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Uranium dissolution in hyperalkaline TMA-OH solutions: Preliminary results

Christelle Cachoir[a]*, Sonia Salah[a], Thierry Mennecart[a], Karel Lemmens[a]

[a]*Belgian Research Nuclear Centre (SCK-CEN), Boeretang 200, 2400 Mol, Belgium*

Abstract

Leaching experiments were performed with depleted UO_2 powders in tetramethylammonium solutions (TMA-OH) at pH 13.5 and 12.5, and at different UO_2 surface area to volume of solution (SA/V) ratio's to determine the solubility and the dissolution kinetics of UO_2 at high pH in absence of cations dominating cementitious waters (Ca,Na, K).
The solubility of UO_2 increased from pH 12.5 to 13.5 and by increasing the SA/V ratio up to 100 m^{-1}. However, no known U secondary-phases were predicted by geochemical calculations to control the measured U-concentrations. A two-step dissolution process was put forward: 1-a fast initial rate, surface controlled and hydroxo promoted and 2- a sorption process at low SA/V ratio or a continuous residual dissolution process at high SA/V ratio.

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1. Introduction

The Supercontainer design is the current reference design for the geological disposal of spent nuclear fuel in Belgium[1]. The main characteristic of this design is to provide a multi-barrier system to contain and isolate the radioactive waste from the biosphere. The immobilized waste is inserted into a canister, which is surrounded by different engineered barriers, like the overpack (carbon steel), the buffer (= Ordinary Portland Cement based concrete) and the stainless steel envelope. The concrete buffer is expected to impose a high pH environment on the long-term. In 2005, a research programme was started at the Belgian Nuclear Research Centre (SCK•CEN) to

* corresponding author. Tel.: +3214333129.
E-mail address: ccachoir@sckcen.be

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evaluate the stability of UO_2, as analogue of real spent fuel in such environment. In a previous work[2], it was demonstrated that the high pH did not increase the soluble U(IV) concentrations in synthetic cementitious pore waters, but it increased the soluble U(VI) concentrations due to formation of uranyl-hydroxo complexes. Besides this, it was stressed that presence of alkali and/or alkaline-earth elements, especially calcium may strongly favour the U(VI)-complexation and/or U-colloid formation, which may result in the precipitation of Ca- U(VI) phases such as $CaUO_4$ or $CaU_2O_7{\times}3H_2O$.

In order to better understand the processes taking place in cementitious systems, this paper presents a new set of experiments performed in hydroxide solutions (TMA-OH) in order to avoid colloid formation on the one hand and to minimize the interaction of uranium with alkali and/or alkaline-earth elements present in cementitious waters (i.e. Na, Ca and K) on the other hand.

2. Experimental details

All leaching experiments were performed in a glove box at 25 – 30°C in PTFE containers under Ar atmosphere with pO_2 below 2 ppm and pCO_2 below 0.1 ppm.

Depleted UO_2 pellets were cut into slices of 3 mm thickness or crushed, sieved and washed in MilliQ water to recover the fraction of 50-100 µm without fines. An average grain size of 88 ± 32.7 µm was estimated by SEM observations (JEOL 6310). However, a reliable BET measurement was not possible because the specific surface area of the powder was close to the detection limit of the apparatus (Micrometrics-Tristar II 3020 with N_2 gas). Therefore, a mathematical relationship between the BET specific surface area of UO_2 and the UO_2 powder size was established based on a literature survey[3]. Thereupon, a specific surface area of 3.2×10^{-2} $m^2.g^{-1}$ was estimated for the depleted UO_2 powder (50-100 µm). Based on the dimensions of the sliced pellet (Ø= 8 mm and h= 3 mm), the geometric surface area of one single depleted UO_2 pellet was calculated to correspond to 1.76×10^{-4} m^2; no surface roughness correction was considered. The total surface area of the samples is given in Table 1.

Two TMA-OH solutions (TMA-OH pentahydrate ⩾ 97%- T7505 Sigma-Aldrich) were prepared with a hydroxyl concentration $[OH^-]$ representative for the two most important pH domains of the water percolating through the cement/concrete buffer[4] i.e. pH 13.5 and 12.5. An ultrapure MilliQ water, previously degassed by bubbling Argon gas to remove O_2 and CO_2 from the solution, was used to make the TMA-OH solutions. The pH of the (leached) solution were determined with a liquid-filled combination electrode for high pH media (Inlab type -Mettler Toledo), freshly calibrated against dilute standard pH buffers (pH 7, 10 and 13). Redox potentials of all (leached) solutions were measured with a Pt combined electrode with Ag/AgCl reference system (Metrohm). A short equilibration time, less than 5 min, was applied for both pH and Eh measurements.

Table 1 summarizes the six static experiments carried out with depleted UO_2, at three different ratio's of fuel surface area to leachant volume (SA/V of 7, 100 and 257 m^{-1}). In order to reach these SA/V ratio's, a definite amount of depleted UO_2 powder (granulometry of 50-100 µm) and one depleted UO_2 pellet were mixed in 300 mL of TMA-OH solution (Table 1- Exp. 1, 2, 3 at pH 12.5 and Exp. 4, 5, 6 at pH 13.5).

Table 1. Overview of the six static tests with depleted UO_2 in TMA-OH solutions

Experiment	*Target pH*	*UO_2 depleted Mass (g)*	*SA powder*	*SA pellet*	*Total Surface Area*	*Volume*	*SA/V*
			($\times 10^{-2} m^2$)	*($\times 10^{-4} m^2$)*	*($\times 10^{-2} m^2$)*	*(mL)*	*(m^{-1})*
1	12.5	0.06 g powder + 1 pellet	0.2	1.8	0.2	300	7
2	12.5	1 g powder + 1 pellet	3.2	1.8	3.2	300	100
3	12.5	2.4 g powder + 1 pellet	7.7	1.8	7.7	300	257
4	13.5	0.06 g powder + 1 pellet	0.2	1.8	0.2	300	7
5	13.5	1 g powder + 1 pellet	3.2	1.8	3.2	300	100
6	13.5	2.4 g powder + 1 pellet	7.7	1.8	7.7	300	257