



*Dedicated to the memory of
Professor Ioan Silaghi-Dumitrescu (1950 – 2009)*

THE EFFECT OF α -RADIOLYSIS ON THE U(IV)/U(VI) RATIO IN URANIUM-BEARING ORES

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The paper studies the concentration changing of the U(IV) and U(VI) species from uranium-bearing ores, resulted from the α -radiolysis induced by an ^{241}Am irradiation source. Thus, the α particles emitted by the ^{241}Am source, much more intense than those resulting from the radioactive decay of uranium, would split radiolytically the groundwater molecules present in the ores. The primary radiolysis products should initiate some redox processes upon the uranium species, changing their concentrations. The oxidation degree of the U(IV) \rightarrow U(VI) transformation, between 8.3 and 15.5 %, was found.

INTRODUCTION

A lot of investigations have been devoted to the concentration variation of the U(IV) and U(VI) species occurring in uranium ores, as well as to the alteration of the UO_2 present in the nuclear spent fuel, as a result of the radiolysis reactions initiated by the nuclear rays released by either uranium nuclei or fission products, on their interaction with groundwater or aqueous solutions. In this respect, in a subsequent step, the $\text{H}\cdot$ and $\text{HO}\cdot$ primary radiolysis products induce redox reactions upon the uranium species, as well as upon other microelements presented in the irradiated system.¹⁻³ A special case is represented by the study of the mineralogical and chemical composition of the uranium-bearing ore from the Oklo region of Gabon, supporting the idea that the complex radiolysis processes may influence the U(IV)/U(VI) ratio of the ore.⁴

Sattonnay *et al.* investigated UO_2 alteration (oxidation) at the interface with deionized and aerated water, under the influence of the

accelerated α radiations produced in a cyclotron ($\Phi = 3.3 \cdot 10^{10} - 3.3 \cdot 10^{11}$ α -particles/cm²·s).⁵ The U(VI) and H_2O_2 concentrations increased when decreasing the pH values of the irradiated system. The formation of hydrated uranium peroxide, such as metastudtite: $\text{UO}_4 \cdot 2\text{H}_2\text{O}$, on the leached UO_2 surface, was identified after an hour α irradiation, through X-ray diffraction.

The influence of the β radiations ($2.6 \cdot 10^8$ Bq) released by a $^{90}\text{Sr}/^{90}\text{Y}$ source on the alteration of the initially non-irradiated UO_2 in the nuclear reactor, at various pH values, was studied by Clarens *et al.* who noticed that leaching of the solid UO_2 occurs on behalf of the H_2O_2 , previously appeared as a water radiolysis product.⁶ Hanson *et al.* followed the formation of studtite and of metastudtite as corrosion products occurring on the surface of the UO_2 from the nuclear spent fuel after two years contact with the thermalization water, on behalf of the primary $\text{H}\cdot$ and $\text{HO}\cdot$ radiolysis products.⁷

The X-ray diffraction, X-ray fluorescence and scanning electron microscopy (SEM) studies

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evidenced the fact that the two mineralogical species - *i.e.* studtite and metastudtite - are actually acting as intermediary products of the process of uraninite transformation into schoepite. Advanced electrochemical investigations, as well as X-ray photoelectron spectroscopy (XPS) investigations devoted to the alteration of UO_2 in CANDU pellets at $\text{pH} = 8.5-9$ aqueous solutions, by the H_2O_2 resulted from α radiolysis, confirmed the occurrence of several compounds of uranium (VI) as corrosion products.^{8,9}

Min *et al.* asserted that the radiolysis products of phreatic water oxidize the Fe^{2+} ions, thus inducing alteration (hematization) of the hydrothermal deposits of uranium.¹⁰

Rey *et al.* have analyzed in detail the stability of hydrated uranium peroxides: studtite and metastudtite, during irradiation with accelerated electrons at 200 keV, by transmission electron microscopy (TEM).¹¹ On a less intense irradiation ($\Phi = 2.31 \cdot 10^{15}$ electrons / $\text{cm}^2 \cdot \text{s}$) studtite became amorphous, but metastudtite remains crystalline up to more intense irradiations ($\Phi = 7.62 \cdot 10^{17}$ electrons/ $\text{cm}^2 \cdot \text{s}$), which may be explained by the different number of hydration water molecules contained in the two minerals. Such mineralogical structures have been investigated both before and after irradiation with accelerated electrons, both by X-ray powder diffraction and thermogravimetric analysis.

The present paper resumes some previous investigations of ours devoted to the identification of the U(IV) and U(VI) uranium species from uranium-bearing ores or from mining groundwater,

developing various techniques for the separation and recovery of the respective species being here applied.¹²⁻¹⁵

RESULTS AND DISCUSSION

The experimental data are listed in Tables 1-2. Irradiation with an ^{241}Am α -irradiation source resulted in the concentration variation of U(IV) and U(VI) species of the samples. This fact may be explained by some redox processes on the uranium minerals initiated by the $\text{H}\cdot$ and $\text{HO}\cdot$ primary radiolysis products. Both radicals are generated in the radiolytic split of water molecules in the ore samples.

The process of water α radiolysis is much more intense in the presence of the ^{241}Am source, compared to the nuclear radiations emitted through radioactive decay of the uranium nuclei. This fact is proved after a 6 month separate experiment on uranium ores (without ^{241}Am), where $\text{U(IV)} \rightarrow \text{U(VI)}$ transformation degree is practically imperceptible.

As the uranium-bearing ore is a alkaline one ($\text{pH} > 7.5-8.5$), considering its content of dolomite or of other carbonates, the radiolytic split of the water molecules (present as humidity) in the samples under study, during α irradiation with ^{241}Am source, as well as the chemical transformations induced by the primary radiolysis products may be expressed as:¹⁶

Table 1

Chemical composition of the uranium ores

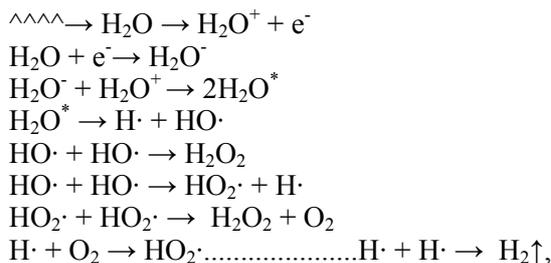
Ore sample	Microelements concentration (mg/g ore)								
	Mn	Cr	Cu	Zn	Fe	Ni	Co	Ca	Ba
1	6.854	0.052	7.006	0.105	41.140	0.108	0.047	3.027	6.750
2	2.077	0.015	2.225	0.496	20.194	0.702	0.078	1.928	1.096
3	2.340	0.015	2.002	0.230	17.767	0.112	0.022	4.670	1.621
4	0.556	0.028	6.493	1.879	6.446	0.826	0.049	5.092	6.125

The experimental data presented throughout the paper have been measured with 95% confidence limits.

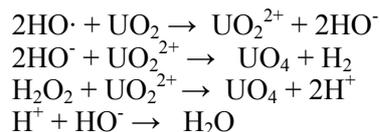
Table 2

Concentration of U(IV) and U(VI) species in uranium ores before and after α irradiation with ^{241}Am

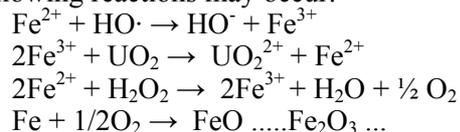
Ore sample	Humidity (g water/g ore)	Natural radioactivity of ore (Bq/g ore)	Uranium concentration (g/g ore) $\times 10^4$				Oxidation degree (%) $\text{U(IV)} \rightarrow \text{U(VI)}$
			Before irradiation		After irradiation		
			[U(IV)]	[U(VI)]	[U(IV)]	[U(VI)]	
1	0.069	12,900	1.521	0.312	1.426	0.338	8.3
2	0.082	19,400	2.356	0.470	2.295	0.526	10.7
3	0.086	34,400	3.962	0.834	3.808	0.981	15.5
4	0.091	17,700	1.978	0.416	1.867	0.538	11.8



and in this case could be occur :



It would be also possible that some microelements from the composition of the uranium ores - which may change their oxidation number through radiolysis - will participate to the redox reactions involving the U(IV) and U(VI) species. For instance, in the case of iron, the following reactions may occur:



The U(IV)/U(VI) oxidation found in this experiment may suggest some initial changing in the mineral composition of the studied ores regarding the similar investigations presented in the literature. As a matter of fact, such redox reactions, developed at the level of the uranium-bearing ores, induced by the H \cdot and HO \cdot primary radiolysis products resulted from the radiolytic decomposition of the groundwater water, were also evidenced by other authors.^{17,18} They drew the attention on the fact that the *in situ* oxidation of uraninite (UO₂) to schoepite (UO₃·2H₂O) is performed through intermediary minerals, such as ianthinite (UO_{2.86}·1.5H₂O), metastudtite (UO₄·2H₂O) and studtite (UO₄·4H₂O), considered as corrosion products of the uranium dioxide subjected to the action of some physical and chemical agents present in the ore, including, too, the radiolysis of the groundwater which leaches the respective ores.

EXPERIMENTAL

Ore samples of 1 kg each have been taken from 4 different extraction areas of a uranium mine. After breaking up ($\Phi = 0.2 - 0.5$ mm) of the ore directly at the extraction site, each sample was preserved in hermetically-closed polyethyleneterephthalat (PET) bottles, in order to maintain its initial humidity. The samples were then subjected to chemical and radiochemical analyses.

The concentration values of the metallic microelements in the ores were determined by atomic absorption spectroscopy (AAS) by using a Perkin Elmer 3300 spectrophotometer, after their dissolution in an acidic medium.¹⁹

The U(IV) and U(VI) species concentrations, both before and after α irradiation, were determined by using a Cecil C-10 UV-VIS spectrophotometer. Firstly, a given amount of uranium ore is held for 4-5 hours in 6M HCl under heating (60-70 °C), in order to selective extract U(VI) specie only. Then, in the same quantity of ore, U(IV) is oxidized to U(VI) using a mixture solution of H₂O₂ and H₂SO₄ (5:1, v:v) under 48 hours heating. After separation from the remained sludge, in both cases, the amounts of total U(VI) were determined spectrophotometrically by using Arsenazo III as a ligand in 6M HCl.²⁰⁻²¹ The absorbance values of formed U(VI) – arsenazo III coordination compounds were measured at $\lambda = 655$ nm. The amount of U(VI) was calculated from the difference of the two measurements : before and after oxidation.

The radioactivity of the four ores samples was determined by means of a Geiger-Müller OTK - 71/S13B (1.5 mg/cm²) detector connected to an VSP -14M electronic counting scaler . The humidity of the ore samples was established by their weighing both before and after their drying at 110 °C, in a drying oven.

The experiments are conducted as follows: 10 g from each ore sample were weighed under thermostatic conditions (controlled humidity) then introduced into 50 ml PET vial in which the ²⁴¹Am source had been previously inserted. The same samples of ore without ²⁴¹Am were used as standards. The vials were hermetically closed with rubber corks, lubricated at the outer surface, to avoid evaporation of the water from the ore, during the experiments. The vials containing the ore samples were mechanically intermittently stirred through complete rotation (360 °), which assures the uniformity at the contact with the ²⁴¹Am ($\Lambda \approx 8.5 \cdot 10^5$ Bq), for 6 months.

CONCLUSIONS

It was investigated the radiolytical oxidation reaction U(IV) \rightarrow U(VI) in uranium ores under the α particles released by an ²⁴¹Am source.

The oxidation degree varies between 8.3 and 15.5 % depending both on the humidity and natural radioactivity of the investigated uranium ores, but in the presence of the ²⁴¹Am source only.

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