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Abstract

In the present work, X-Ray Photoelectron Spectroscopy (XPS) was used to study the effect of water vapor on the UO_2 surface as a function of temperature. The experiments were performed *in situ* inside a high pressure chamber attached to the XPS instrument. UO_2 samples were put in contact with either hydrogen or argon streams, saturated with water at room temperature, and the sample surface evolution was analyzed by XPS. In the case of the water vapor/argon experiments, one experiment at 350ºC was performed and, in the case of the water vapor/hydrogen experiments, the temperatures used inside the reactor were 60, 120, 200 and 350ºC. On one hand, in presence of argon, the results obtained showed that the water vapor in the argon stream oxidized 93% of the U(IV) in the sample surface. On the other hand, the degree of UO_2 surface oxidation showed a different dependence on the temperature in the experiments performed in the presence of hydrogen: the maximum surface oxidation occurred at 120ºC, where 65.4% of U(IV) in the sample surface was oxidized, while at higher temperatures, the surface oxidation decreased. This observation is attributed to the increase of

hydrogen reducing effect when temperature increases which prevents part of the oxidation of the UO_2 surface by the water vapor.

Keywords

UO_2, oxidation, water vapor, hydrogen, temperature

1. Introduction

The corrosion of UO_2 is a fundamental issue related to the behavior of the spent nuclear fuel on both the temporary storage and the final disposal.

During the last decades, many nuclear plants have had to relocate the spent nuclear fuel (SNF) from the pools to dry storage facilities. In the case of Spain, a centralized SNF and High Level Waste temporary storage facility is expected to be in operation in 2018 [1].

Different factors affecting the drying process such as corrosion, presence of residual water, radiolysis, fuel burn-up and temperature, among others, were studied [2]. Several drying methods are applied, being vacuum drying technology the most favorable, often in combination with a purge or cyclic backfill to improve heat transfer between the heat source and any remaining water. Forced helium gas drying is also proposed as an adequate SNF drying procedure [2].

Residual water in the dry SNF might be found as chemically adsorbed as water of hydration associated with oxides. In addition, it might also be present as physically sorbed on exposed surfaces or as free liquid water. The estimations of the residual water in the dry fuel tend to have a large uncertainty because they strongly depend on the knowledge of fuel characteristics.

On the other hand, radiolysis of residual water is known to generate gases, mainly hydrogen and oxygen. The hydrogen production due to alpha radiolysis from water sorbed on uranium

oxides was estimated to range between 0.02 and 0.19% (v/v) of water vapor on the sample [3]. Gamma-radiolysis studies of water absorbed on the surface of uranium oxides gave hydrogen yields ranging from $1.99 \cdot 10^{-2}$ to $5.07 \cdot 10^{-6}$ mmol H_2/g sample [4]. On the other hand, water radiolysis is enhanced on the ZrO_2 surface [5] . This result implies that the radiation-induced yield of hydrogen and oxygen gas will be higher at the fuel cladding surfaces than at the fuel material itself, which should be considered in the long-term "dry" storage strategy.

Considering the presence of residual water in the dry fuel, different studies were performed to study the interaction of the UO_2 surface with water vapor. It was found by Hedhili et al. [6] that the water molecule was completely dissociated on the UO_2 (001) plane, the O atoms were incorporated in the surface and oxygen seemed to diffuse through the UO_2 bulk. On the other hand, studies performed on the behavior of water vapor in contact with stoichiometric uranium dioxide determined that H_2O was adsorbed onto the UO_2 surface by means of X-Ray Photoelectron Spectroscopy (XPS) [7,8] . A recently published review on surface reactions of uranium oxide powder, thin films and single crystals [9] evidences that the UO_2 surface is oxidized of by water vapor.

However, the redox reaction between water and UO_2 might be influenced by other redox species in the gas phase, as hydrogen, and there is no information on the result of this three-species interaction. For this reason, in this work, the effect of both water vapor and hydrogen on the surface oxidation of UO_2 is studied by using XPS. The knowledge of this interaction is not only necessary in the field of the dry storage, but also in the SNF geological disposal, where high amounts of hydrogen could be present due to the anoxic corrosion of the canister [10] together with water vapor due to fuel temperature.

2. Materials and methods

2.1 Reactants

Non-irradiated UO_2 particles from synthetic uranium dioxide provided by ENUSA (Empresa Nacional del Uranio S.A., Spain) with a diameter lower than 75 μm were pressed to make a cylindrical pellet with 1 mm maximum thickness and 13 mm diameter. Later on, the UO_2 was placed into a sample holder, without using any adhesive, and introduced inside the SPECS Ultra High Vacuum (UHV) system.

Two different gases were used to carry out the experiments: H_2 and Ar with 99.999% of purity from Messer (Germany).

2.2 XPS platform

XPS was used to study the UO_2 surface evolution. The spectra were recorded in a SPECS system equipment with an Al anode XR50 source operating at 150 W and a Phoibos MCD-9 detector. The accuracy in binding energies is ± 0.1 eV at a pressure lower than 10^{-8} mbar.

In situ experiments were performed under atmospheric pressure in a high pressure cell (HPC-20) integrated in the SPECS UHV platform without exposing the sample to the air. Two types of experiments were carried out. Some experiments were performed with a gas stream (15 mL/min) that was bubbled through Millipore water at room temperature and then the flow was introduced to the HPC where the temperature was increased smoothly by an infrared lamp and measured with a thermocouple in direct contact with the sample holder. From data reported in the literature [11,12] the amount of water introduced into the reactor was estimated to be ca. $3.5 \cdot 10^{-4}$ $ml_{H2O} \cdot min^{-1}$ at 25ºC. For the rest of the experiments, the gas stream was in direct contact with the sample, without water. In all the experiments performed the gas flow was supplied via a mass flow controller from MKS (USA) and evacuated by the pumping system. Once the experiments were finished, the HPC was pumped out to make the vacuum inside the chamber and transfer the sample directly to the analysis chamber. A

summary of the conditions for the whole set of experiments performed can be found in Table I. At the end of each treatment, the sample was transferred to the analysis chamber to get an XPS spectrum.

For data processing, the CasaXPS program (Casa Software Ltd., UK) was used and the O1s peak was chosen for reference at 529.7 eV. The procedure to analyze the U $4f_{7/2}$ band involved a fitting routine with a Shirley background and curves with 70% Gaussian 30% Lorentzian [13]. Uranium oxidation state was determined by the de-convolution of U $4f_{7/2}$ peak into U(IV), U(V) and U(VI) based on the distances among them and the typical spectrum characteristics of each oxidation state. In addition, U $4f_{7/2}$ peak positions, as well as number of satellites were considered (Table II).

3. Results and Discussion

3.1. Initial Surface Composition

Figure 1 shows that the $U4f_{7/2}$ peak of the sample as prepared was situated at 380.1 eV of Binding Energy (BE) and a double satellite peak appeared after $U4f_{5/2}$ band at 5.9 and 8.5 eV from $U4f_{5/2}$ (ΔBE). Although the $U4f_{7/2}$ peak position could be attributed to U(IV) in Table II [14], the presence of a double satellite proved that the UO_2 surface was partially oxidized. Consequently, the surface composition was determined by the $U4f_{7/2}$ peak de-convolution. The results obtained are shown in Table III, giving a surface composition of $(U^{IV}_{0.5},U^{V}_{0.262},U^{VI}_{0.238})O_{2.37}$. This oxidized surface compound was the result of either the sample pre-treatment and/or the contact with the atmosphere prior to the experiments.

3.2. Reduction treatments

Different approaches were tested to check the best way to get a reduced U(IV) surface, using a hydrogen stream at both different temperatures and times of exposition (Table I). T-H_2(350)

was performed at 350ºC for 10 minutes and T-H_2(500) was performed at 500ºC for 20 minutes. While T-H_2(350) was not enough to give an UO_2 stoichiometry at the surface of the sample, T-H_2(500) treatment reduced the surface to stoichiometric UO_2. In Figure 1 the spectra after this last treatment can be observed and its main characteristics are listed in Table III. This spectrum characteristics are attributed to U(IV) as can be seen by comparing UO_2 XPS and the ones obtained after T-H_2(500) [9,15–17]. Therefore, this last treatment was performed before each subsequent experiment, in order to have UO_2 at the sample surface and follow the UO_2 surface evolution before and after the experiments.

3.3. Effect of water vapor/argon stream on the UO_2 surface

In order to determine the effect of water vapor on the UO_2 surface, the reduced sample was put in contact with an argon stream bubbling through a saturator at room temperature with MILLIPORE water (T-Ar-H_2O). The experimental temperature inside the reactor was set at 350ºC (see Table I).

The results showed that the surface of the solid was oxidized after performing the experiment, with contributions of both U(V) (57.1 %) and U(VI) (35.8 %) (see Table III). This oxidation effect of water vapor was observed in previous studies where it was determined that water vapor enhanced the oxidation either through the oxygen diffusion into the UO_2 lattice or by forming hydrated oxidized products on the surface [18–20]. The formation of a reduced core-oxide shell structure cannot also be ruled out.

3.4. Effect of water vapor/hydrogen stream on the UO_2 surface

Once the sample was reduced to UO_2 again, it was put in contact with hydrogen and water vapor from the saturator, experiment named T-H_2-H_2O(350) (see Table I).

Table III lists the spectrum characteristics and Figure 2 shows the deconvolution of the U $4f_{7/2}$ photoemitted electrons. As observed, the U(IV) is the main contributor with a value of 64.2% and the percentages of U(V) and U(VI) are 20.4 and 15.4 %, respectively. The oxidation of the sample is corroborated by the appearance of a second satellite peak.

As it can be seen, at the end of the experiment the surface was less oxidized than in the experiment in the presence of Ar, pointing to the effect of hydrogen attenuating the oxidation.

A comparison could be made between T-H_2-H_2O(350) and T-Ar-H_2O experiments looking at Figure 3. In both experiments UO_2 surface was oxidized but the uranium oxidation state in T-H_2-H_2O(350) experiment was lower than in the T-Ar-H_2O experiment. Indeed, the oxidized states in T-H_2-H_2O(350) experiment, both U(V) and U(VI), were equal to the U(VI) percentage obtained after the argon experiment. Therefore, the U(V) observed in T-H_2-H_2O(350) experiment was completely oxidized to U(VI) when argon was used instead of hydrogen. From these results it is clear that hydrogen inhibited part of the sample oxidation. However, this was not enough to completely avoid surface oxidation.

3.5. Effect of temperature on the oxidation process

Three more temperatures (60ºC, 120ºC and 200ºC) were evaluated in the experiments with water vapor/hydrogen stream: T-H_2-H_2O(60), T-H_2-H_2O(120) and T-H_2-H_2O(200) (see Table I), in addition to the previous T-H_2-H_2O(350) experiment.

After performing T-H_2-H_2O(60) experiment, the spectrum showed similar characteristics to the typical U(IV) spectrum except for the presence of a second satellite. Therefore, the U $4f_{7/2}$ band was de-convoluted and the results showed that the amount of U(IV) was the highest of all three oxidation states (see Table III). This result was similar to the one obtained in T-H_2-H_2O(350) experiment that also showed U(IV) as the main oxidation state.

The spectrum recorded for the T-H_2-H_2O(120) experiment showed that the solid surface was even more oxidized than the one obtained at 60ºC . The results of U $4f_{7/2}$ de-convolution showed that the amount of U(V) and U(VI) were 30.4 and 35.0 %, respectively. These values were higher than the ones obtained at 60ºC. Therefore, the water vapor oxidizing effect is enhanced at 120 ºC.

The spectrum recorded for the T-H_2-H_2O(200) experiment, according to the experimental data, showed that the solid surface was more reduced than the one obtained after the T-H_2-H_2O(120) experiment. Nevertheless, this result is within the measurement error and, therefore, this statement is not conclusive.

In Figure 4 the evolution of the surface oxidation state is shown as a function of temperature. Two different trends can be observed: (1) an increase of the uranium oxidation state with temperature until 120ºC; and (2) a decrease of the oxidation state at temperatures higher than 120ºC. Furthermore, U(IV) was the predominant oxidation state again at 350ºC, which could be explained assuming that higher temperatures may increase the reduction effect of hydrogen.

4. Conclusions

In this work, the effect of hydrogen and water vapor on UO_2 as a function of the temperature was studied *in situ* by XPS to determine the surface composition of the sample according to the reported spectrum characteristics of U(IV), U(V) and U(VI).

Experiments performed under an argon stream at 350ºC showed that the amount of water introduced to the HPC was enough to oxidize the sample surface.

On the other hand, the results obtained in the presence of hydrogen showed that H_2 limits the oxidation of UO_2 in contact with water vapor at 350ºC compared to argon.

Temperature had an important impact on the overall oxidation process in the water vapor/hydrogen experiments. At 60ºC, the surface was oxidized and the oxidized phases represented approximately 41% of the uranium on the solid surface. In the temperature range 60-120ºC, the oxidation increases progressively and U(IV) was oxidized to U(V) and U(VI). At 120 and 200ºC the sample reached similar oxidation states. At higher temperatures the oxidation decreased; reaching the minimum oxidized state at the maximum experimental temperature (350ºC).

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Tables

Table I Experimental conditions summary that relates the ID Name used in this work with the main conditions.

ID Name	Gas	Water saturation	Temperature (ºC)	Time (minutes)
T-H_2(350)	H_2	No	350	10
T-H_2(500)	H_2	No	500	20
T-Ar-H_2O	Ar	Yes	350	10
T-H_2-H_2O(60)	H_2	Yes	60	10
T-H_2-H_2O(120)	H_2	Yes	120	10
T-H_2-H_2O(200)	H_2	Yes	200	10
T-H_2-H_2O(350)	H_2	Yes	350	10

Table II Published main spectrum characteristics of three identified uranium oxidized states

Oxidized State	BE U4$f_{7/2}$ (eV)	ΔBE satellite (eV)
IV[a]	379.5 – 380.0	6.7
V[b]	380.0 – 380.6	8.0 – 9.0
VI[c]	380.8 – 381.4	4; 10

a. [9,15–17]

b. [21,22]

c. [21,22]

Table III List of the main characteristics of the U 4f band for each T-H_2-H_2O (i) and T-Ar-H_2O treatment realized focusing at the Binding Energy and the FWHM of the U4$f_{7/2}$ peak, the relative position of the two observed satellites refereed to the U 4$f_{5/2}$ peak position and the percentage of U(IV), U(V) and U(VI).

Treatment	**BE U4$f_{7/2}$ (eV)**	**FWHM U4$f_{7/2}$ (eV)**	**ΔBE satellite 1 (eV)**	**ΔBE satellite 2 (eV)**	**U(IV) (%)**	**U(V) (%)**	**U(VI) (%)**
Initial	380.0	2.6	6.2	8.7	50.0	26.2	23.8
T-H_2(500)	379.7	2.0	6.7		100	0	0
T-H_2-H_2O(60)	379.9	2.5	6.5	9.0	59.1	19.7	21.2
T-H_2-H_2O(120)	380.3	2.6	5.8	8.5	34.6	30.4	35.0
T-H_2-H_2O(200)	380.1	2.6	5.9	8.5	37.7	25.4	36.9
T-H_2-H_2O(350)	379.8	2.4	6.4	9.1	64.2	20.4	15.4
T-Ar-H_2O	380.5	2.6	5.5	8.2	7.1	57.1	35.8

Figures

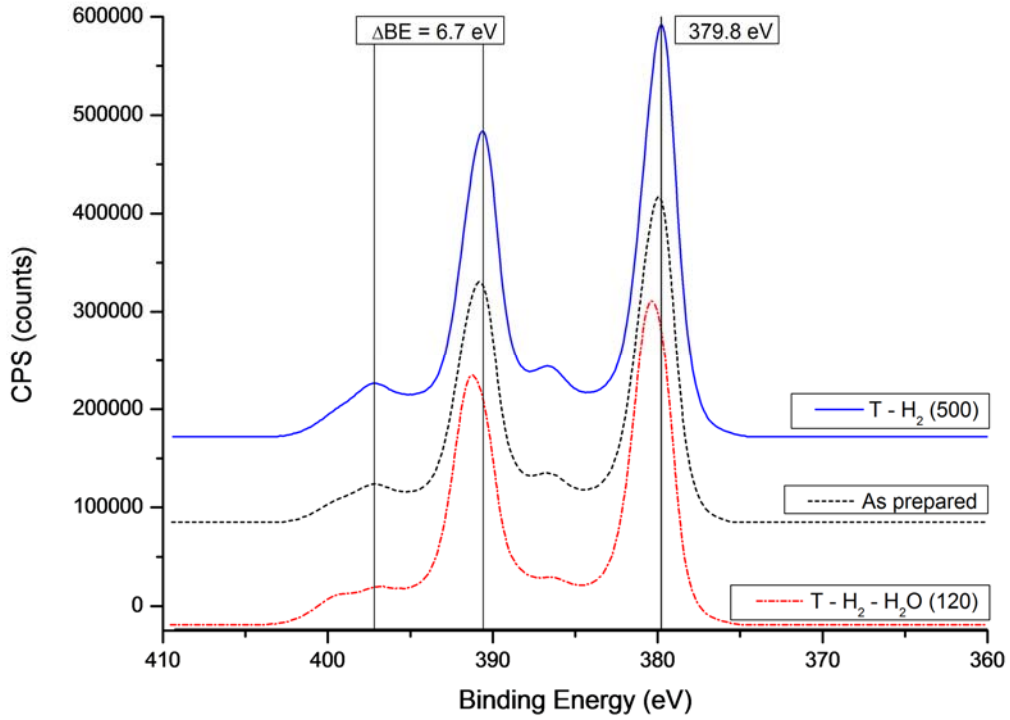

Figure 1 Collection of spectra obtained for T-H_2(500), sample as prepared and T-H_2-H_2O(120) experiments. In this figure, the lowest U $4f_{7/2}$ position can be observed together with the ΔBE of the satellite and the sharpness of each band.

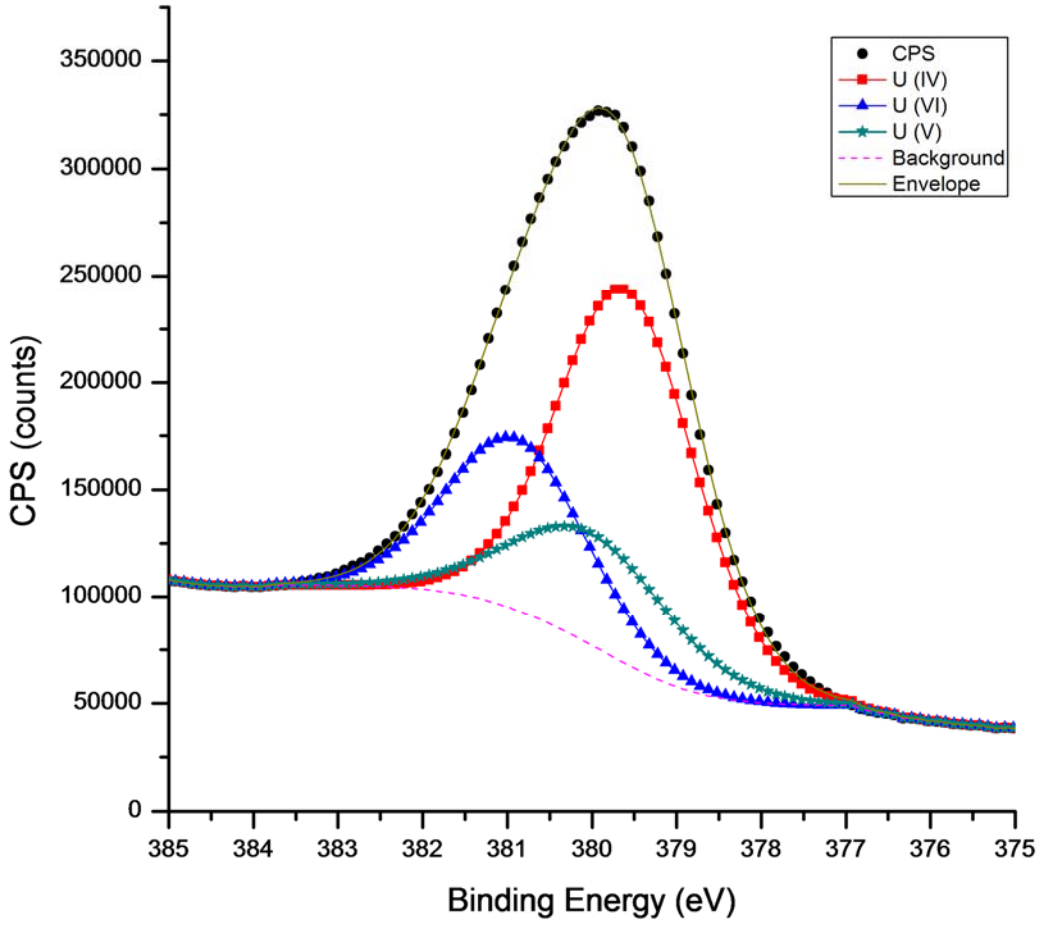

Figure 2 Deconvolution of the U $4f_{7/2}$ band from the spectrum obtained after performing T-H_2-H_2O(350)

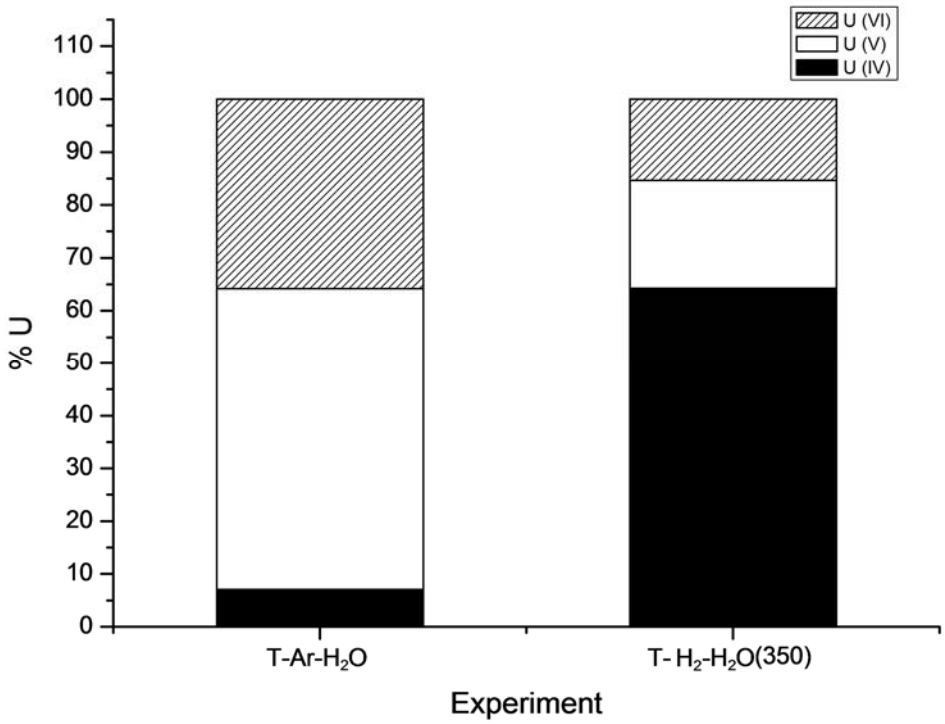

Figure 3 Surface uranium species percentages in T-Ar-H_2O and T-H_2-H_2O(350) experiments.

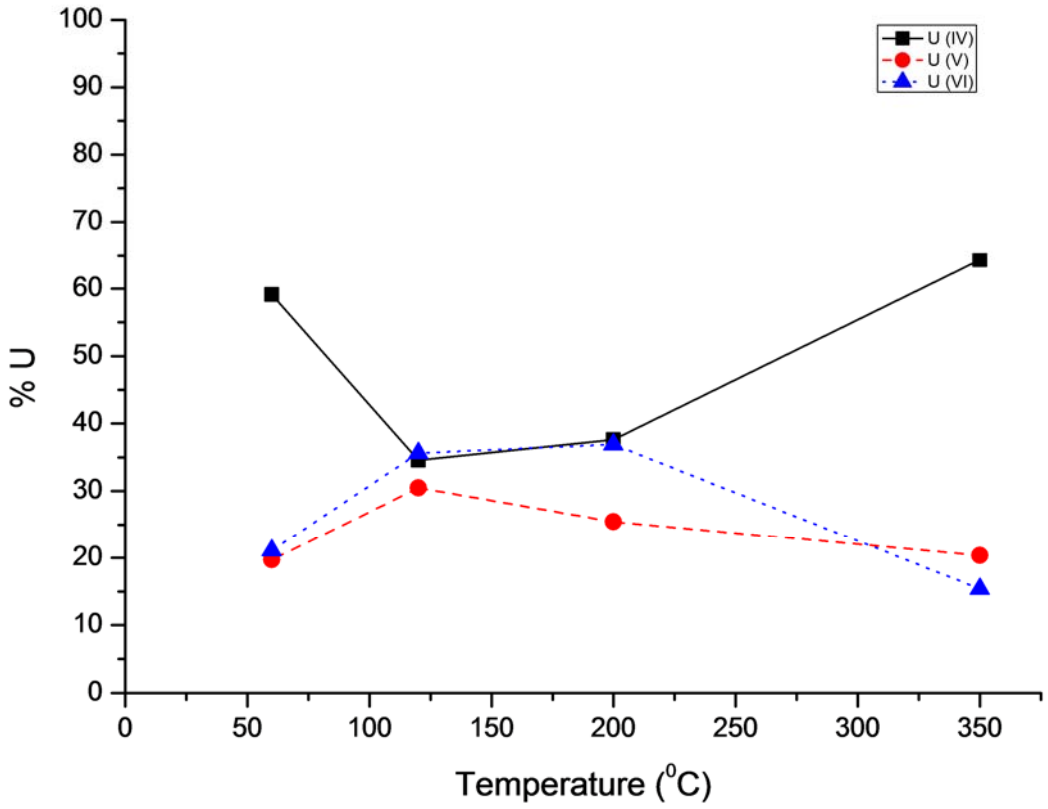

Figure 4 Evolution of surface uranium oxidation states percentages obtained after all the T-H_2-H_2O(i) treatments as a function of temperature. ■ U(IV), ● U(V) and ▲ U(VI).