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OBSERVATION ON THE CHEMICAL COMPOSITION OF MINE WATER IN BANAT DISTRICT

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Environmental pollution caused by the radioactive and heavy metals is still an actual problem. There are in Romania many areas, where those phenomena are very active. The present work aims to point out and to discuss the results of the chemical analysis of mine water samples collected from a site affected by uranium mining activities. Those results are useful for the identification and development of the most appropriate treatment technologies in order to clean those mine waters according to the law enforced.

Keywords: mine water, uranium, heavy metals, chemical composition

1. Introduction

Radioactive pollution generated by uranium mining activity represents a major problem of our society. Therefore a large variety of remediation technologies such as ionic exchange [1-5], adsorption on different materials [6-30], biosorption, bioreduction [31-47], flotation [48, 49], complexing processes [49-52], co-precipitation[48,49], redox processes [53,54], solvent extraction [55-58], reverse osmosis [59], liquid membrane separation [60-62] have been developed in order to clean the contaminated water.

Romania has a rich tradition in uranium ores exploitation and processing activity located in Banat region, Eastern Carpathians and Apuseni Mountains [63-65]. From those activities large amounts of low radioactive wastes piled up in heaps and wastewaters have resulted. They consist in [64]:

- 1000 ha land surface contaminated by natural occurring radioactive elements;

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- over 150 deposits containing about 6 mil. m^3 of radioactive waste resulted from uranium ores exploitation;
- 2 tailings ponds containing at about 6 mil. tones of radioactive material resulted from uranium ores processing.

The mine waters represent another significant contributor to the environmental radioactive pollution. They result from the following resources:

- weathering water;
- water originated from the ground-water table resulted due to the infiltration of the surface water into the lithological formations of the ore body;
- underground water accumulated by the aquifers formations opened by the exploration/exploitation mining works;
- industrial water used for wet drilling mining exploitation, for dusting prevention and for the hydraulic filling of the excavation caves.

Today the mining works in Banat region are either closed or subjected to the ecological reconstruction process.

The present work aims to point out and to discuss the results of the chemical analysis of mine water samples collected from uranium mining site located in Banat region.

2. Experimental activity

Mine water samples have been collected from the following points:

- 100 m downstream creek Jitin;
- the creek underneath a low-radioactive waste pile;
- the inside of a gallery;
- the gallery entrance;
- the gallery exit;
- Natra creek before the confluence with Lisava creek;
- Lisava creek after the low-radioactive waste pile;
- Natra creek after the confluence with Lisava creek;
- Downstream Ciudanovita stream;
- Upstream Ciudanoviţa stream;
- Settling pond Ciudanovita;
- Settling pond Lisava;
- Before the wastewater treatment plant.

They have been analyzed using AAS, spectrophotometry and volumetry.

3. Results and discussions

The results of the chemical analysis of the collected mine waters samples are showed in Figs. 1-9.

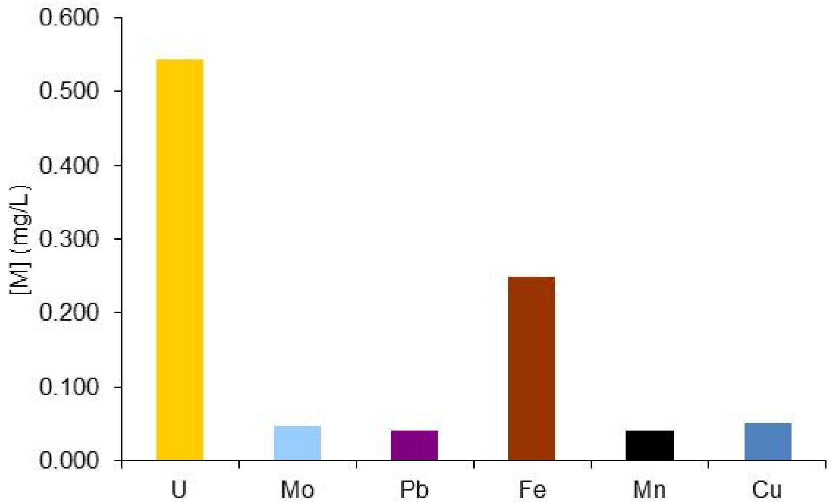

Fig.1 Radioactive and heavy metals concentration of the mine water sample collected at 100 m downstream creek Jitin

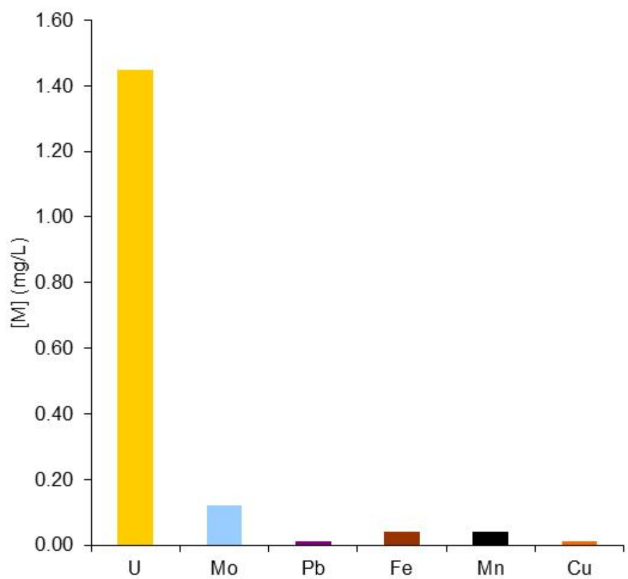

Fig.2 Radioactive and heavy metals concentration of the mine water sample collected from the creek underneath a low-radioactive waste pile

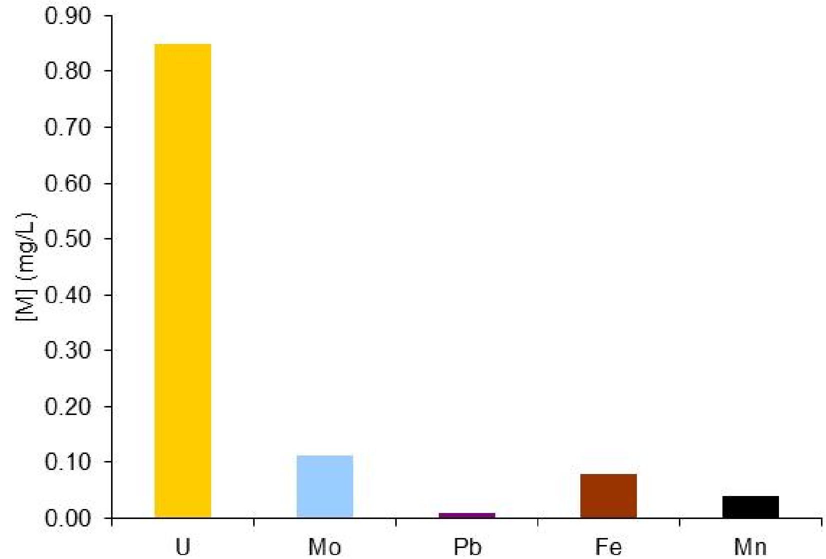

Fig.3 Radioactive and heavy metals concentration of the mine water sample collected from the inside of a gallery

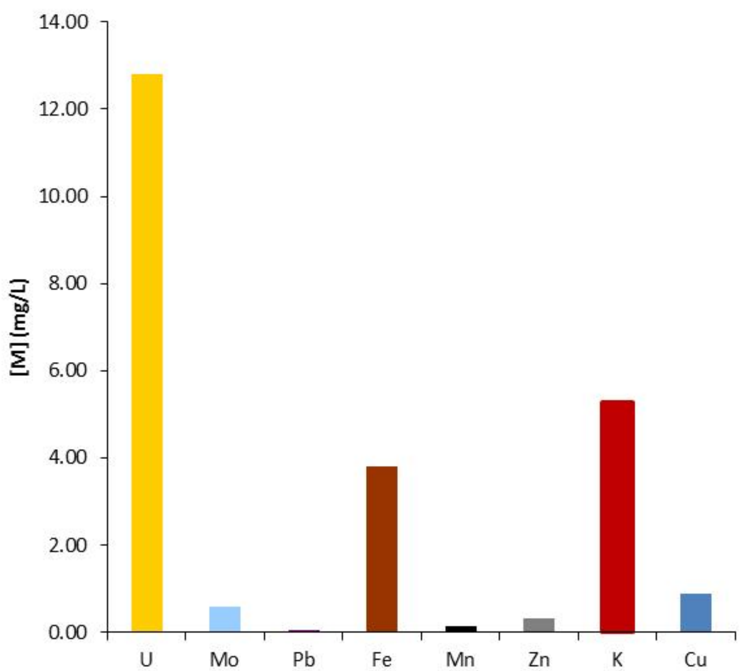

Fig.4 Radioactive and heavy metals concentration of the mine water sample collected from the gallery entrance

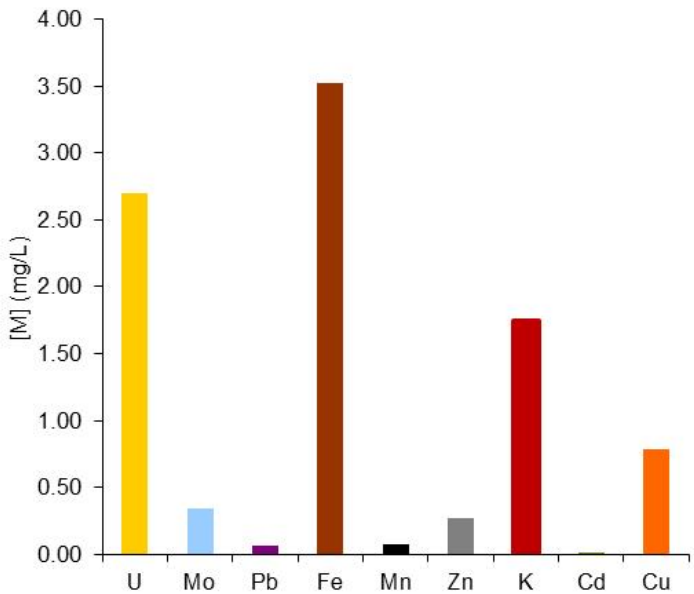

Fig.5 Radioactive and heavy metals concentration of the mine water sample collected from the gallery exit

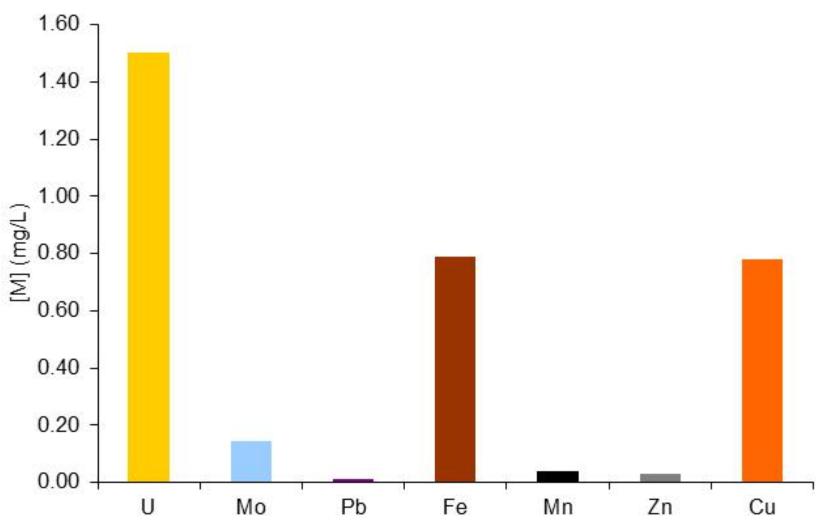

Fig.6. Radioactive and heavy metals concentration of the mine water sample collected from Natra creek before the confluence with Lisava creek

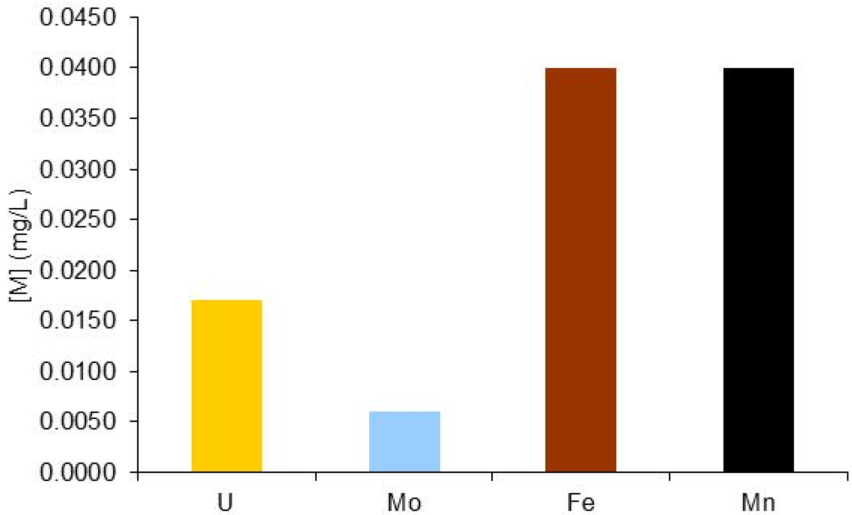

Fig. 7. Radioactive and heavy metals concentration of the mine water sample collected from Lisava creek after the low-radioactive waste pile

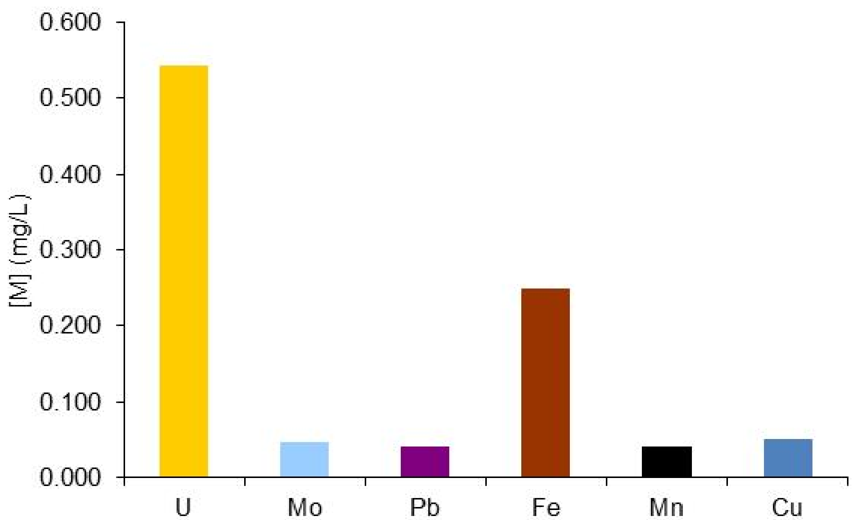

Fig.8 Radioactive and heavy metals concentration of the mine water sample collected from Natra creek after the confluence with Lisava creek

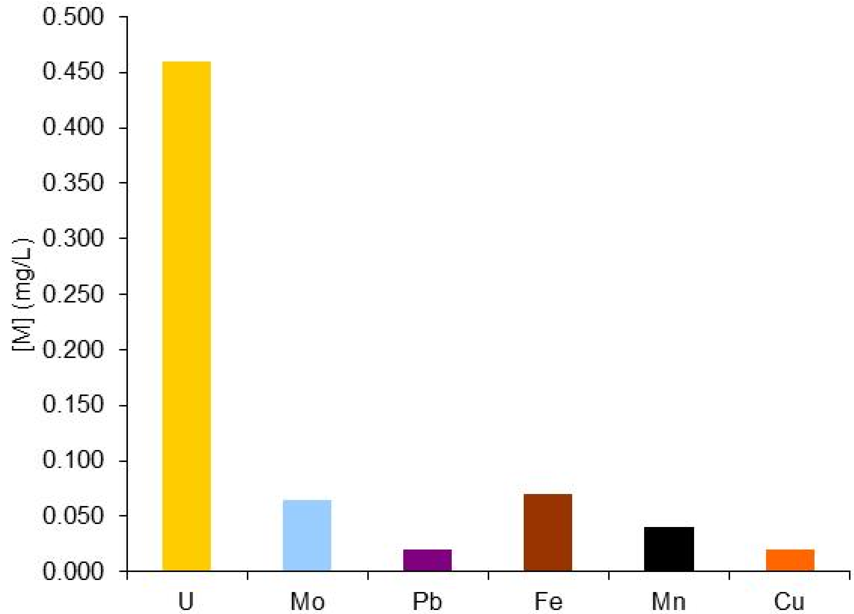

Fig.9 Radioactive and heavy metals concentration of the mine water sample collected from upstream Ciudanovita stream

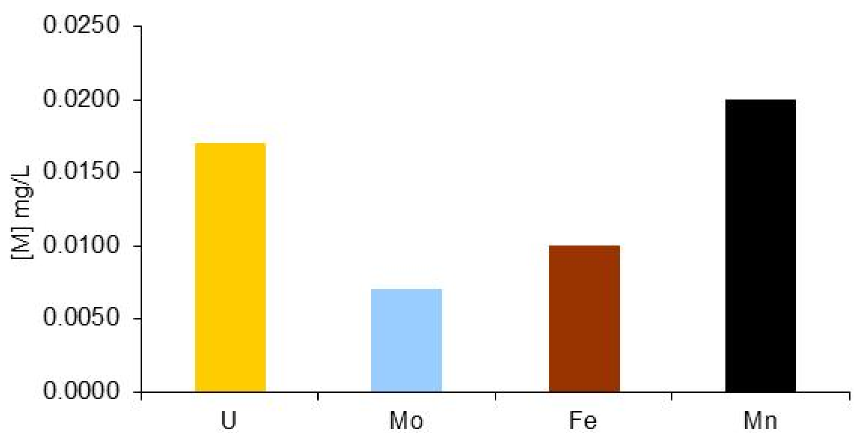

Fig.10 Radioactive and heavy metals concentration of the mine water sample collected from upstream Ciudanovita stream

It can be observed that the radioactive and heavy metals contents have a large range of variation. So that, the highest uranium (U) content is recorded by the water sampled at the entrance of the gallery, namely 12.8 mg/L (fig.3) and the smallest one by the water sampled from Lisava creek after the low-radioactive waste pile, respectively 0.017 mg/L (fig.10).

Other metals contents range as follows: iron (Fe) 0.04 mg/L (fig.2) to 3.8 mg/l (fig.5); molybdenum (Mo) 0.01 mg/L (fig.7 and 10) to 0.59 mg/L (fig.4); lead (Pb) 0.01 mg/L (fig.1-3) to 0.04 mg/L (fig.8); manganese (Mn) 0.02 mg/L (fig.10) to 0.13 mg/L (fig. 4); copper (Cu) 0.01 mg/L (fig.1 and 2) to 0.89 mg/L (fig.4); zinc (Zn) 0.03 mg/L (fig. 6) to 0.33 mg/L (fig.4); cadmium (Cd) is detectable in one sample: 0.01 mg/L(fig.5); potassium (K) is detectable only in the water sampled from the entrance and the exit of the gallery namely 1.75 mg /L (fig.5) and respectively 5.27 mg/L (fig.4).

Table 1 shows chemical composition of the mine water sampled from the settlement ponds from Ciudanovita and Lisava. All those samples were collected in autumn, when the weather was rainy.

Table 1

Chemical composition of the mine water sampled from the settlement ponds

Sample symbol	Sampling point	U mg/L	Mo mg/L	Cu mg/L	Cr mg/L	HCO_3^- mg/L	SO_4^{2-} g /L	CCO_{Mn} mg/L
A	Settlement pond Ciudanovita	0.58	0.1	0.02	0.01	0.8296	0.084	22.79
B	Settlement pond Lisava	3.12	0.371	0.20	-	1.3176	0.134	64.24

A mine water sample collected before the water treatment station in summer pointed out high concentrations of U, Mo, Cu and Cr (fig.11).

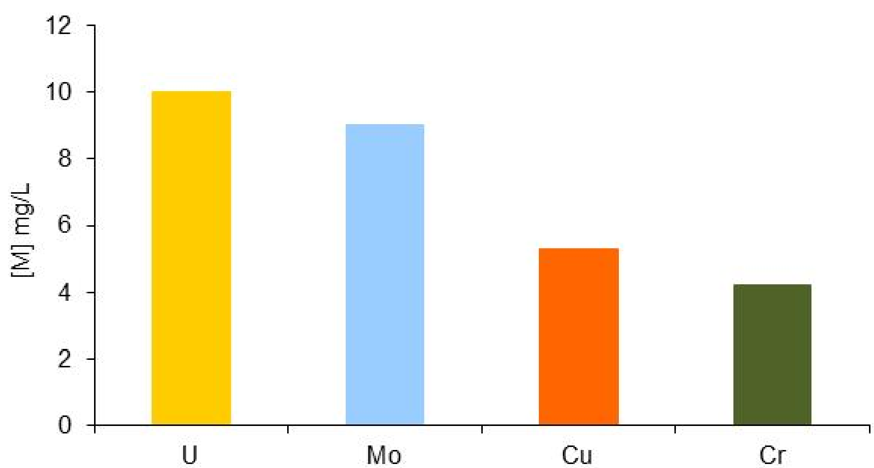

Fig.11 Radioactive and heavy metals concentration of the mine water sample collected before the wastewater treatment plant in Lisava

Table 2 shows the admitted concentrations limits of the heavy metals of the water stipulated by the law and regulations enforced [65].

Table 2

Limit values of heavy metals uptake by the sewage and industrial waste waters discharged into the hydrological network

No.	Metal	Value (mg/dm^3)	Analysis method
1	Lead (Pb^{2+})	0.2	[66]
2	Cadmium (Cd^{2+})	0.2	[67]
3	Total chromium (Cr^{3+} + Cr^{6+})	1.0	[68]
4	Hexavalent Chromium (Cr^{6+})	0.1	[68]
5	Ionic total iron (Fe^{2+}, Fe^{3+})	5.0	[69]
6	Copper (Cu^{2+})	0.1	[70]
7	Nickel (Ni^{2+})	0.5	[70]
8	Zinc (Zn^{2+})	0.5	[70]
9	Molybdenum (Mo^{2+})	0.1	[71]
10	Total manganese (Mn)	1.0	[72]

The National Government stipulates the limit value of radioactive metals uptake by the wastewater in the operation authorization of the legal entities working with this type of effluents.

The results are useful for the assessment of the heavy metals and uranium accumulation in case of a mine water containing 12,8 mg U(VI)/L, 0.586 mg Mo(VI)/L, 0.04 mg Pb(II)/L and 0.89 mg Cu(II)/L and with an average flow rate of 60 m^3/h. Figs. 12-14 display the accumulations corresponding to 1 hour, 24 hours and 1 month.

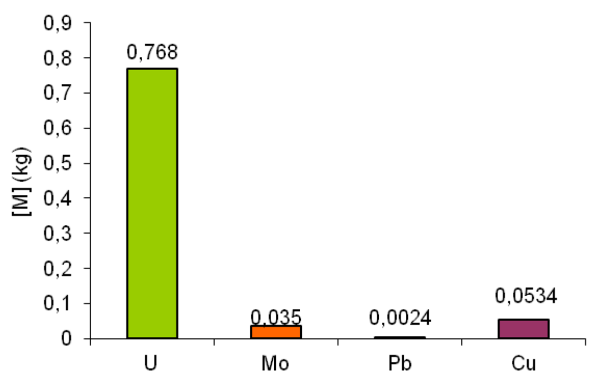

Fig. 12 Heavy metals and uranium amount accumulated in one hour corresponding to the average flow rate of 60 m^3/h

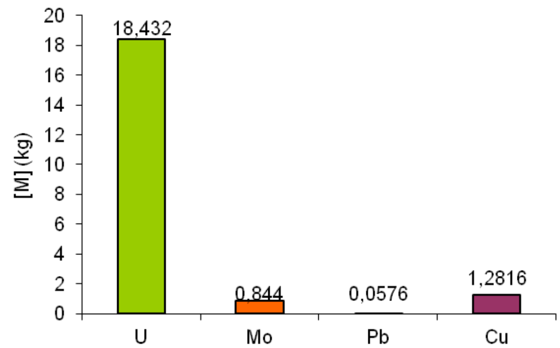

Fig. 13 Heavy metals and uranium amount accumulated in 24 hours corresponding to the average flow rate of 60 m^3/h

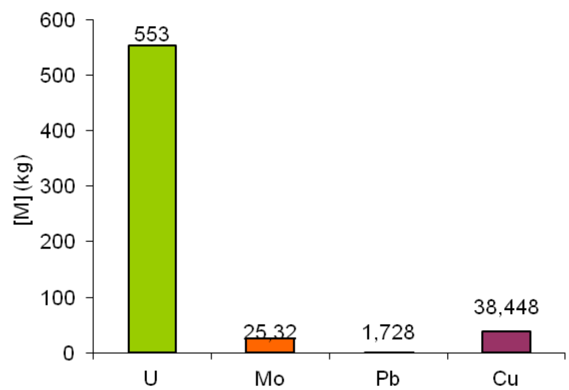

Fig. 14 Heavy metals and uranium amount accumulated in one month corresponding to the average flow rate of 60 m^3/h

4. Conclusions

The chemical analysis pointed out the presence of the contamination with uranium and heavy metals, which it is influenced by the weathering phenomena and the chemical composition of the uranium ore body. Therefore it is mandatory to develop new highly effective and environmental friendly wastewater treatment technologies. Considering the advantages and disadvantages of the main technological solutions displayed in table 3, Dissolved Air Flotation technique could be a viable solution due to its specific characteristics: selectivity, amenability, low reacting time (up to 5 minutes), small amounts of wastes generation, high separation efficiency, possibility to be applied for the separation of ionic, molecular, colloidal and micro-dispersed species of inorganic or organic nature.

Table 3

Uranium and heavy metals separation methods' advantages and disadvantages

Separation method	Advantages	Disadvantages	References
Complexing processes	Selectivity, high preconcentration capacity, efficiency.	Limited application, time consuming, expensive and toxic reagents	[1-8]
Co-precipitation	Allows separation of the dangerous pollutants in small amounts	Requires large amounts of specific reagents to remove very small amounts of contaminats resulting high volumes of toxic sludge	[48,49]
Redox processes	Pollutants immobilization, rapid separation	Reaction products instability caused by the pH variation, reagents toxicity, complex set up, toxic waste source.	[48,49]
Ionic exchange	Rapid kinetics	Weak selectivity for the metallic ions present in poor aqueous sources due to the presence of the competing ions	[1-5]
Solvent extraction	Well-defined process	Solvent loss during the extraction process, toxic and inflammable reagents utilization, third phase occurrence, environment pollutant	[6,8]
Adsorption on different materials	Relatively simple technology, industrial applicable, highly selective, chemical stability, high efficiency.	Slowly kinetics, competitive ions presence significantly decrease the adsorption efficiency, difficulties at the recovery of the uploaded material, passivity of the active surfaces, time consuming, poisoning, low mechanical resistance	[6-30]
Biosorption, bioreduction	Environmental friendly, accessible materials, selectivity, resistance to the aggressive environment	Highly expensive, biomass growing difficult conditions (nutrients, temperature, pH), limited adsorption capacity.	[31-47]
Flotation (Ion flotation, sorbtion-flotation electroflotation, precipitate flotation, colloidal adsorbing flotation etc)	High selectivity, adaptability, high separation efficiency, possibility to be applied for the separation of ionic, molecular, colloidal and microdispersed species of inorganic or organic nature.	Electro-flotation is energy-consuming, flotation with dispersed gas requires high quality and resistant porous material **therefore the Dissolved Air Flotation technique is preferred.**	[73-90]

The gas bubbles generated by pressured water expansion are homogenous and smaller-sized comparing to the ones provided by other techniques, so that they provide an optimum mass transfer from the liquid phase towards the foam increasing the separion efficiency.

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