

Identification of Uranium Species Released from the Waste Glass in Contact with Bentonite

벤토나이트와 접한 유리고화체로부터 유출된 우라늄 화학종의 규명

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Abstract

Yellowish uranium compounds were enriched at the interface between a Ca-bentonite block and a waste glass, containing about 20% uranium oxide, in contact with the block due to the dissolution of uranium by a synthetic granitic groundwater in Ar atmosphere. The uranium compound formed for 6 years leach time was identified as a beta-uranophane $[\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2\cdot 5\text{H}_2\text{O}]$ using XRD, IR and mass spectrometer. The solubility of the beta-uranophane was measured to be about 10^{-6} mole/L in de-mineralized water at 80°C .

Key words: Uranium alteration, Waste glass, Bentonite, Uranophane, Leaching

요약

칼슘-벤토나이트와 접한 약 20%의 우라늄 산화물을 함유한 유리고화체가 알곤 분위기에서 모의 화강암지하수에 의해 침출되었을 때 노란색의 우라늄화합물이 벤토나이트와 고화체의 경계면에 농축되었다. 6년간의 침출후 형성된 우라늄 화합물이 beta-uranophane $[\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2\cdot 5\text{H}_2\text{O}]$ 임을 XRD, 적외선 스펙트럼과 질량분석기를 이용하여 확인하였으며, 이 화합물의 용해도를 80°C , 탈이온수에서 측정된 결과 약 10^{-6} mole/L 이었다.

중심단어 : 우라늄변형체, 유리고화체, 벤토나이트, Uranophane, 침출

I . Introduction

In order to reuse spent PWR fuel as the fuel of a CANDU reactor and to reduce the repository requirements for the direct disposal of spent PWR fuel, a DUPIC(Direct use of spent PWR fuel in CANDU reactor) program has been jointly studied in cooperation with AECL, KAERI and US DOE since 1991 [1]. From the OREOX (Oxidation and reduction of oxide fuel) process, by which a spent PWR fuel could be re-fabricated as a DUPIC fuel, the scrap of uranium oxide could be generated. This scrap accompanies fission products and is highly active, and therefore should be stabilized in a monolithic form. Preliminarily a vitrification process has been recommended for the solidification of the scrap [2]. For the isolation of radioactive nuclides from biosphere, the waste glass containing the scrap is filled in a metal container and disposed in a deep underground. The container would be surrounded with bentonite in the bore hole located at a few hundred meter below ground level according to the Korean concept [3] of a multi-barrier system for the disposal of high level radioactive wastes. After corrosion of metal container, the waste glass could be directly contacted with the bentonite.

To support the performance assessment of the DUPIC fuel cycle, the long-term corrosion behavior of a simulated waste glass containing about 20% of the scrap, has been studied under repository conditions. This paper describes the investigation of the uranium alteration phases formed on the surface of a simulated uranium-containing borosilicate waste glass in contact with a domestic Ca-bentonite block during the corrosion in a synthetic granitic groundwater up to about six years.

II . Experiment Procedure

Disc-shaped specimens of the simulated borosilicate waste glass were prepared by a molding method. The stoichiometric amounts of SiO_2 , B_2O_3 , Na_2CO_3 , fly ash and U_3O_8 (Table 1) were mixed and heated in alumina crucibles at 1200°C for 2 hours. A waste glass cylinder was made by pouring the molten waste glass into a preheated stainless steel mold with a diameter of 18 mm, annealed at 500°C for 1 hour and then cut to about 2.5 mm thickness. The surface of each waste glass specimen was polished with a 1000 grit SiC sandpaper and cleaned ultrasonically in petroleum ether, isopropanol and acetone, in sequence [4].

The overall flow scheme for the leach test is shown in Fig. 1. Each waste glass specimen was sandwiched between two Ca-bentonite blocks, compacted to 1.4 Mg/m^3 in a stainless steel leach cell (Fig. 2). Ar-purged synthetic granitic groundwater (Table 2) as leachant flew through the leach cells placed in an oven at 80°C with a flow rate of about 1.0 ml/day. Each of the leach cells was dismantled periodically. A little bit detailed procedure is described in the previous paper [5].

The surfaces of the glass specimens before or

Table 1. Compositions of reactant and product as a simulated waste glass (wt. %).

Reactant		Product ^a	
SiO_2	16	SiO_2	38.99
B_2O_3	12	B_2O_3	12.10
Na_2CO_3	27	Na_2O	16.26
U_3O_8	20	UO_2	19.35
Fly ash	36	Al_2O_3	9.22
		CaO	0.51
		MgO	0.25
		TiO_2	0.37
		K_2O	0.78
		Fe_2O_3	2.17

^aProduct of glass was analyzed only the major elements.

after leaching were observed and analyzed using X-ray diffractometry (XRD Siemens D5000), time of flight - secondary ion mass spectrometry (TOF-SIMS; Physical Electronics PHI7200) and infrared spectrometry.

To measure briefly the solubility of the altered uranium species, the yellowish uranium compound was collected by scraping both surfaces of the bentonite and the waste glass, and placed in 10 ml of demineralized water in a Teflon bottle. The bottle was kept for 3 weeks at 80°C and then the solution was filtered with a 0.2 μm filter. The uranium

Table 2. Composition of ground water before and after passing a leach cell.

Element	Before passing a leach cell	After passing a leach cell ^a
	Concentration (mg/L)	
K	1.8	ND ^b
Ca	15	0.4
Mg	1.6	0.2
F	5.6	13
SO ₄	12	ND ^b
Cl	38	39
Na	58	57
HCO ₃	87	ND ^b
Si	-	39
pH	7.8	7.7

^a The concentration of ions was measured after 300 days leaching.

^b Non detected.

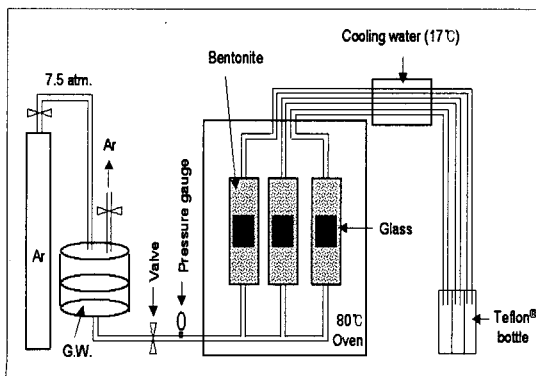


Fig. 1. Schematic diagram of dynamic leach test.

concentration of the solution was measured by using inductively coupled plasma mass spectrometry (ICP-MS; VG Elemental X7).

III. Results and Discussion

Fig. 3 shows the XRD patterns of the yellowish materials formed on the surface of the bentonite blocks in contact with the waste glass specimens leached up to about 6 years. XRD peaks of the bentonite obtained from a 6-years leaching test are well matched to those of a crystalline beta-

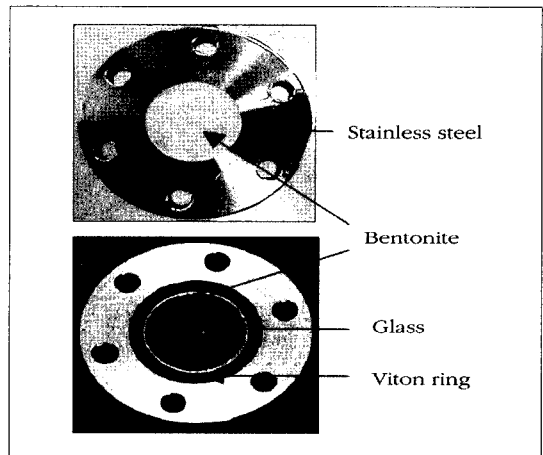


Fig. 2. Photograph of a pair of leach cell.

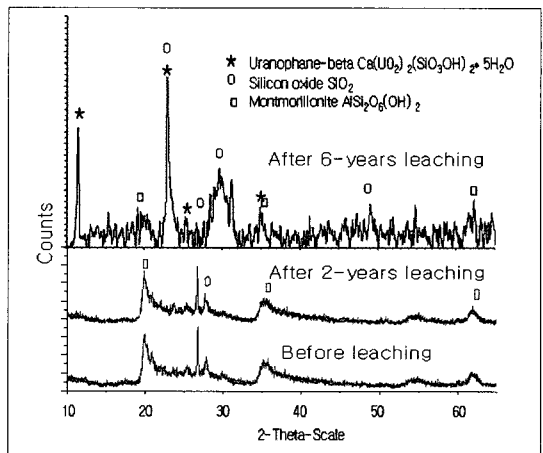


Fig. 3. XRD patterns of the surface of the bentonite blocks in contact with the waste glasses leached up to about 6 years.

uranophane, $\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O}$ [6]. Korzeb et al. [7] suggested the following reaction for the formation of uranophane:

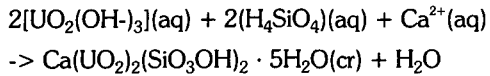


Fig. 4 shows the mass spectrum of this specimen and the speculative chemical forms of each peak. The mass spectrum indicates that the newly formed mineral on the altered layer of the specimen had the functional groups of CaO, SiO_4 and UO_2 peaks. Near 1000 and 3400 cm^{-1} in an IR spectrum also indicates that the mineral is a type of uranophane [8].

Wang [9] and Wronkiewicz et al. [10] have reported that the sequence of alteration phases of spent fuel would be as follows: uraninite \rightarrow (uranyl hydrates \rightarrow) uranyl silicate \rightarrow Ca-uranyl silicate.

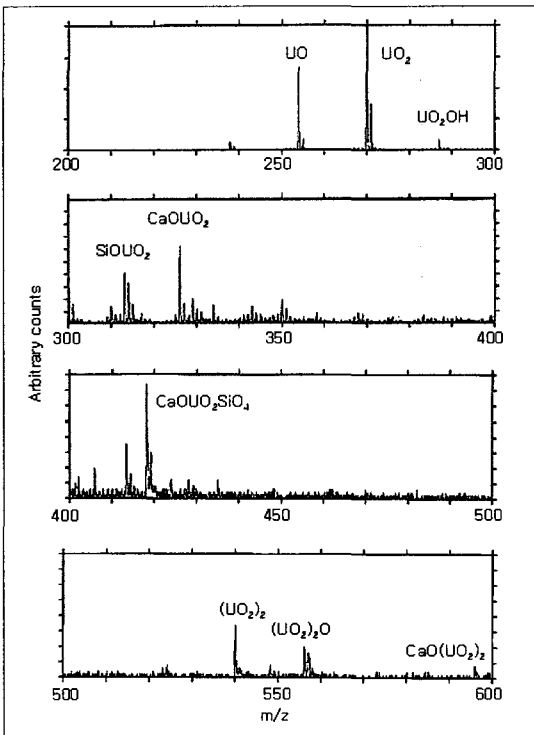


Fig. 4. Mass spectrum of the secondary mineral on the leached waste glass and its speculative chemical forms.

However, no peak related to the intermediates as well as beta-uranophane was observed on the surfaces of the bentonite blocks in contact with the other waste glass specimens leached up to about 2 years. This result indicates that the uranium released from the waste glass in contact with a Ca-bentonite buffer by an alkaline granitic groundwater was slowly altered into a beta-uranophane. Uranophane was found after elapse of three years in a drip test of spent fuel at 90°C at Argonne National Laboratory [10].

There was no XRD peak corresponding to soddyite and renardite which are well known as the major secondary uranium minerals [11]. And also schoepite which is known to be formed on spent nuclear fuel in contact with water under oxidizing conditions [12] was not found in this test because schoepite is stable in environment with low pH and low activities of dissolved silica and Ca [13].

The solubility of the beta-uranophane collected from the leached waste glass was about 1×10^{-6} mole/L at 80°C, which is lower than the extrapolated value (about 5.6×10^{-6} mole/L) of an uranophane in the HATCHES database at ambient temperature [8].

IV. Conclusions

The beta-uranophane with a solubility of approximately 1×10^{-6} mole/L at 80°C was formed as a secondary uranium mineral when a waste glass containing uranium is leached in a domestic Ca-bentonite buffer by a granite water. However, other uranium silicate compounds such as soddyite and renardite were not found.

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