

The Conceptual Model for the Transport of ^{226}Ra , U_{nat} and Heavy Metals with Infiltrating Rainfall from the Tailing Dump into the Underlying Soil

M. Bragea*, D. Perju**, M. Poiana***, C. Cristache****, G. Branzei*

*Institute of Public Health Prof. Dr. Leonida Georgescu, V. Babeș 16, 300226, Timisoara, Romania,
Phone: +40-256 492101, Fax: +40-256 492101 E-Mail: mbragea@yahoo.com, WWW: <http://www.ispt.ro>

**"Politehnica" University of Timișoara, Faculty of Industrial Chemistry and Environmental Engineering, P-ța Victoriei 2, 300006 Timisoara, Romania, Phone: +40-256-403000, Fax:+40-256-403021, E-Mail: delia.perju@chim.upt.ro, WWW: <http://www.upt.ro>

***Banat's University of Agricultural Sciences and Veterinary Medicine, Faculty of Food Processing Technology, Aradului 119, 300645, Timisoara, Romania, Phone: +40-256-494023, Fax: +40-256-200296, E-Mail: atenapoiana@yahoo.com, WWW: http://www.usab_tm.ro

****National Institute of R&D for Physics and Nuclear Engineering "Horia Hulubei", Radioactive Waste Management, Atomistilor 407, P.O.Box MG-6, Bucharest-Magurele, Romania, Phone: +40-21 457-44-40, Fax :+40-21 457-44-22, E-Mail: ocarmen@ifin.nipne.ro, WWW: <http://www.nipne.ro>

Abstract: This paper describes the geochemical processes regulating the migration of heavy metals and radionuclides in uranium mining tailings site Ciudanovita, Caras Severin and to examine the depth-scales of concern resulting from the interaction of different mechanisms. Contaminants of concern for the management of uranium mill tailings include radium 226, uranium 238 and heavy metals (e.g. Ca, Fe, Al, Ni, K, and Na). Residual tailing pyrite oxidation was found to be the critical factor in the transfer of metals and radionuclides to seepage water.

Keywords: tailing dump, heavy metals, pyrite, radionuclides, dynamic model

1. Introduction

Accurate prediction of the transport of toxic metals and radionuclides in the subsurface of inactive mining sites is critical to the assessment of environmental impacts and the development of effective remediation technologies.

Understanding the physical and chemical processes present that influence the migration of contaminants is essential to mitigating the environmental problems associated with this sites. However, contaminant fate and transport in the subsurface are known to be controlled by complex hydrological and geochemical processes.

Because of the variety of hydrogeological and climatic factors existing in an area, each tailings site and the selection of the optimum disposal option must be independently evaluated. To a limited extent, geological, hydrological and geochemical variables can be selected and modified, either by process selection or in the tailings managements. For example, the amount of water remaining with the solid tailings can affect the quality and quantity of the seepage from the tailings into local ground water.

The purpose of this work was to investigate the geochemical processes regulating radionuclides and heavy metals migration in the uranium mining tailings of the Ciudanovița, Caraș-Severin and to examine the depth trend of major radionuclides and other contaminants. For estimating the flux of radioisotopes out of the tailings mass, it is essential to know the major association of radioisotopes with different minerals, the relative fraction

in the particulate and soluble phases, and the mechanisms which control the migration of the radionuclides. In many cases the ore bodies are associated with metal sulphides such as pyrite and marcasite which are not desired products and are released to the tailings as part of the radioactive waste.

Upon weathering, these metal sulphides are readily oxidized, producing acid mine drainage conditions from these tailing piles which is of considerable environmental concern. Radium is hypothesized to be co-precipitated mainly gypsum, other metal sulphates (e.g., jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) with minor influence of such precipitates as $\text{Al}(\text{OH})_3$ [2].

In the tailings, the main mechanisms of interest are precipitation –dissolution reactions, pyrite oxidation, and adsorption onto surfaces, solid state diffusion, pore water diffusion, pore water complexation and hydrological transport.

The oxidation of pyrite and other iron sulphides produces highly acidic conditions within the radioactive waste with the subsequent water containing significant concentrations of iron, sulphate, heavy metals and trace radionuclides. The migration of such poor quality tailings water either by surface run-off or sub-surface groundwater can lead to serious deterioration in the quality of adjacent natural water systems. The potential for pyrite oxidation should, however, persist for decades in abandoned tailing dumps.

2. Materials and methods

For a good simulation of the action of the infiltration water through the tailing dump on the elements migration in solid phase we designed a physics dynamic model which diagram is presented in figure 1. The purpose of this model would be for a better quantitative understanding of a physics mechanisms and the processes of the contaminants transport released into the water from the tailing dump. The experimental installation made by many glass columned, has allowed the study of radionuclide extracting and their migration from the tailing into the water. The glass column (4), with 800 mm length and the 30 mm diameter is scheduled in the upper and lower part with a tap for regulation of the flow capacity (2) and (6), which allows the flow with certain speed. Into the same lower part the glass column is scheduled with a layer of glass silk (5) used as holder. Into the glass columned were introduced well known quantities (200 g) of the samples from Ciudanovita, sampled from three different depths (0 -100 mm, 500-600 mm, 1000-1200 mm). The tailing was eluted with acidulated distilled water, H_2SO_4 , 0,5 M until a pH comprised about 4-5. This was conceived for simulation of acid rainfall or forming some little quantities of sulfuric acid through the geochemical processes (e.g. pyrite). The flow speed was measured by a chronometer.

The elution water was collected monthly over a year and examined by means of chemical and radiochemical analyses, ascertaining the pH, the ^{226}Ra and U_{nat} concentrations, as well as the Fe, K, Ca, Al, Ni and Na concentrations, by following methodologies:

- The pH of the eluted solution was measured with a Piccolo digital pH-meter
- ^{226}Ra were determined by measuring the alpha radioactivity of the Ra sulfate precipitate, separated radio-chemically, together with the Ba and Pb sulfates. The chemical efficiency of the precipitation method is 89 %
- We highlighted the U_{nat} , after the chemical processing, with the color reaction, using a PAN indicator (1.2-pyridil-azo-2-naftol) and afterwards we measured its radioactivity. The chemical efficiency of this method is 83%.

The alpha measurements were made with a counting assembly FHT 1100 with a proportional counter with gas circulation and relative efficiency of 26 %.

The Fe, K, Ca, Al, Ni and Na concentrations were determined with an atomic absorption spectrometer (Varian AA-110).

3. Results and discussion

The tailing dump can contain minerals associated in various quantities: zinc, aluminum, chrome, potassium, manganese, etc.

In many uranium minerals are considerable quantities of sulfites which represent an important issue in the evaluation of the further behavior after the dump closing.

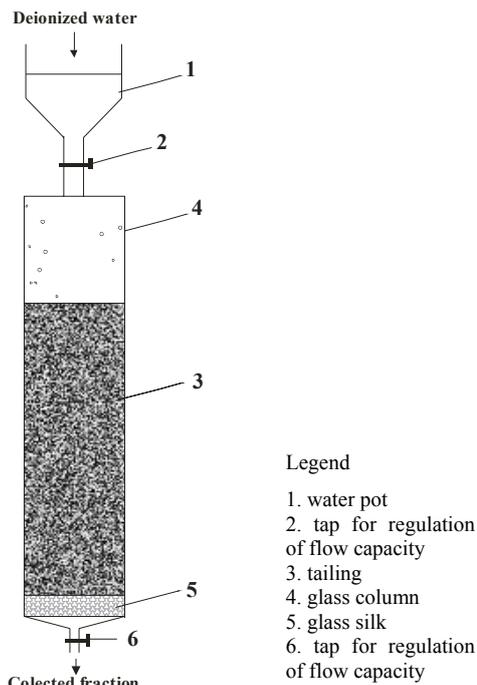


Figure 1. Schematic representation of installation for extraction study in dynamic regime

Metals and radionuclide are not uniformly distributed in the solid material from the tailing dump [1].

In figures 2 – 5 are represented the metal quantities which are in the extraction solution for one volume V and a before settled time T for physics dynamic model.

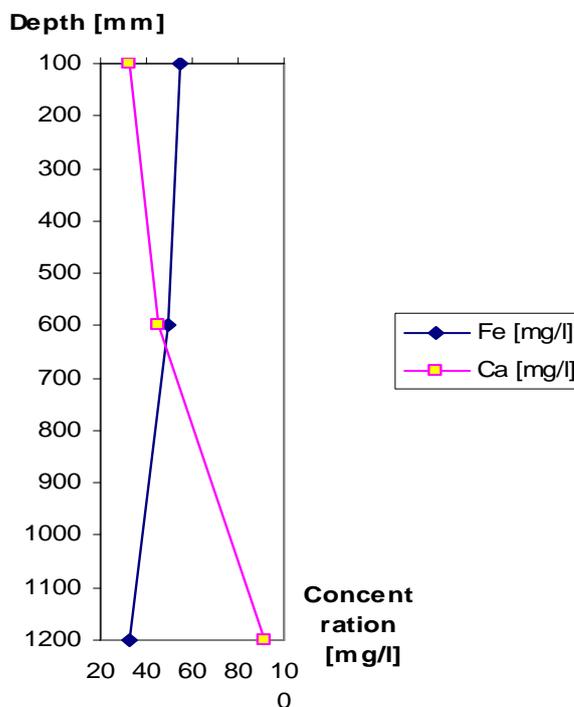


Figure 2. Depth of migration related to concentration of Fe and Ca in the tailing dump

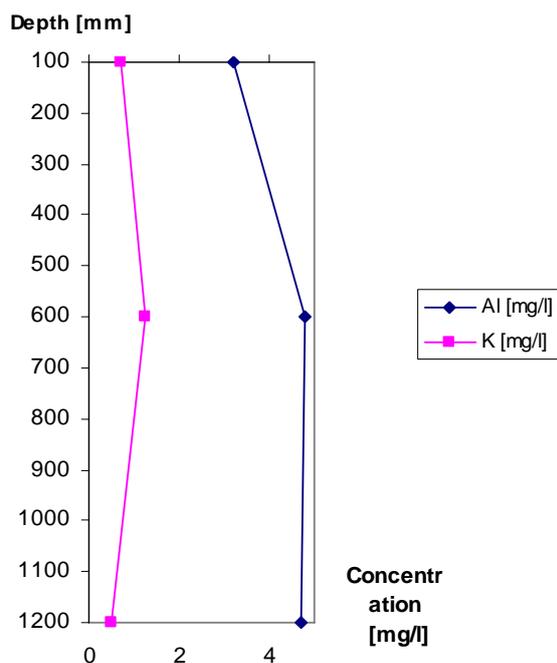


Figure 3. Depth of migration related to the concentration of Al and K in the tailing dump

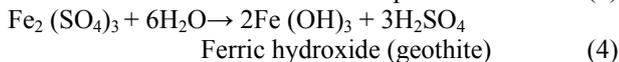
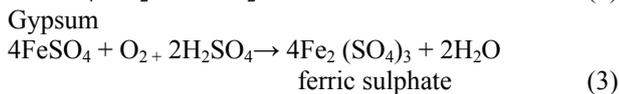
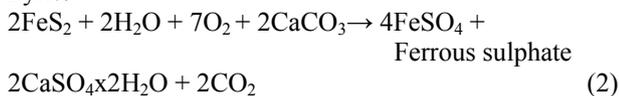
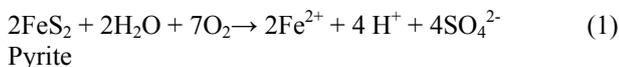
The pH was 1,1 at 0-100 mm depth, 1,2 at 500-600 mm and 2,1 at 1000-1200 mm. The rate of migration of metals and radionuclides to the surface is dependent upon the amount of moisture present, as well as the pH.

The concentration of Fe was 54,6mg/L at 100mm depth, 59,6 mg/L at 600mm and 38,7 mg/L at 1200mm (fig.2).

The low pH, and high sulphate and iron, suggests that pyrite oxidation is predominantly occurring in a relatively narrow zone near the surface tailing.

In the solutions phase the iron is variable from the highest values in the upper layers with lower decrease. Pyrite oxidation produces highly acidic conditions within the tailings which causes leaching of metals and radionuclide.

The formation of acid and iron sulphates occurs by the following chemical steps (1, 2, 3, and 4) [3]:

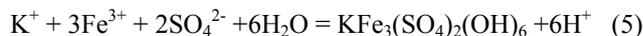


The Fe^{3+} ion presence is a co precipitate for the uranium, and explain the fast elution of the uranium after the first phase (fig.4).

Concentration of K and Al (fig.3) are 0,72 mg/L, respectively 3,2 mg/L at 100m depth, 1,24 mg/L

respectively 4,8 mg/L at 600 mm and 0,52mg/L and 4,7mg/L at 1200mm depth. Possible sources of K derived from dissolution of K feldspar, smectite and illite present as silicate gangue minerals.

Precipitation of potassium jarosite is shown by the following reaction:



This equation suggests that Fe and SO_4 are consumed and H is liberated at a 3:2:6 ratios. Precipitation of potassium jarosite liberates six moles of H, contributing to the generation of an acidic solution. Equation (5) depends on relative concentration Fe produced from minerals undergoing dissolution within tailing pore water.

A major source of acidity in the tailings impoundment is the reprecipitation of Al in hydroxide and hydroxyl-sulfate phases, because these phases consume base (OH^-) and decrease the pH according to the reactions (6, 7) [4]:

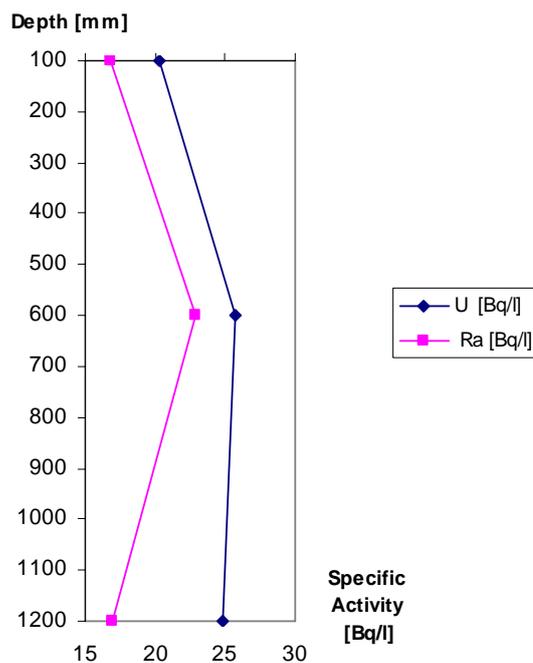
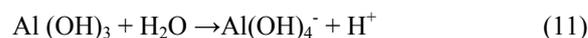
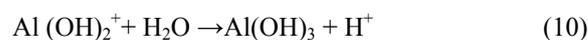
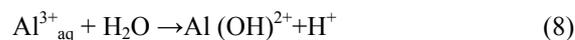


Figure 4. Depth of migration related to the concentration of the U_{nat} and ^{226}Ra in the tailing dump

As the pH increases, the aluminum and iron ions consume hydroxyl hydrolyzes (8, 9, 10, 11), result by a decrease in pH:



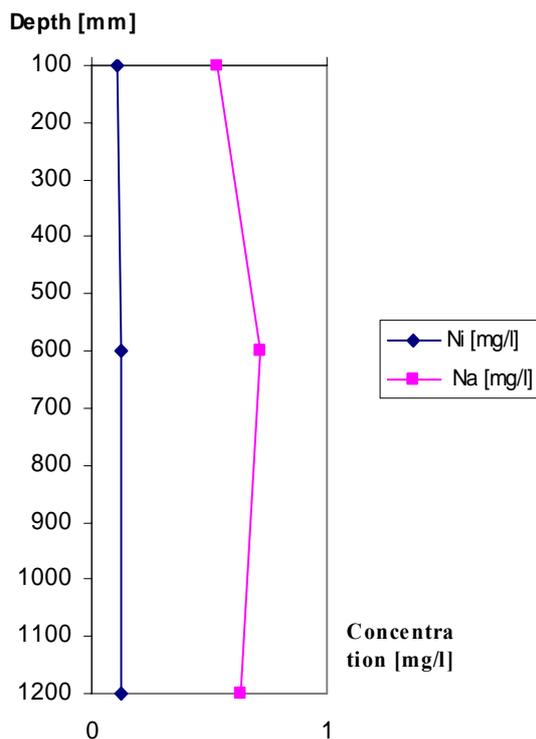


Figure 5. Depth of migration related to the concentration of Ni and Na in the tailing dump

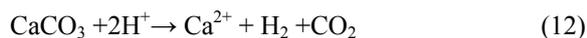
As the tailings become weathered, chemical, biochemical and geochemical changes occur within the impoundment area. The flux and availability of water are of the most important parameters affecting the chemistry of the tailings and the migration of contaminants through the tailings. The water acts as a transport mechanism for cationic and anionic constituents, as well as influencing the solubility and migration of salts.

Ni, Na (fig.5) and U_{nat} (fig. 4) shows higher concentrations in lower layers than at the surface (0,10 mg/L for Ni and 0,53 mg/L for Na at 0-100 mm depth, respectively 0,127 mg/L for Ni and 0,63 mg/L for Na at 1000-1200 mm depth).

The specific activity of U_{nat} was 20,32Bq/L at 0-100 mm depth, 25,69 Bq/L at 500-600 mm and 24,82 Bq/L at 1000-1200 mm.

On the other hand Ca (fig.2) and Ra (fig. 4) show a different distributions model. Concentration for Ca was 32,4 mg/L at 0-100 m, 45,6 mg/L at 500-600 mm and 91,2 mg/L at 1000-1200 mm depth.

The calcite in the aquifer reacts with the infiltration water (12, 13). [4]:



In consequence their availability for migration is quite high.

Ra is not uniformly distributed in the solid material from the tailing dump. Investigation have shown that specific activity of ^{226}Ra was 16,87 Bq/L at 0-100 mm,

22,89 Bq/L at 500-600 mm and 19,67 Bq/L at 1000-1200 mm. Radium exists in the divalent state and, as an alkaline earth, most closely resembles the chemistry of barium, Insoluble inorganic radium compounds include sulphate carbonate, while soluble forms of halides and nitrates exist [9].

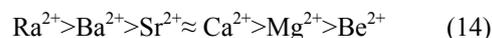
The radium, probably exists in the tailings in several forms, as $RaSO_4$, precipitated during the leaching, around the solid ore particles; associated with jarosite, $KF_3(SO_4)_2(OH)_6$, or with lime ($CaSO_4 \cdot x2H_2O$) or with neutralized hydroxides $M(OH)_2$ [4].

Insufficient data are available to indicate whether the radium is substituted into the jarosite and gypsum lattices as a cation, or whether it exists as a co-precipitate or precipitate adsorbed onto sulphate compounds or minerals [8]. This form or species of radium in the tailings will have an important effect on the relative mobility of radium throughout the impoundment area.

The metal hydroxides already made and particularly those by Fe and Mn have the ability to fix the radionuclides. The cation exchange equilibrium is dominated by columbic interactions between cations and the fixed groups of the exchanger material [5].

In the first phase only the ^{226}Ra was washed and it was in combinations with certain solubility.

The ^{226}Ra solubility is influenced by the common ion effect. The chemical properties of the ^{226}Ra are manifest similarly with other metals earth alkaline cations, which are very predictable in their behavior. When ionic hydration effects predominate, the ions of smaller hydrated radius tend to displace ions of larger hydrated radius, and the affinity for adsorption can be written as (14) [6]:



In some situation the co-precipitation can take place with other solids as carbonates, sulfates or iron oxides, in the case of the ^{226}Ra , but in general the behavior of these elements will be lead by the ion exchange process and from this reason there are sensitive at the changes in ionic power.

Thus, co-precipitation with Ca would be a much more probable mechanism [1]. Adsorption of ^{226}Ra decrease when Ca is in the infiltration water and Ca fights for the places of adsorption. This means that Ca has the tendency to interact with rainfall water and to make crust of $CaCO_3$.

In the same time, in the upper layer it take place the precipitation of amorphous hydroxide of Al, Fe, U_{nat} , as well as the precipitation of soluble sulfates (Ba and Ra).

The U_{nat} sorption onto iron and Mn oxide can be major extraction processes of U from eluted solution [7]. U found in this phase is not in isotopic equilibrium with U dissolved in the same system.

This means the metal transfer speed between two phases is little. If U (VI) is reduced at U (IV) the precipitation can take place and the mobility of U_{nat} is decreasing.

In alkalescent conditions the anionic species of uranyl hydroxyl dominate the chemistry of dissolved U (VI) [7].

Because the tailings are so heterogeneous, and the chemical changes occurring over time during weathering are so dynamic, many facets must be considered and the data interpreted and related.

4. Conclusions

We can observe that metal ion presence generate chemical interactions. The experimental results give a reasonable approximation of a water flow through the surface of tailing dump.

The experimental data about the metals concentration in the infiltration waters suggest that the presence of these in the tailing dump are generating chemical reactions and physical process as precipitation, adsorption, and delay phenomenon.

According to what we have seen earlier it is clear that in pyrite uranium tailings the pyrite oxidation of some other sulfuric metals is one of most important issue for the environment, in evaluation of abandonee tailing dump under the rainy climate. The pyrite oxidation is an important phenomenon in surfaces layer of unsaturated tailing area. The oxidation produces on the tailing surface acid conditions which causes the lixiviation of heavy metals and radionuclide.

With infiltration, the reaction products gradually migrate downwards. The co-precipitation and adsorption of hard metals and of the radionuclide occupy an important place in the neutralization area.

Although this not alter the major conclusion given above, it presents a complicating factor in that it shows that the chemical characteristics observed at a particular point and at a particular time can be the result of not only the local geochemical processes, but also of translocation processes. Interpreting trends in chemical profiles a purely equilibrium geochemical basis could, therefore, lead to inappropriate hypotheses.

The tailing dump should be covered with a layer of clay material and other of soil. Re-vegetation of the whole area could also be considered. These actions would favor the reduction of water infiltration and oxygen penetration. As a consequence the pyrite oxidation processes would be reduced as observed in the deep layers of the tailings in the dump.

REFERENCES

1. Belzile, N., Lecomte, P. and Tessier, "Modelling the transport of radioactive contaminants in water" *Environ. Sci. Technol.*, 23, **1999**, pp.1015-1025,
2. Bird, G. A., Stephenson, M. & Cornett, R.J. Size "Distribution of iron and manganese species in freshwaters" *Geochim.Cosmochim.Acta* 47, **1993**, pp.731-745.
3. Bolistreri, L.S., Box, E. S. "Assesing the influence of Radium Pyrite and carbonate Minerals on the geochemistry", *Environmental Sci. Technol.* 33, **2004**, p.3347-3353.
4. Clevenger, T.E. "Use of sequential extraction to evaluate the heavy metals in mining wastes." *Wat.Air.Soil.Pollut.*, **1998**, 50, pp.241-54.
5. Dearlove, J.P.L, Green, D.C. & Ivanovich, M. "Uranium transport and partitioning of U, Th and Ra isotopes between solid and aqueous phases in the Krunkebach mine, Federal Republic of Germany" *Sci. Basis Nucl. Waste.Manag.*, XII, **2001**, p.927-32.
6. Fressel, M.J., Koster, H.W. "Radium in Soil": The Environmental Behaviour of Radium, Vol.1, *Technical Reports Series* no. 310 IAEA, **1990**, pp.323-345.
7. Fernandes, H. M., Veiga, L.H.S., Franklin, M.R., Veiga, L.H.S., Prado, V.C.S. & Taddei, J.F." Environmental impact assessment of uranium mining and milling facilities: A study case at the Poços de Caldas uranium mining and milling site, Brazil" *J. Geoch. Explor.*, **1998**, pp.56-68.
8. Reiga, L. H. S., Amaral, E., e, E.D. & Fernandes, H. M. "Radioactive and non radioactive pollutants as contributors to the human health risk at mining areas" *Proceedings of 9th International Conference of Heavy Metals in the Environment*, CEP Consultants, Toronto, Canada, **1993**, pp.45-51,
9. Skeaff, J.M., Problems In the separation of radium from uranium ore tailings, *Hydrometallurgy* , **2000**, pp .249-257,