# Could the calixarenes be a viable solution for radioactive decontamination of mine waters from Romania?

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**Abstract.** The present paper shall briefly overview the past of the Romanian uranium industry and its current state. Then it will present the features of the radioactive contaminated mine waters and the treatment methods used for their decontamination. The advantages and the disadvantages of the decontamination method will be pointed out. The main updates concerning the calixarenic derivatives behavior towards uranium will be presented.

## Uranium industry in Romania

Since 1950s the Romanian uranium industry met its top development, when uranium-bearing ores were found by radiometric investigations and aerial gamma prospecting in three main areas, namely Banat, Apuseni Mountains and Eastern Carpathians (Georgescu D., Popescu M. and Aurelian F, 2004).

Since 1952 until 1962, uranium ore was directly extracted and exported to the former Soviet Union, respectively to the Silimäe ore processing plant in Estonia. On 1962, its shipment to the Soviet Union was stopped and it was stockpiled nearby the mining pits. Since 1978 the stockpiled ore beside the new extracted one began to be processed when Feldioara plant was commissioned. Beside that the specific technological researches were tightly related with scientific studies about wastes treatment, mining activities closure and ecological restoration of affected areas by extraction and processing uranium ores (Popescu I.C. et. al., 2005).

Under the complex international context and due to the public concern increasing about the radiological risk and the radioactive contamination threats, the uranium extraction and processing activities were almost closed in Romania, following the European pattern, and the entire scientific interest was shifted towards the environment radioactive decontamination within the areas affected by uranium exploration, exploitation and processing activities.

We have to underline the fact that the information concerning the uranium industrial activity is still classified and protected by the secrecy law.

The main assignments for the research scientist teams were to elaborate extraction flow sheets and projects in order to process the Romanian uranium ores, to purify yellow-cake and to produce nuclear pure uranium dioxide powder.

## Main aspects concerning the environmental radioactive pollution and exposure pathways

The environment radioactive pollution is caused mainly by the flow of water on horizontal and vertical direction that enhances the chemical reactions such as leaching processes and rocks' weathering. Other chemical reactions may be initiated either by the microbiological processes or the biofilms occurrence on the surface of the minerals and they are consisting mainly in the minerals' and other elements' oxidation. The most complex chemistry could be observed in cases when the organic compounds are included into the rock mass and the degradation processes will significantly influence the environmental chemistry for the rest of contaminants. Biological contaminants degradation will determine the releases of different gases such as methane,, hydrogen sulfide, carbon dioxide or ammonia.

One of the most important possible exposure pathways is the use of contaminated aquifers or rivers as sources for potable water or for irrigation of crops and watering the livestock.

The air contamination is based on the re-suspension of dust or releases of radon, which may occur. So the inhalation and the contamination of surroundings represent secondary pollution sources.

## Radioactive contaminated mine waters features and the decontamination methods used

As it is already known the uranium industry is a significant pollution source, which generated huge amounts of radioactive contaminated wastewaters. A very important part of them is represented by the mine waters, which are a serious threat for the environment and for the people living nearby as well.

The interaction between radioactive contaminated mine waters and environment is very complex because it depends on a lot of factors such as the pH and temperature of water; the uranium ore body geological nature; environmental conditions (aerobic or anaerobic environment); the microorganisms' presence, etc. So to identify the most appropriate and economic feasible solution from the radioactive decontamination viewpoint in order to treat the mine waters contaminated by the radionuclides could be a very difficult challenge.

Before 1989, among the other assignments, in Romania, to recover the uranium from mine waters was a national strategic objective for the research scientists involved in the uranium industrial activity. It was also important to come up with a viable solution using indigenous reagents and substances. Therefore a lot of research studies were performed using different types of ion exchange resins. The most promising one was called VIONIT AT1, a strong basic anionite, fabricated in Romania by the Chemical Plant Victoria from Ramnicu Valcea, which was able to uptake around 100 mg U per 1 mg of resin. Other alternative methods for the recovery of uranium were tested in lab as well.

One of many options was to create a new sort of adsorbent by chemical extraction of the humic acids contained by an indigenous sort of charcoal and to impregnate them into an inert support. Despite the fact that the test results were encouraging respectively the uranium uptake was of about 300 mg / g of humic acids in situ investigations pointed out the inefficiency of this method as the uranium's recovery concerns because only about 3 mg U /g of product were up-taken.

The ionic flotation, uranium precipitation using limestone and iron sulfate, adsorbtion on other adsorbents were also studied as radioactive decontamination methods.

In practice (Popescu I.C., 2005) the methods used for the treatment of radioactive contaminated mine waters could be grouped in:

- Physical methods mainly based on the adsorption, absorption and ion exchanging processes using organic or inorganic compounds;
- Chemical methods that involve redox reactions;
- Biological methods that involve the microorganisms' growth reaction based on electron transfer mechanism.

The control analysis performed out lined the following list of mine water contaminants, which should be removed according to the Romanian specific regulation enforced: solid suspension matter, which proved to contain natural radionuclides, especially uranium and radium; solubilized uranium due to the conjugated action of more favorable factors on the way covered by the underground water through the mine; radium, which is present as an equilibrium element of the radioactive disintegration of uranium.

It has to be underlined the fact that in mine water, all the contaminants listed above have presented content values higher compared to the Romanian safety limits. By time, it has been observed a decrease of this concentration; in fact the variation of this concentration depends on the mining activity intensity and on the quality of the mined ore.

Between 70's and early 80's the concentration of solids in suspension had values higher than 10 g/L, uranium content was frequently higher than 4 mg/L and the radium content was about 0.5 Bq/l. On 1999 mine water analysis showed that ore solid suspension values were less than 5 g/L, uranium content between 1.5-2 mg/L and radium between 0.1-0.3 Bq/lL

Our research scientists' team elaborated a technical flow sheet following the research studies results in order to radioactively decontaminate the mine waters. On its basis a treatment plant was erected and the flow sheet is presented by fig.1.

The other potential contaminants, such as heavy metals, especially mercury and arsenic reached a concentration under the safety limits and thus there will be no need for additional treatment of mine water because of them.

Our most recent chemical analysis of mine water samples showed they have a relative complex composition such as suspended materials ~10 mg/L, uranium present as $Na_4UO_2(CO_3)_3$ ~1.6 mg/L, nitrates ~20 mg/L, sulfates ~0.20 mg/L, chlorides ~0.30mg/L, calcium ~40 mg/L, molybdenum (II) 0.20 mg/L, magnesium ~20 mg/L, $NaHCO_3$ ~ 1000 mg/L. The pH of the water ranges from strong basic to low acidic.

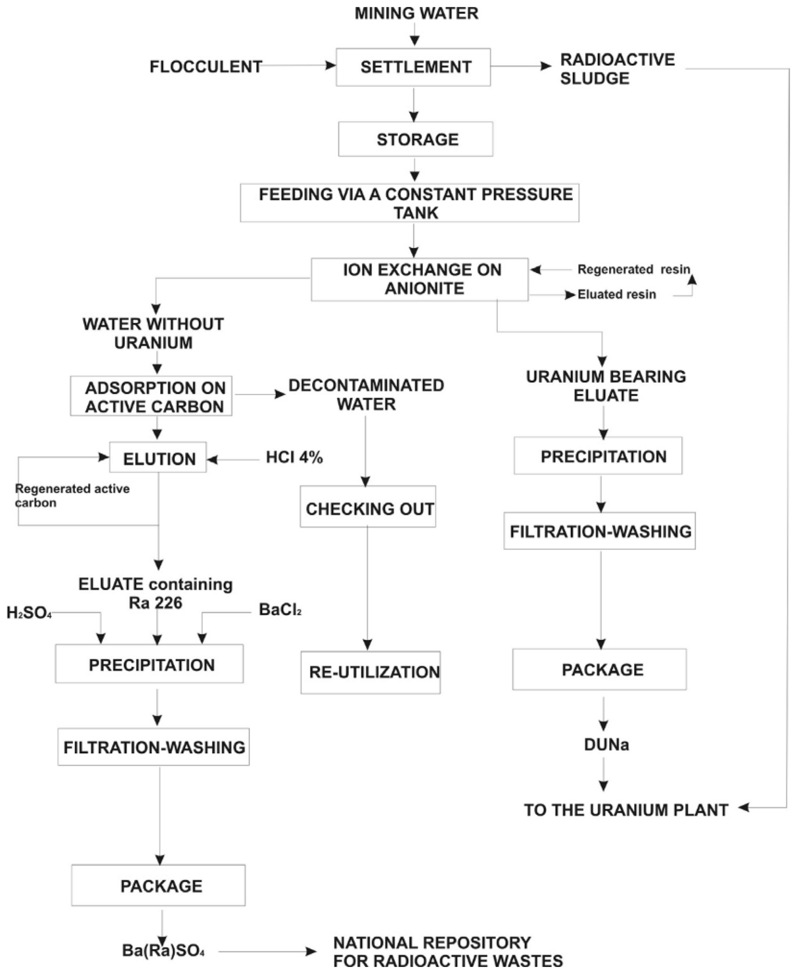


**Fig.1.** Radioactive mine waters decontamination flow sheet.

## Could the calixarenes be a viable solution for the radioactive decontamination of the mine waters?

Despite of their extremely encouraging results each one of the above mentioned procedures presents some weak points such as is the case of the bioremediation processes, where everything is beautiful until the poor micro-organisms die and all the radionuclides accumulated by their bodies return into the natural circuit.

It is important not to ignore the fact that now the science made significant progress in getting to understand intimately the chemical behavior of uranium and his progenitors at molecular level such as in the supramolecular chemistry's case and has reached a point in which is able to filter molecules (see the reverse osmosis units, nano- and ultra-filtration ones as well). Unfortunately the last ones are in many cases too expensive to afford it.

Many research studies have been carried out worldwide in order to synthesize extremely selective organic molecule able to discriminate between the competing ions, to retain uranium and to discriminate the radioactive mine water.

In their quest for the appropriate answer they discovered a very promising class of organic compounds known as calixarenes (Schmeide, K, et. al. , 2002). Calixarenes are macrocyclic molecules formed by 4, 6 ore 8 para-substituted phenolic units linked by methylene bridges ortho to the OH functions (fig.2).

Thus, molecules of different ring sizes are formed. It has been reported recently that the ones especially designed are suitable to separate uranium from aqueous solutions. They have huge potential for industrial applications depending on their structure such as in the case of the uranium detecting sensors (Becker A. et. al., 2005), in determination of uranium contents in the human body fluids (Baglan N., et. al. 2005), separation of cesium and strontium, lanthanides sequestration

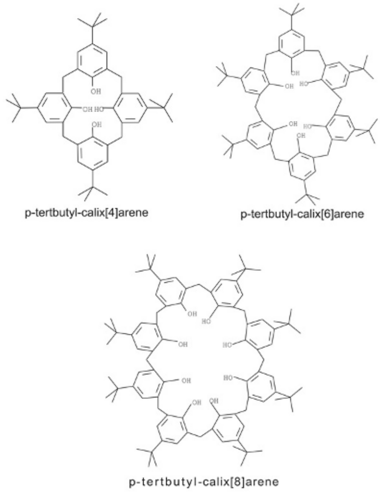


**Fig.2.** Calix[n]arenas structures (where n=4, 6 or 8).

(Perin R. et. al., 1993), separation of neutral organic molecules, uranium recovery, accelerators for instant adhesives, heavy metals separations (Nechifor) and so on.

Tests performed on synthetic solutions conducted to recent reports concerning the high selectivity for uranium of the calix[6]arenas functionalized with carboxylic or hydroxamic groups on the lower rim (Schmeide, K, et. al., 2002).

## Conclusions

Romanian uranium mining is a very important source of pollution because it generates is a very important source of pollution because it generates huge amounts of radioactive contaminated wastewaters. The mining water represents a very important part of them and their chemical composition depends on many different environmental factors. The recent research reports' results indicate that the calixarenas could be a very good answer to the potential difficulties in decontaminating radioactive mine waters. Whether they are suitable or not for it, that can be found out only by carrying out new research studies.

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