# Study of the chemical leaching of uranium from several mineralogical layers

Marian Raileanu[1], Rodica Calmoi[1], Catinca Simion[1], Gabriel Barbir[2], Alexandru Cecal[1]

[1]"Al.I. Cuza" University, Department of Inorganic Chemistry, 11–Carol I, 700506 Iasi, Romania, E-mail: cecal@uaic.ro
[2]Uranium National Company, Suceava Branch, Crucea - Romania

**Abstract.** The purpose of the present work was to study the oxidation of uranium species coming from different samples of some Romanian uranium ores at U(VI), in the presence of the following oxidizing agents: $KMnO_4/H_2SO_4$, $H_2O_2$ and royal water. It was established that the highest capacity of leaching is shown by $KMnO_4/H_2SO_4$ that achieved values of ca. 100% in about seven days. This chemical reaction was explained through the chemical and mineralogical composition of the studied samples.

## Introduction

Uranium, a naturally occurring radioactive element, is a primordial constituent of the earth crust (Chopin et al, 1995, Plant at al, 1999). Even though, until the beginning of the XX century, its concentration was extremely low in the biosphere; after 1945, uranium started to be mined and milled and enriched in its fissile isotope $^{235}U$. Therefore, in the areas of uranium plants, its concentration increased to values exceeding the maximum accepted limits (Tykva and Berg, 2004). The same happened in the areas where are activities connected to the reprocessing of spent nuclear fuel elements.

If speaking about lower oxidation states (III, IV and V) it should be mentioned that uranium is insoluble in water. In the presence of the oxidant agents and water, solubility change rapidly when U(VI), as uranyl ion, $UO_2^{2+}$ appeared. Therefore, the following aspects must be considered:

- performance of activities connected to the cycle of the nuclear fuel elements without environmental release of U(VI)

- the quantitative extraction of uranium from the ore; therefore the risk of oxidation by the pluvial waters of the traces of U(IV) to $UO_2^{2+}$, when the latest passes to the surface waters must be eliminated (Blackman, 2001).

Taking into account the above-mentioned aspects, the aim of the present study is to test (at laboratory scale) some oxidizing agents that may perform the quantitative leaching of $UO_2^{2+}$ ions from different uranium ores. The study has in view the correlation of the leaching capacity with the chemical and mineralogical composition of the studied samples.

## Materials and methods

Six uranium ore samples (marked from "1" to "6") obtained from some Romanian uranium mining areas were subjected to the chemical leaching. They had different contents of uranium and their chemical and mineralogical composition ranged between various values.

The uranium ores were broken by grinding in agate ball mill. The grains size distribution determined by sieving is: 0.10 mm $< \phi <$ 0.125 mm (3.9 %), 0.09 mm $< \phi <$ 0.10 mm (6.4 %), 0.08 mm $< \phi <$ 0.09 mm (14.6 %), 0.071 mm $< \phi <$ 0.08 mm (56.2 %), 0.063 mm $< \phi <$ 0.071 mm (13.8 %), 0.056 mm $< \phi <$ 0.063 mm (5.1 %) (Cecal et al, 2000).

The content of the heavy metals in the studied samples was determined after the dissolution in 1 M $HNO_3$ or 1 M HCl with a UV-VIS Carry 210 spectrophotometer. To establish the mineralogical association of the uranium, the powder sample was analyzed by X-ray diffraction. For the purpose, a Dron 2.0 diffractometer with $CoK_{\alpha(1+2)}$ $\left( \overline{\lambda} = 1.79019 \right)$ radiation filtered with iron was used.

The following liquid reagents were used: (a) arsenazo III: 0.0352 g in 50 ml buffer solution (Keil 1979). (b) buffer solution: 75 ml acetic acid solution 0.2 M in 925 ml sodium acetate solution 0.2 M. (c) solution 0.1 M potassium permanganate – concentrate sulfuric acid 1:3 ($v$:$v$).

In order to perform the leaching experiments, 1 g from each ore sample was contacted with 50 ml of oxidizing mixture. In order to determine the amount of dissolved uranium (as $UO_2^{2+}$ ions), from each sample, 1 ml clear solution was extracted at different moments (24, 48, 72, 168 and 336 hours). The pH was corrected to 3.0, using small volumes of 1 M NaOH or 1 M HCl solution. The correction of pH is done because the cation, as acceptor of electrons, may be considered a poli-alkaline acid able to react with many other alkaline substances, with several coordination's number. After the correction of pH, 1 ml arsenazo III solution was added, and afterwards it was completed with 50 ml buffer solution. The absorbance at the wavelength of 665 mm was read, using as standard the solvent with which the extraction was made. Taking into account this absorbance, there was calculated the extracted amount of uranium as $UO_2^{2+}$ ions.

The concentration of the other elements in the uranium ores composition was established by means of atomic absorption spectrometry.

**Table 1.** The chemical composition of the analyzed samples.

| Sample | Zn | Cu | Fe | Mn | Pb | Ni | Co | Cr | Cd | U |
|--------|------|-----|----|------|------|-----|----|------|------|------|
|        |     |     |    |      | ppm  |     |    |      |      |      |
| 1 | 3.28 | 7.3 | 84 | 6.5 | 7.1 | 114 | 56 | 17.8 | 0.65 | 560 |
| 2 | 3.28 | 5.1 | 70 | 5.5 | -[1] | 54 | 32 | 17.8 | 0.70 | 430 |
| 3 | 0.30 | 5.5 | 56 | 4.5 | -[1] | 60 | 32 | 12.7 | 1.20 | 380 |
| 4 | 5.66 | 8.0 | 61 | 6.5 | 7.1 | 84 | 60 | 12.7 | 8.00 | 140 |
| 5 | 0.89 | 4.7 | 75 | 6.5 | 7.1 | 48 | 36 | 12.7 | 0.50 | 480 |
| 6 | 5.66 | 6.2 | 65 | 10.5 | 53.4 | 84 | 44 | 22.9 | 8.30 | 2450 |

[1] no data

**Table 2.** The mineralogical composition of the uranium sample number "1".

| Mineral | Chemical formula | Abundance, % |
|---------|------------------|--------------|
| Quartz | $SiO_2$ | 55.00 |
| Ankerite | $CaMg_{0.77}Fe_{0.23}(CO_3)_2$ | 11.20 |
| Sanidine | $K(AlSi_3O_8)$ | 8.30 |
| Muscovite | $[SiAlO_{10}Al_2(OH)_2]K_2$ | 4.70 |
| Thucolite | $(U,Th,Pb)(CO_3)_x$ | 3.75 |
| Biotite | $K_2(Fe_{2.76}Mg_{2.32}Ti_{0.55})(Al_{2.41}Si_{5.58}O_{20})(OH)_2$ | 3.00 |
| Hematite | $Fe_2O_3$ | 2.60 |
| Blende + Pyrite | $ZnS+FeS_2$ | 1.10 |
| Pyrochlore | $(Na,Ca,U)_2(Nb,Ta)_2O_6(OH,F)$ | 0.35 |

## Results and discussion

The heavy metals' content of the studied uranium ores samples used in the leaching experiment is presented in Table 1.

For illustration, the mineralogical composition of the sample labeled with "1" is presented (Table 2). This uranium ore sample has a molar mass M = 344.8 and is crystallized in the cubic system (a = 10.42 Å, crystallographic group Fd3m). (Ianovici et al., 1979).

For the samples 2-5, the concentration of the quartz is higher as 55% and those of the other minerals are lower, but the relative abundance is almost the same. The "sample 6" has a concentration in thucolite and pyrochlore higher as presented in Table 2.
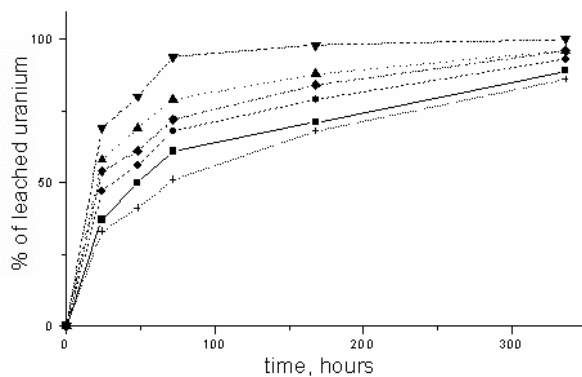
It can be observed that uranium exists in two distinct mineralogical associations, thucolite and pyrochlore. Both of them are extremely hard because uranium is part of the crystal lattice. At the same time, the high content of quartz (55 %) suggested a leaching method based on the acid treatment type.
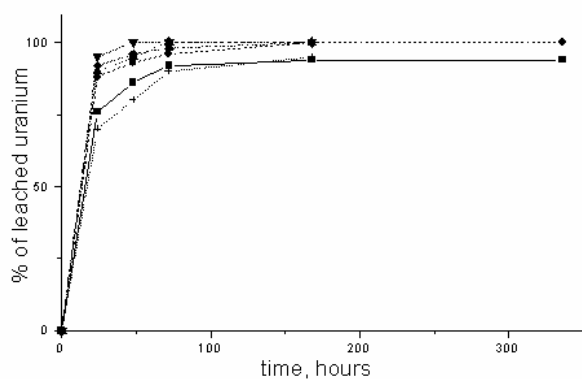
(a)
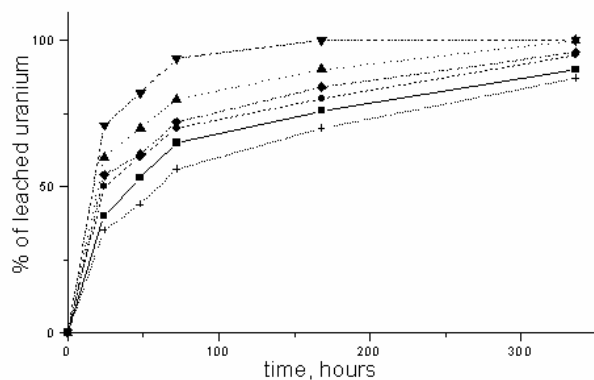


(b)



(c)

**Fig. 1.** The time dependence of the uranium leaching using: $KMnO_4/H_2SO_4$ (a), $H_2O_2$ (b) and $HCl+HNO_3$ 1:3, *v:v* (c) (■: ore "1", ●: ore "2", ▲: ore "3", ▼: ore "4", ♦: ore "5", +: ore "6").

In-situ leaching of uranium ores

The leaching phenomenon has its origin in the *"in situ"* oxidizing action of the atomic or molecular oxygen on the species of uranium in intermediate oxidation level, according to the most probable chemical reaction:

$$UO_2 + [O] + 2H^+ = UO_2^{2+} + H_2O$$
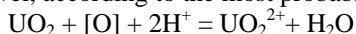
The results of the leaching experiments are summarized in the Figures 1.

It can be noticed the oxidizing/leaching capacity of the intermediate species of uranium to U(VI), in the case of all the studied oxidizing agents. The efficiency of the process reaches values of approximately 100 % after seven days of contact in the oxidizing system; in case of $KMnO_4/H_2SO_4$ system, the process is taking place faster. The higher concentrations of uranium (sample number "6") involve higher extraction efficiency, the process being limited by the time factor.

From the Figs. 1, a good efficiency of the leaching process can be noticed. This efficiency is related to the solution of $KMnO_4/H_2SO_4$ where the effect of the interferences is manifested at the end of the experiment only (Komersova et al, 2001). In case of royal water, a constant increase of the absorbance along with the whole experiment can be noticed, thus meaning a high efficiency of this acids mixture in the way that the whole extraction was made during a 24 hours time interval, until the first reading of the absorbance was performed.

For all experiments, higher the concentration of quartz and lower concentrations of thucholite and pyrochlore, lower the extraction degree of uranium as $UO_2^{2+}$ ions.

A part of the microelements: Fe, Ca, Ni, Cr in the sludge, which remains after the uranium leaching, should be considered for the further chemical treatments with the view to be separated.

## Conclusions and perspectives

The dissolution of six uranium ore samples and the leaching of the reduced species of uranium to U(VI) were studied in the presence of $KMnO_4/H_2SO_4$, $H_2O_2$, and royal water. All the oxidizing agents led to remarkable results that could not be achieved in case of the alkaline or the microbiological leaching. It can find an explanation in the property of the strong acids to destroy the mineralogical matrix that includes uranium.

In the given conditions, the waste contains just traces of uranium that are not leading to the radioactivity increase of the environment. In addition, these micro quantities must be retained, if it considers the large volume of depleted uranium that gathers in the areas of the mining exploitations. Due to the fact that for small concentrations the chemical methods are not presenting any interest from the costs point of view, the using of microbiological methods of leaching/ storage have to be considered.

## Acknowledgement

## References

Al-Jundi J, Werner E, Roth P, Hollriegl V, Wendler I, Schramel P (2004) Thorium and uranium contents in human urine: influence of age and residential area. J. Environm. Radioactivity 71: 61-70.

Blackman Jr, WC (2001), Basic hazardous waste management, 3rd edition, Lewis Publishers, Boca Raton, pp. 211.

Cecal A, Humelnicu D, Popa K, Rudic V, Gulea A, Palamaru I, Nemtoi Gh (2000) Bioleaching of uranium (VI) from poor uranium ores by means of cyanobacteria. J. Radioanal. Nucl. Chem. 245 (2): 427–429.

Cecal A, Popa K, Craus ML, Patachia S, Moraru TR (2002), On the bioleaching of $UO_2^{2+}$ ions from a Romanian poor uranium ore. J. Radioanal. Nucl. Chem. 254 (1): 81–84.

Chopin GR, Rydberg J, Liljenzin JO (1995) Radiochemistry and Nuclear Chemistry. Butterwoth - Heinemann, New York, pp. 110.

Ianovici V, Stiopol V, Constantinescu E (1979) Mineralogy, EDP, Bucharest, pp. 239.

Keil R (1979) Hochselektive spektralphotometrische Spurenbestimmung von Uran (VI) mit Arsenazo III nach Extraktionstrennung. Fresenius Z. Anal. Chem., 279: 384-387.

Komersova A, Bartos M, Kalcher K, Vytras K (2001) Some new methods of indirect determination of metals based on adsorption and complexation properties of arsenazo III azo dye. Coll. Czech. Chem. Comm., 66: 456-464.

Tykva R, Berg D (2004) Man-made and natural radioactivity in environmental pollution and radiochronology. Kluwer, Dordrecht, p. 114.