

Thorium-234 Electrodeposition Using Ionic and Aqueous Uranyl Solutions

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Electrodeposition process of natural uranyl many has several deposit possibilities, since the process variables and uranium natural isotopes and secular equilibrium may induce the formation of several uranium compounds. One of these deposit possibilities is the strong beta-emitter thorium-234. The present work showed that pulsed polarization and 2-propanol natural uranyl solution (50 mM [U]) induced the formation of intense beta-emission in the samples, with activity beta-alpha ratio reaching levels of 300, which is much higher than the secular equilibrium ratio around 1. The natural decay of the deposited samples showed that the beta-emitter as most probable element to be thorium-234 within a pertinent regression exponential decay curve adjustment ($R^2=0.998$) giving a typical experimentation value for half-life as 22.88 days. This value was found lower than the typical 24.10 days for thorium-234 (specific activity of 85.69×10^{13} Bq/g), probably due to activity contribution of uranium-235 daughter, thorium-231 (specific activity of 19.67×10^{15} Bq/g), which beta-decays having half-life of 25.6 h. Further experimentation with pulsed polarization of the cathode (0 to -15V; 12.5 Hz – duty time = 87.5% and process time varying until 3600s) also showed that thorium-234 depends on solution acidity, solution usage and deposition time. XRD spectra suggests that the deposit would be probably a combined structure of uranium-thorium hydride, which decomposes with time.

Introduction

Thorium is a natural radioactive element with atomic number 90, being the second of 5f actinide series. Its chemistry is similar to that of the lanthanides and Group IVB, such as Ti, Zr and Hf, displaying a dominant +IV oxidation state. The thorium electrochemistry predicts standard potential for $\text{Th}^{4+} | \text{Th}^{3+}$ couple varying between -3 to -3.7 V. Thorium is more acidic than the lanthanides, but less acidic than U, which is expected by its larger ionic radius (Th, 1.08 Å). There are 30 isotopes of thorium with masses ranging from 209 to 238. This element is one of the most widely used tracers of particle cycling in the world's oceans. Its extensive usefulness is due to both the well characterized production rates of thorium isotopes, as ^{234}Th and ^{230}Th from their soluble uranium parents (^{238}U and ^{234}U), and their high particle reactivity in seawater (1).

In this work, we are especially interested in ^{234}Th , which is a radioactive daughter of natural ^{238}U decay emitting an alpha particle(2), as shown in Figure 1.

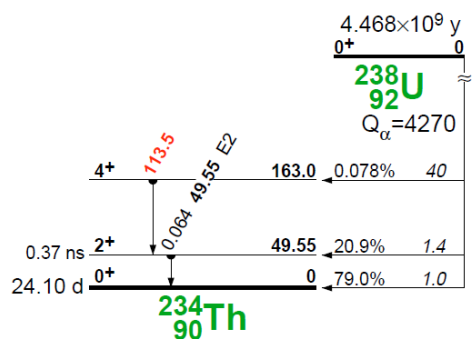


Figure 1. Natural decay of ^{238}U followed by ^{234}Th , according to Firestone(2)

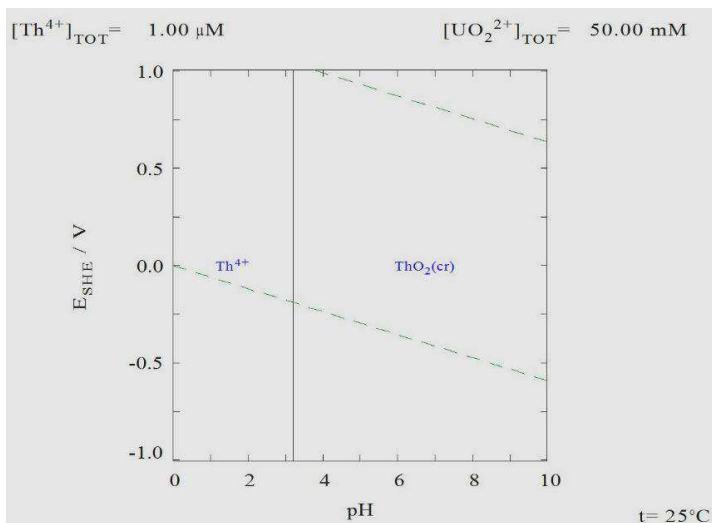
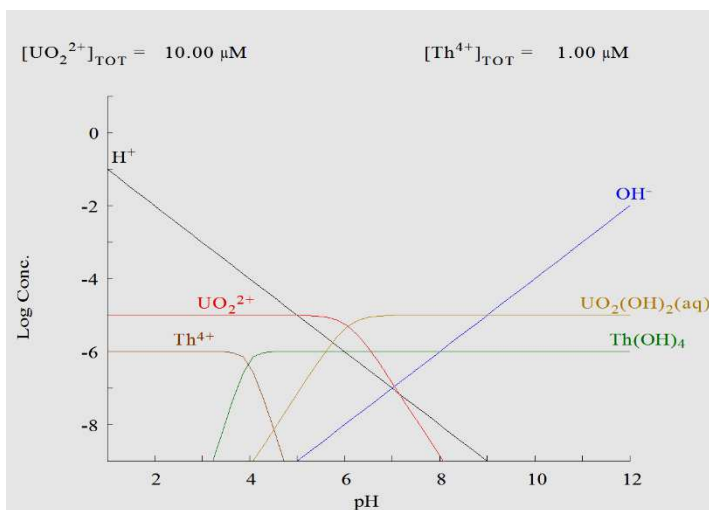


Figure 2. (Above) Equilibrium concentration vs. pH of the system uranyl; (Below) Pourbaix Diagram of uranyl solution containing ^{234}Th traces.

The isotope ^{234}Th ($4n+2$) decays with a half-life of 24.1 days to ^{234}Pa , with a half-life of 6.70 h with a beta emission energy of 0.20 MeV, followed by a quick natural decay towards $^{234\text{m}}\text{Pa}$, with a half-life of 1.17 min, emitting an intense beta radiation in the order of 2.29 MeV transmuting towards ^{234}U . This short-lived thorium isotope has been used as a tracer for a variety of transport processes in aquatic systems(1,3–8).

Chemically, UO_2^{2+} has preferential deposition with OH^- if compared with Th^{4+} as shown in Figure 2, displaying the equilibrium concentration diagram versus pH for uranyl aqueous solution, with low concentration of thorium and uranyl. It reveals that thorium hydroxide precipitation is slightly preferential to uranyl hydroxide in pHs higher than 3. In uranyl acidic solution below pH=1, the prevalence of ionic state for Th^{4+} and UO_2^{2+} is higher, which may lead to formation of hydrides.

Experimental

The uranyl nitrate solution $\text{UO}_2(\text{NO}_3)_2$ was prepared by leaching nuclear pure U_3O_8 [11] using nitric acid. The concentrated nitrate solution was diluted in 2-propanol to a concentration of 0.05 mol.L^{-1} of natural uranium. The uranyl-thorium electrodeposition experiment used this acidic aqueous and ionic solution as electrolyte, with pH~1, adjusted by p.a. nitric acid.

The electrochemical cell for uranium electrodeposition was a vertical quartz tube, supported by a polypropylene structure, containing the electrolyte solution inside the cell. The cathode opening, where the electrodeposition took place, sealed the cell bottom with the help of a rubber O-ring covered with Teflon. This experimental device exposes a 2-cm^2 area of cathodic electrode to the electrolyte. The experiments used AA6061 aluminum alloy coupons, which were heat treated at 450°C during 1 hour, and ground with emery paper #600, rinsed at NaOH for 2 minutes and duly degreased with acetone. All aluminum coupons were electroplated to receive a nickel layer described elsewhere(9,10). After this operation, the coupons were degreased with acetone and assembled in the cathode position of the cell. The ^{234}Th electrodeposition experiment used 30 ml of uranyl solution in the electrochemical cell. The counter electrode was a platinum wire with large anodic area. The used reference electrode was Ag/AgCl. The pulsed cathodic polarization followed these settings:

1st Experimental Phase: Solutions: 50mM [U] in $\text{UO}_2(\text{NO}_3)_2$ in 2-propanol (ionic solution: 140 experiments) and 50mM [U] $\text{UO}_2(\text{NO}_3)_2$ in bidistilled water (aqueous solution: 98 experiments). Use of direct cathodic polarization $-15 \text{ V}_{\text{Ag/AgCl}}$ using direct cathodic polarization during 1200 s. Use of pulsed cathodic polarization of $-15 \text{ V}_{\text{Ag/AgCl}}$ during 70 ms (“on”-stage) followed by 10 ms (“off”-stage) with a frequency of 12.5 Hz Duty time: 87.5%, during varying time periods until 3600 s.

2nd Experimental Phase: specific tests with 50mM [U] in $\text{UO}_2(\text{NO}_3)_2$ in 2-propanol, in the range of 0.7 to , acidified with HNO_3 at 30°C . It was used pulsed polarization in galvanostatic way, from 600 s to 3600 s, with frequency of 12.5 Hz, time-on during 70 ms at cathodic current of -50 mA and time-off during 10 ms at 0 mA. An specimen of pulsed potential in current vs. time graph is seen at Figure 3.

The radiological data of alpha and beta emission counting was made by Ludlum α , β -Counter 3030p. Bruker D8 Advance was used to get the XRD diffractograms.

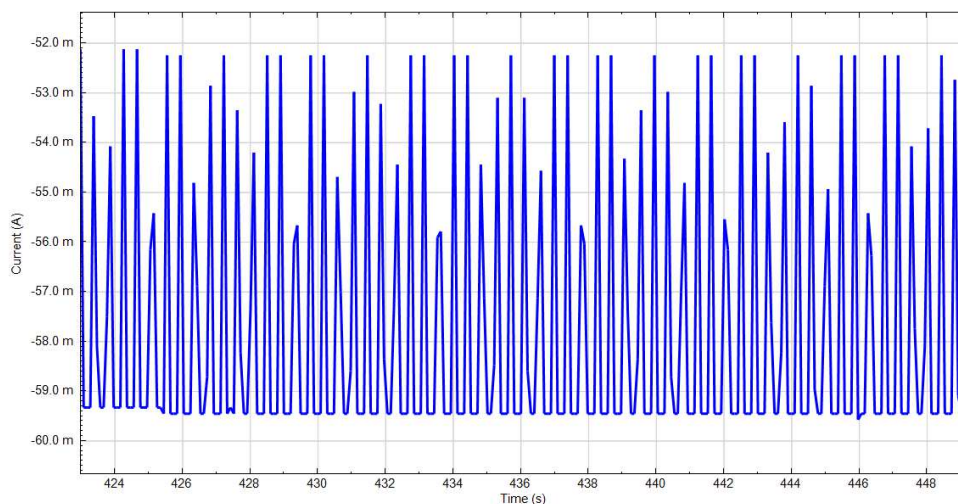


Figure 3. Specimen of pulsed polarization in a electrodeposition experiment using a solution of 50mM $\text{UO}_2(\text{NO}_3)_2$ in 2-propanol, with potential cycling of $-15 \text{ V}_{\text{Ag}/\text{AgCl}}$ during 70 ms (“on”-stage) followed by 10 ms (“off”-stage) with a frequency of 12.5 Hz, during 1200 s.

Results and Discussion

Figure 4 represents the results of first experimental phase as a whole. It shows four graphs of β/α ratio versus pH dispersion containing data from aqueous and 2-propanol solutions and having been submitted to direct and pulsed polarization. Accounting that the β/α ratio is in log-scale, this phenomenon showed deposition preference for a β -emitter, probably associated with uranium-deposition following certain experimental conditions.

As a first observation of the graph, the solution acidity is determinant to induce the β -emitter deposition. It appears that higher acidity is relevant to obtain higher β -emitter deposition. Roughly analyzing the graphs, we can see that direct polarization and aqueous solution has been relevant to some extent to deposit β -emitter, but β/α ratio stayed under 10. This is understood for the present work as an indication of a feeble preference for β -emitter to deposit under these conditions. However, when 2-propanol uranyl electrolyte was associated to pulsing potential, very higher level of β/α ratio was obtained, when the ratio levels reached higher ratio values, beyond 100. We may consider this as a proof for the preferential electrodeposition of β -emitter compared to α -emitter (uranium compound) in these special conditions.

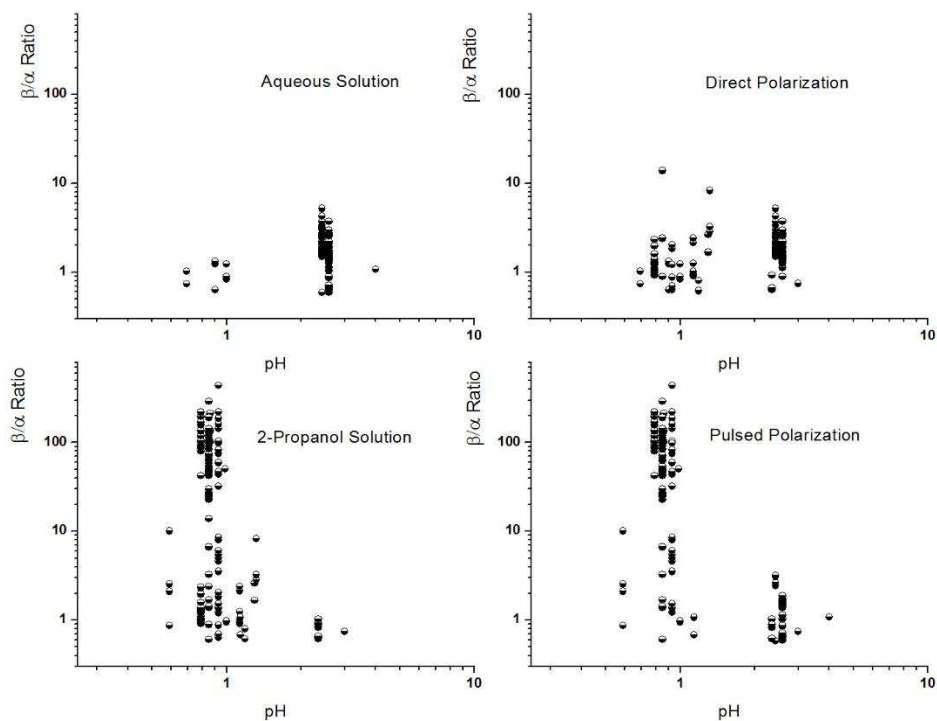


Figure 4. Results of β/α ratio, varying with pH, from electrodeposition experiments taking into account the solution type (aqueous and ionic) and the electrodeposition method (direct and pulsed). Experiments: 238 in total; 98 aqueous and 140 ionic; 110 using direct polarization and 128 using pulsed polarization.

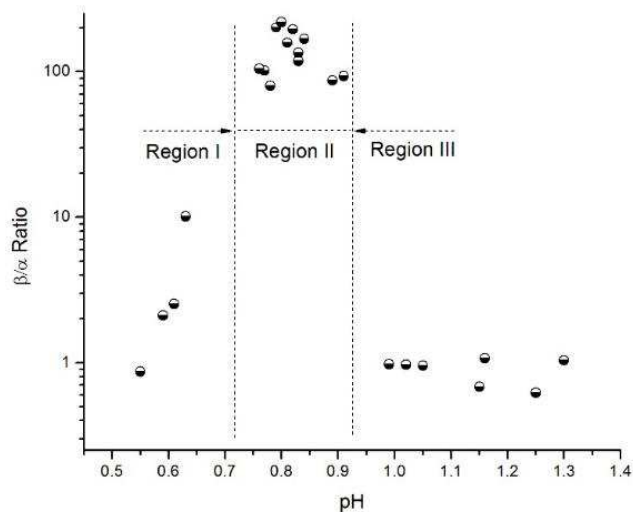


Figure 5. The β/α ratio vs acidity of uranyl 2-propanol solution

Analyzing the samples of the second experimental sequence, where the samples were submitted only to pulsed electrodeposition using 2-propanol solution, we can see immediately the experimental dependence from pH level, where higher β/α ratio was reached, where pH approaches 0.8, in region II, as could be seen in Figure 5.

In order to certify about the nature of β -emitter, we made β -counting during 106 days after the electrodeposition with several samples were controlled. Figure 6 shows a typical decay curve (Sample 430D), which had a fitted equation ($R^2 = 0.998$) done by equation 1:

$$A \left(\frac{\text{Bq}}{\text{cm}^2} \right) = 0.992 + 88.663 e^{-3.505 \cdot 10^{-7} \cdot t} \quad [1]$$

Where A is the β -activity in Bq/cm^2 and t , the time in seconds. Considering the decay constant, indicated in the curve equation as $\lambda = 3.505 \cdot 10^{-7}$, the mean-life, calculated by $t_{1/2} = \ln(2)/\lambda$, indicates that the mean-life was $t_{1/2} = 22.88$ days for the experimental deposition. The found mean-life is 5.06% less than the theoretically $^{234}\text{Th} > ^{234}\text{Pa} > ^{234\text{m}}\text{Pa} > ^{234}\text{U}$ decay mean-life of 24.10 days.

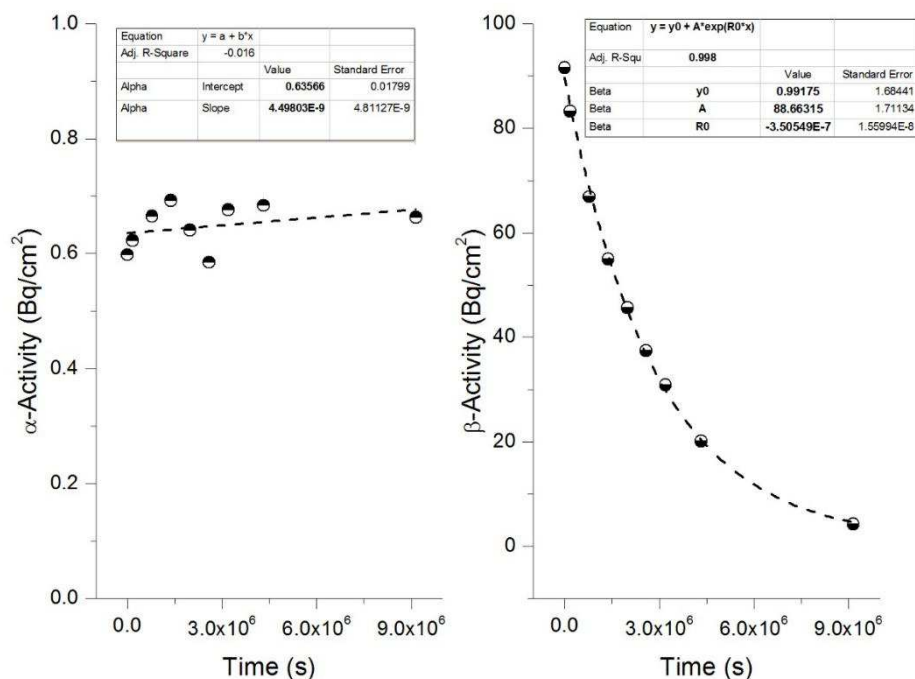


Figure 6. Results of α and β -activity (Bq/cm^2) of a typical sample (Sample 430C), during 106 days after pulsed electrodeposition of uranium compound associated β -emitter.

Some variance is expected from using a natural uranium solution, where other uranium isotopes are present, for instance ^{235}U (0.72 wt%) which also produces ^{231}Th . This thorium isotope decays to ^{231}Pa , by β -emission, with mean-life of 25.6 h. Chemically speaking, both thorium isotopes behave in the same way, so within an acceptable error, we can say that we are dealing mostly with ^{234}Th decay in this

experimental work, as the β -emitter, with some mean life displacement by ^{231}Th , towards lower values. The variation of α -emission, as indicated in the Figure 6, has no virtual alteration along the period of α -counting, so there is no major phenomena concerning to uranium isotopes variation, since uranium isotopes themselves are not β -emitter, being practically only α -emitters.

Figure 7 presents a typical SEM micrographic uranium-thorium deposit obtained from 2-propanol uranyl solution, under pulsed polarization during 3600 s. As seen in this picture, the uranium deposit is incrustated in nickel substrate structure in convenient places. The deposition appeared not to be linked with high faulty sites of the substrate, as the U-deposits do not appear convincingly at the grain boundaries. It is likely that the U-deposits may be linked to nickel crystalline structure serving as anchorage to nucleate and grow the uranium deposit associated with thorium.

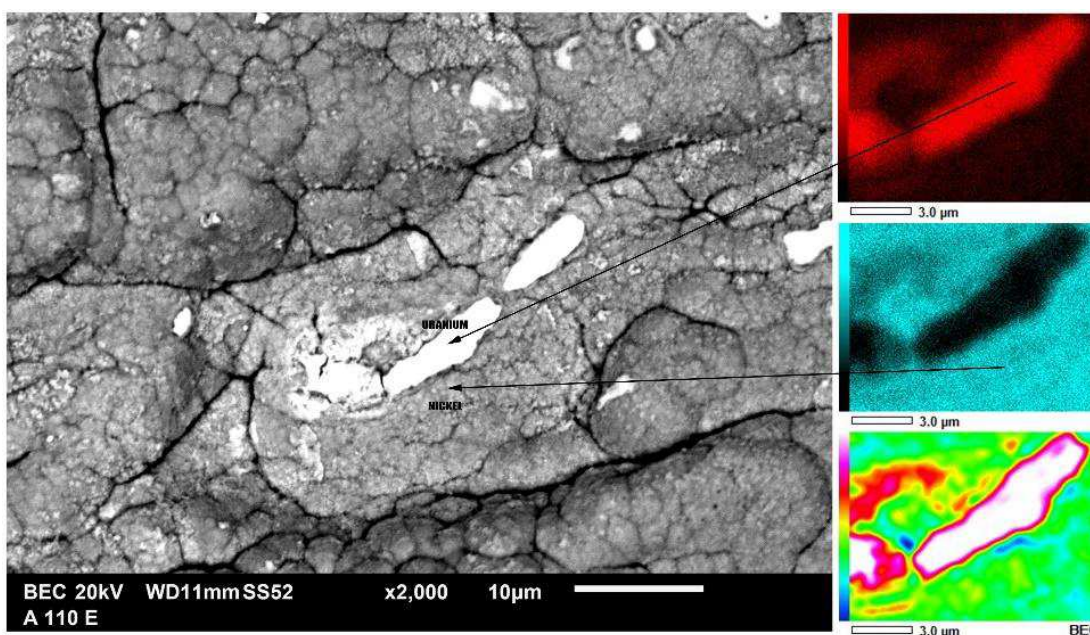


Figure 7. Typical micrography after pulsed polarization of 2-propanol uranyl solution during 3600s from experimental phase 2.

SEM with EDAX did not show any indication of thorium presence. The expected level of thorium is very low, even with an incremental β -emitter deposition, which proved to be mostly ^{234}Th as proved above. Based on the level of ^{234}Th specific activity of 856.9×10^{12} Bq/g, the amount of obtained activities at the level up to 1000 Bq/sample would represent contents in the order of 10^{-10} grams/sample. This content level is hardly detectable even in modern ICP analyzers, mainly when this amount is dispersed over the surface as tiny areas in the microstructure, as shown in Figure 7. Nevertheless, this ^{234}Th deposit was properly detectable in β -counters due to the prominent activity of ^{234}Th .

As shown in Figure 8, during the second phase of experiments, the usage of the same solution was sequentially made. It proves that there is an influential effect of solution usage sequence and the corresponding response for increasing and decreasing the β/α ratio. The experiments carried out during 3600 s showed better image of the

result, as the ratio increased up to the fifth and then decreased onwards. The decreasing is a natural phenomenon, since the depleting of β -emitter in the original solution is expected to reach exhaustion after some period of usage. This is factual, since a linear decreasing happened consistently from the fifth to the eighth usage. Furthermore, the β/α ratio increases unexpectedly during the first five solution usages. There is no trivial explanation to this, probably due to chemical behavior of uranium and thorium in isopropanol uranyl solution under powerful pulse polarization during a long period. A probable explanation for this solution “preparation”, increasing the ^{234}Th deposition amount, would be the reduction of UO_2^{2+} (Uranium-VI) to U^{3+} , which may happen in favorable conditions of high acidity and under intense pulsing potential from -15 V to zero and backwards.

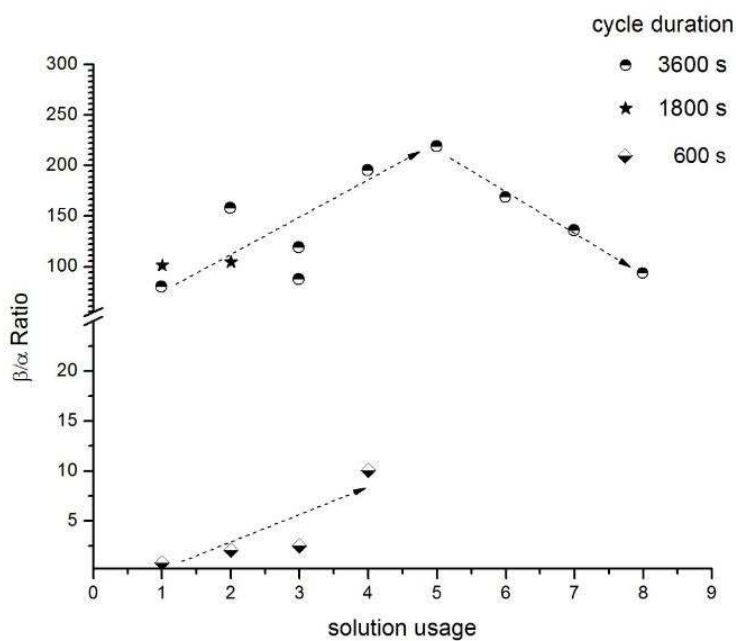


Figure 8. Solution usage during the electrodeposition and the response of β/α ratio.

The ions U^{3+} and Th^{4+} under a great amount of H^+ would form uranium and thorium hydrides, which may deposit within an entangled U,Th-microstructure over the substrate. Probably, ^{234}Th atoms enter into the microstructure as a substitutional atom. There is a probable indication that this may be happening by means of XRD diffractograms of the some sample. One diffractogram was made just after the deposition and the other after 150 days, as shown in the Figure 9.

The diffractogram displacement after 150 days is probably due to recrystallization of amorphous uranium hydroxides and oxides that mostly characterizes the peaks of whole spectrum. However, during this stay period, the level of β -emission decreased enormously following the ^{234}Th decay pattern (mean-life: 24.1) in the analyzed sample from 7687 to 230 cpm.

It is noticeable that the XRD background drop is not regular through the whole spectrum. In the region of $2\Theta > 25^\circ$ the BG drop is more intense than in lower angles. This is the region where the 100%-intensity peaks of uranium hydrides surge. As shown in the lower position of this figure, the powder simulation of UH_3 (from several PDF cards as in indicated in Figure 9) distinguishes the regions where hydrides may appear. This might be an indication of [U,Th]-hydride formation embedded in the amorphous background. This hydride phase tended to disappear during the open-air stay period, since uranium hydride oxidizes eagerly, as ^{234}Th transmuted to ^{234}U , replacing ^{234}Th atoms in the structure. Nevertheless, this topic shall be investigated more deeply.

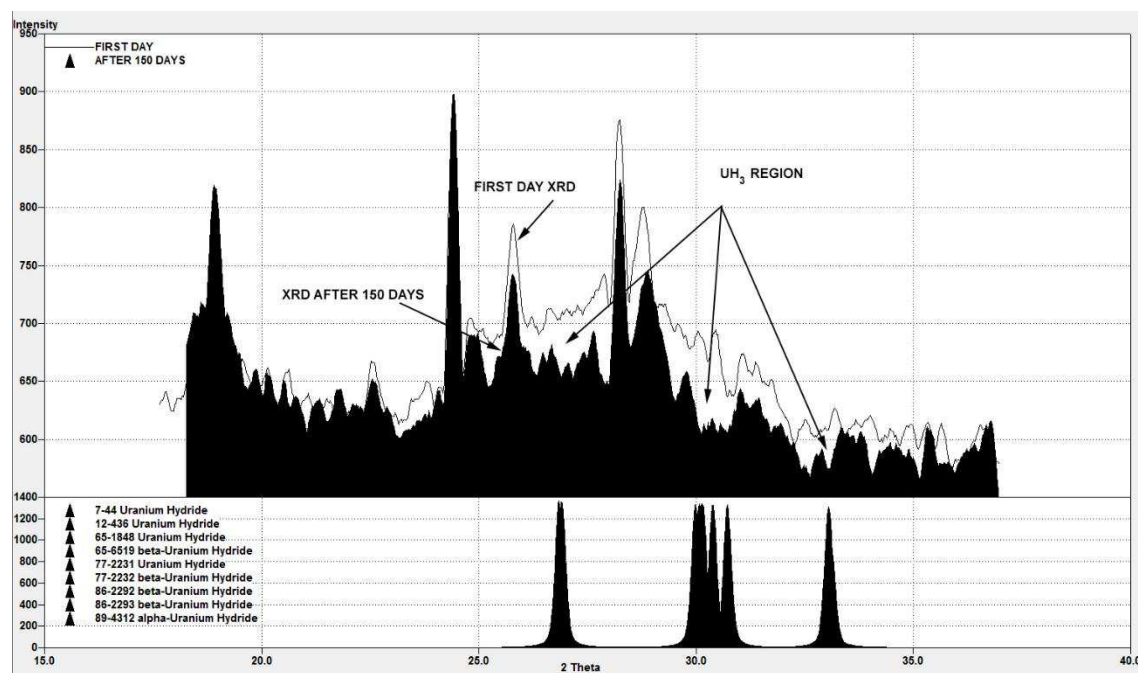


Figure 9. XDR diffractograms of the same sample (A41110E), initially with β -counting of 7587cpm (line) and the darker diffractogram made after 150 days, when β -decayed to 230 cpm. Below, there are 100% peaks of several uranium hydrides.

Conclusions

These work experimentation showed that it is possible to deposit mostly ^{234}Th , which is daughter from ^{238}U , from a solution natural $\text{UO}_2(\text{NO}_3)_2$ 50mM [U], acid (pH around 0.8) by means of pulsed polarization electrodeposition, using 12.5 Hz and duty time as 87.5%. The solution sequential usage showed initially an increasing amount of β -emitter deposition, inducing to the concept that a “solution preparation” was taking place during this sequencing. The proposed explanation was the probable reduction of uranyl into the $\text{U}^{4+} \rightarrow \text{U}^{3+}$, which, in acid solutions and high cathodic pulsating potential from 0 to -15V, would be formed. It would promptly combine with H^+ (concentrated in cathodic area) inside a high acidic media. This condition leads to the deposition of uranium hydrides, which could carry the cation Th^{4+} into its structure. The content level of ^{234}Th is less than 10^{-12}g , which is difficult to be detected in conventional chemical methods, but promptly detected by β -counters, since it has high specific β -activity.

In XRD diffractogram analyses, the uranium hydride regions were depleted in the background, after 150 days of time gap. As the uranium hydrides are unstable in the presence of oxygen, the time stay was sufficient to transform hydrides into oxides and hydroxides. During this period, ^{234}Th transmuted into ^{234}U and reduced exponentially the emission of beta rays. The microstructure showed dispersed areas of uranium deposit, not covering the substrate, which exhibited a tendency of not depositing on grain boundaries, but over the nickel crystallized substrate. This is an indication of coherent nucleation and growing of hydrides over the nickel microstructure.

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