. 2. Variation of Leach Rate of Uranium in Various Leachants at 25°C

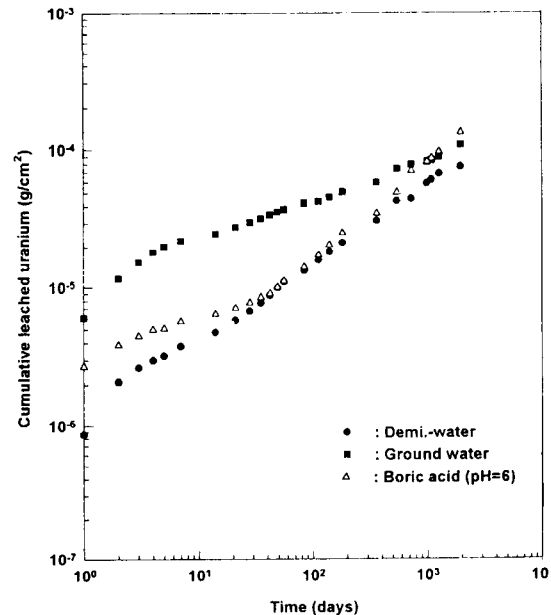


Fig. 3. Cumulative Amount of Uranium in Various Leachants at 25°C

ulative amount of uranium leached in three leachants at 25°C. As shown in this figure, the cumulative

amount of uranium leached in groundwater at 25°C is much higher than those in the demineralized water and boric acid solution. This high uranium leach rate in the synthetic groundwater at room temperature seems to be caused by enhanced uranium solubility due to complex reaction with carbonate species in groundwater. In general, the theoretical solubility of uranium in the synthetic groundwater at 25°C is higher than that in demineralized water assuming that U₃O₈ is the solid phase of uranium[13], because the species in groundwater, such as carbonate and phosphate, complex with the uranyl ions to enhance the solubility of uranium. Therefore, it is reported that the theoretical solubility of uranium in demineralized water under oxidizing conditions is about 6×10^{-5} gU/L at pH=6, but in synthetic groundwater this value is about 9×10^{-1} gU/L[13]

The fractional release rates of uranium leached over the total leach period for three leachants are summarized in Table 2. This fractional release rate or factor of uranium was calculated as follows :

$$F_r(\text{day}^{-1}) =$$

$$\frac{\text{cumulative U concentration} \times \text{leachant volume}}{\text{g inventory of U per pellet} \times \text{total leach period}} \quad (2)$$

Although the leach rate in groundwater was the highest in all the leachants over initial 100 days of leach periods, the fractional release rates of uranium in all leaching solutions at 25°C have the similar values over the whole leach period, not depending on the leachant as shown in Table 2. The effect of temperature on the leach rates of uranium will be dis-

cussed as following.

(3) Effect of temperature on leach rate

The kinetic effects with temperature variation in the range of 25~75°C on the leach rate of uranium were studied in three leachants. Figs. 4~6 display the variation of uranium leach rate with temperature in demineralized water, synthetic groundwater and boric acid solution at pH=6, respectively. The temperature effects on the fractional release rates of uranium in three leachants are also given in Table 2. Although the scatter in the data after 50 days in the demineralized water and boric acid at 50°C is too great to draw any conclusion, the leach rates of uranium at 75°C were overallly higher than those in both demineralized water(Fig. 4) and boric acid solution (Fig. 6) at 25°C. To identify these phenomena at 50°C, the second leaching experiments for 200 days in both demineralized water and boric acid solution have been carried out. The leach rates in the second experiments are somewhat different from those in the first experiments because another unpolished UO₂ pellets were used. As shown in Figs. 7~8, the leach rates increased with temperature. The observed increase in the leach rate of uranium with temperature in both the demineralized water and boric acid at pH=6 may be due to the oxygen diffusion-controlled reaction in the absence of complex ions. There is an another evidence for considering the oxygen diffusion-controlled reaction as the rate-determining step. Assuming Arrhenius behavior between 25 and 75°C, the calculated activation energies for both demineralized water and boric acid at pH=6 was about 26~31 kJ/mol. This activation energy for the oxidative dissolution of UO₂ is in accord with those reported by Aronson(21~42 kJ/mol)[18], Johnson et al. (15~30 kJ/mol)[19], Pearson and Wadsworth(28 kJ/mol)[20] and Thomas(20 kJ/mol)[2].

Even though there are some scattered data in the results, the uranium leach rate in synthetic groundwater was clearly independent on temperature vari-

Table 2. Fractional Release Rates of Uranium With Various Leachants at Various Temperatures

| Leachant | Temperature(°C) | | |
|----------------------|----------------------|----------------------|----------------------|
| | 25°C | 50°C | 75°C |
| Demi. water | 1.7×10^{-8} | 3.4×10^{-8} | 1.1×10^{-7} |
| Groundwater | 2.4×10^{-8} | 2.7×10^{-8} | 2.4×10^{-8} |
| Boric acid (pH=6) | 2.9×10^{-8} | 6.8×10^{-8} | 1.3×10^{-7} |

Unit : day⁻¹

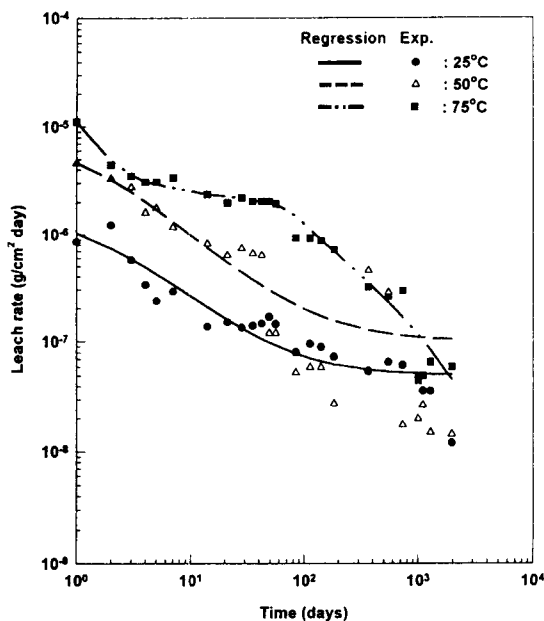


Fig. 4. Variation of Leach Rate of Uranium Depending on the Temperature in Demi-Water

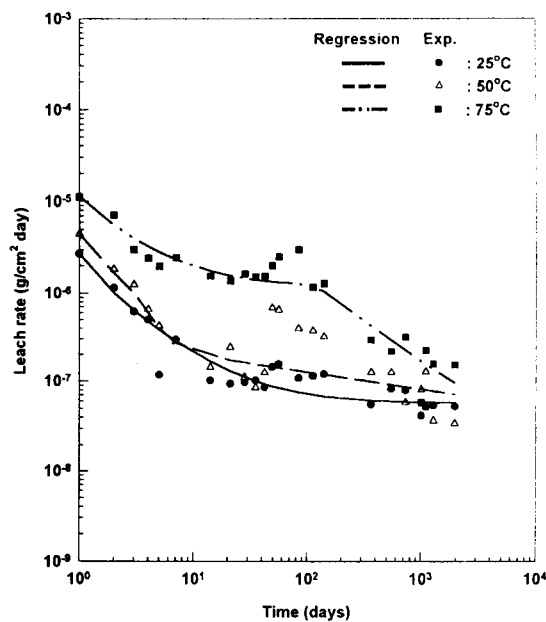


Fig. 6. Variation of Leach Rate of Uranium Depending on the Temperature in Boric Acid(pH=6)

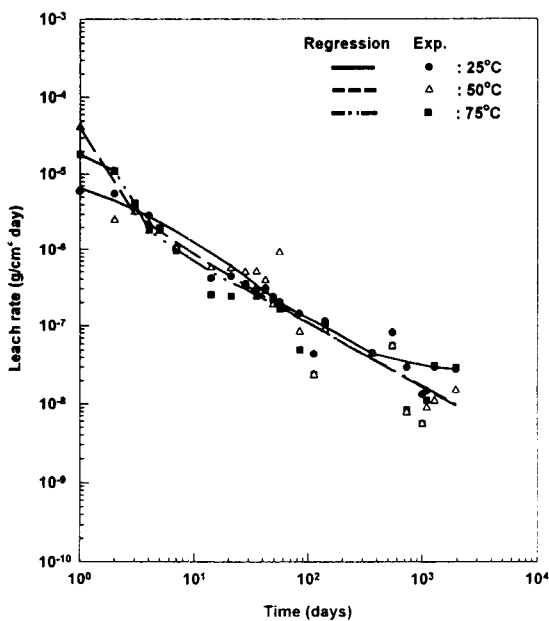


Fig. 5. Variation of Leach Rate of Uranium Depending on the Temperature in Groundwater

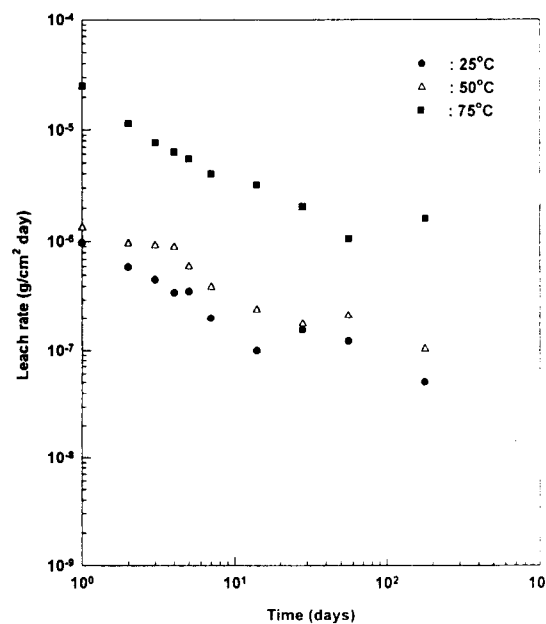


Fig. 7. Variation of Leach Rate of Uranium Depending on the Temperature from the Second Leach Tests in Demi-Water.

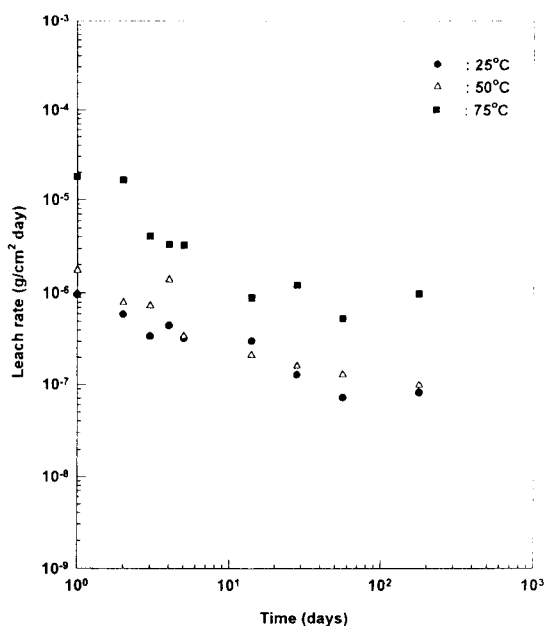


Fig. 8. Variation of Leach Rate of Uranium Depending on the Temperature From the Second Leach Tests in Boric Acid at pH=6.

ation as shown in Fig. 5, but Thomas[2] reported that uranium leach rate from the unirradiated CANDU UO_2 fuel in synthetic groundwater over 7~8 days decreased as temperature increases. This observed decrease in the leach rate may be due to passivating layer on the surface. Leach rate of uranium in synthetic groundwater at 25°C could mainly be controlled by the complex reaction of uranyl ions with carbonate ions[2] rather than oxygen diffusion-controlled reaction. Under oxidizing conditions, UO_2 dissolves to form the uranyl species UO_2^{2+} and its hydrolysis products[3]. The carbonate and phosphate species in groundwater complex with the uranyl ion and enhance the solubility of UO_2 . But no variation of leach rate of UO_2 in groundwater with increasing temperature may be due to the local deposition of passivating uranyl phases, such as NaUO_3 and $\text{Na}_2\text{U}_2\text{O}_7$, which precipitate at high temperatures and high alkalinities[21], after the release of UO_2^{2+} into solution[2].

(4) Effect of surface oxidation state on leach rate

This leach rate is limited by the solubility of UO_2 since the groundwater flow under disposal conditions is very slow. The solubility of UO_2 depends on the geochemical conditions, the chemical stability of UO_2 , the leaching mechanism of UO_2 and the oxidation state. After leach tests, the surface oxidation state of UO_2 pellets was analyzed by X-ray diffractometry (XRD, Rikaku). As shown in Figs. 9~11 and Table 3, XRD examination showed that UO_2 surface oxidized to $\alpha\text{-U}_3\text{O}_7$ phase with UO_2 minor phase at 25, 50°C and U_3O_7 phase at 75°C.

In the absence of strongly complexing anions, It is reported that the anodic oxidation of unirradiated CANDU UO_2 fuel in neutral or alkaline solutions proceeds with the initial surface formation of U_3O_7 , followed by the formation of U_3O_8 . A partially passivating layer of UO_3 may form in alkaline solution while a nonpassivating layer of $\text{UO}_3 \cdot n\text{H}_2\text{O}$ may form in neutral solution[23]. Shoesmith et al.[23] studied the

Table 3. X-ray Diffraction Data of UO_2 Pellet Leached in Demineralized Water at 75°C($\alpha\text{-U}_3\text{O}_7$ Phase, d in Å).

| $hkl(\text{U}_3\text{O}_7)$ | $d(\text{U}_3\text{O}_7), \text{Lit.}^{(a)}$ | $hkl(\text{U}_3\text{O}_7), \text{Lit.}^{(a)}$ | $d(\text{U}_3\text{O}_7), \text{Obs.}^{(b)}$ | $hkl(\text{U}_3\text{O}_7), \text{Obs.}^{(b)}$ |
|-----------------------------|--|--|--|--|
| 111 | 3.14 | 100 | 3.14 | 100 |
| 200 | 2.713 | 30 | 2.721 | 35 |
| 002 | 2.696 | 20 | N.D. ^(c) | — |
| 220 | 1.926 | 20 | 1.927 | 46 |
| 202 | 1.918 | 25 | N.D. | — |
| 311 | 1.645 | 20 | 1.644 | 42 |
| 113 | 1.628 | 15 | N.D. | — |
| 222 | 1.567 | 15 | 1.575 | 10 |
| 400 | 1.366 | 5 | 1.365 | 8 |
| 004 | 1.349 | 5 | N.D. | — |
| 331 | 1.253 | 10 | 1.253 | 18 |
| 313 | 1.246 | 10 | N.D. | — |
| 420 | 1.223 | 10 | 1.228 | 4 |
| 204 | 1.210 | 10 | 1.202 | 1 |

(a) Ref. [22].

(b) Observed data after 5.4 years in Demineralized Water at 75°C.

(c) N.D.: Not Detectable

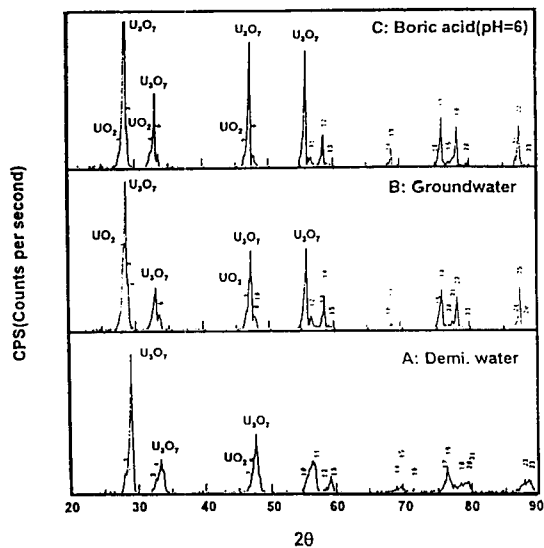


Fig. 9. X-ray Diffraction Pattern of Oxidized UO_2 Fuel in Various Leachants for 5.4yrs at 25°C .

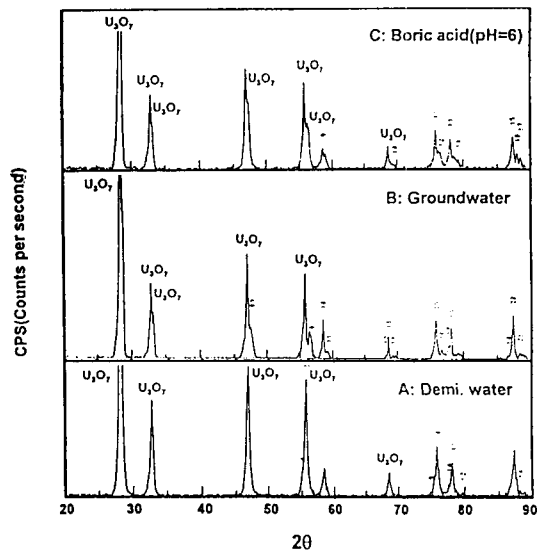


Fig. 11. X-ray Diffraction Pattern of Oxidized UO_2 Fuel in Various Leachants for 5.4yrs at 75°C .

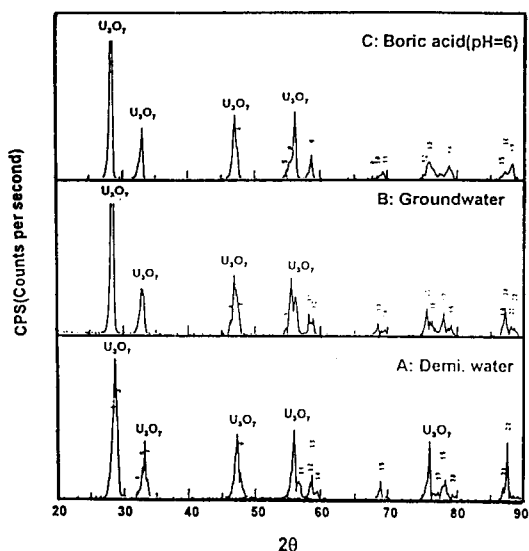


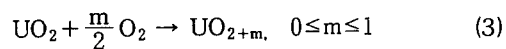
Fig. 10. X-ray Diffraction Pattern of Oxidized UO_2 Fuel in Various Leachants for 5.4yrs at 50°C .

anodic oxidation of UO_2 by electrochemical method in carbonate solutions, and if the carbonate ions in solution exceed 10^{-2} mol/L the oxidation of the U_3O_8 surface layer to U_3O_{10} does not occur and dis-

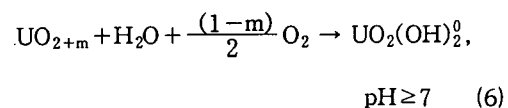
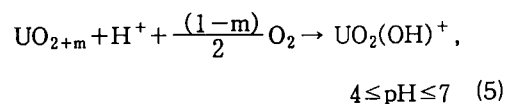
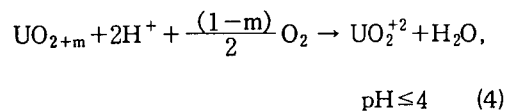
solution progresses through the formation of uranyl carbonates.

Wang and Katayama[10] suggested that the leaching mechanism of UO_2 can be presented as following steps.

(1) surface Oxidation

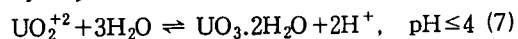


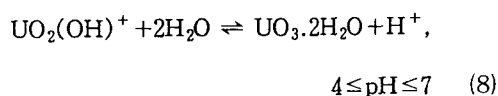
(2) Oxidation-Dissolution



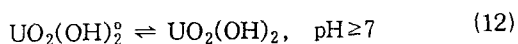
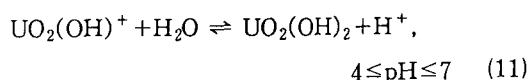
(3) Transport

(4) Hydrolysis-Film Formation ($25-75^\circ\text{C}$)





(5) Hydrolysis-Crystal Growth (150°C)



Since U_3O_8 and $\text{UO}_3 \cdot n\text{H}_2\text{O}$ phases on the UO_2 surface were not detectable even after leach test in our experiments, and the concentrations of dissolved uranium species in leachant were considerably below saturation values[13], leach rates obtained from our experiments were unlikely influenced by the formation of particulate UO_3 -hydrates. Therefore, the leach rates of uranium in both the demineralized water and boric acid at $\text{pH}=6$ may be controlled by the oxidation of UO_2 surface to U_3O_8 ($m=0.33$ in Eq.(3)) and film dissolution as uranyl(UO_2^{2+}) ions by Eq.(4). It is generally reported that U_3O_8 phase is composed of 2U(IV) and U(VI) and the solubility of U(VI) in aqueous solution is much higher than that of U(IV) [24]. This result may be another evidence that the leaching behavior of uranium from UO_2 fuel is controlled by oxidative-dissolution of UO_2 surface. But unfortunately the passivating uranyl phases of the NaUO_3 and $\text{Na}_2\text{U}_2\text{O}_7$ on the UO_2 surface leached in groundwater were not detected.

4. Conclusions

The leach test of unirradiated UO_2 fuel pellets has been carried out for 5.4 years with parametric variations of the leachant composition and temperature under the air-saturated conditions.

The leach rates in all leachants sharply decreased over the 10 days of initial leaching period and ten-

ded to be slowly decreased after initial high leach rates. Over initial 100 days of leach periods, the leach rate in groundwater was the highest in all leachants and no significant differences were observed between leach behavior in demineralized water and boric acid solution($\text{pH}=6$). But these leach rates in all the leachants around 2,000 days at 25°C appeared to be reached the steady rates in the range of $1 \sim 5 \times 10^{-8}$ g/cm². day. The leach rates of uranium in both demineralized water and boric acid at $\text{pH}=6$ increased as temperature increase, except some scattered data. It may be shown that the leaching behavior of uranium from UO_2 fuel in both the demineralized water and boric acid would be controlled by the surface oxidative-dissolution reaction of UO_2 . But the leach rate of uranium in groundwater was independent on temperature variation. This result shows that the leach rate of uranium in groundwater at room temperature could mainly be controlled by the complex reaction of dissolved uranyl ions with carbonate ions and that no variation of leach rate of UO_2 in groundwater with increasing temperature may be due to the local deposition of passivating uranyl phases, which precipitate at high temperatures and high alkalinities. However, the passivating uranyl phases, such as the NaUO_3 and $\text{Na}_2\text{U}_2\text{O}_7$, on the UO_2 surface leached in groundwater were not detected.

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