In situ Decontamination of the Mine Waters from Uranium Mining Activities

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Experimental studies using mine waters from Banat-Romania area, in discontinuous single contact of phases led to the selection of optimal reactive materials, depending on the distribution coefficient, K_d, We established that this process parameter in connection with to the used solids respects the chain : K_d for activated carbon type AC 20 G > K_d for apatite > K_d for activated carbon type MN with P > K_d for zero-valent iron > K_d for indigenous natural zeolite from Slanic Prahova area > K_d for indigenous natural zeolite from the Mirsid area. When these materials are used for fixed bed mine water decontamination has been obtained a time increasing of uranium immobilization. In the effluent we obtained less than 0.048mg / L after 120 h for an influent having an uranium content of 1.72 mg/L. Chemical mechanisms for uranium recovery on the selected materials are appropriate for low uranium content in mine waters. The fixed bed mine water decontamination experiments shown that these material types can be used for development of permeable reactive barriers.

Keywords: uranium compounds, mine water, contamination, distribution coefficient, reactive permeable barrier

Permeable reactive barriers (BPR) are a technological procedure for polluted waters decontamination, especially for mining waters. It operates by passing of a stream with radioactive contaminated water, over a reactive material which transforms dissolved contaminants in a form friendly to the environment (degradation products less harmful or species immobilization). The BPR downstream concentration of dangerous species will be low, so permitted by the regulations in force [1, 2].

The main characteristics of BPR that distinguishes this technique from other currently used methods are: depollution technology refers only to the range of dissolved polluting substances, that is, it differs from techniques that are acting on the polluted soil, either primary or secondary sources of pollution; the BPR works passively with the respect to treated waters but inside it a species transfer and reaction occurs; the contaminant species transfer inside of BRP improves natural groundwater flow by absence of pumping or injection system, etc.; the reaction treatment in BRP uses reagents that allow degradation or adsorption of pollutants, diminishing to a minimum the intervention and maintenance frequency (at least in most situations); this technology leads to a physical separation between an upstream hydraulic compartment and a downstream one, of a polluted aqueous fluid; downstream concentration of the pollutant shall obey the conditions set by a regulatory authority;

The basic components of a permeable reactive barrier (BPR) are [4-6]:

- hydraulic component that involves the two major types of configuration: the continuous wall system, figure 1, the most commonly used in North America (Continuous Wall-CW or Continuous Reactive Wall-CRW) and the Funnel & Gate-F & G system, figure 2, the most commonly used in Europe;
- reactive component is composed of materials that lead to reactive pollutant removal from water treated by different processes (chemical degradation, chemical shape modification and adsorption,etc).

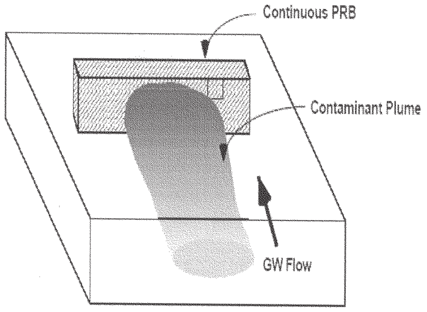

Fig. 1 .BRP continuous well

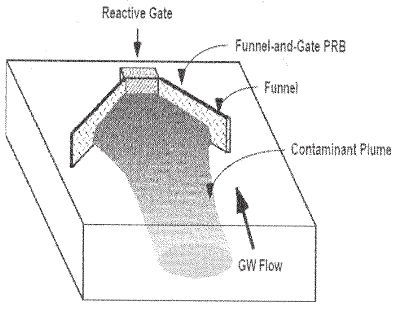

Fig. 2. BRP Funnel & Gate

International researches [7] on a wide range of materials used for uranium mine waters show that the decontaminations by BRP are adsorption, substitution and precipitation based. Reactive materials tested with satisfactory results for permeable reactive barriers of adsorption or substitution are the activated carbon, ion-exchange resins, iron (III) oxides and oxi-hydroxides, magnetites, peats, humic salts, lignites, coals, phosphate compounds, titanium oxides and zeolites. The optimum reactive materials for the precipitation inside of reactive barriers are biodegradation microorganisms, iron (II)

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carbonate, iron (II) hydroxide and iron (II) sulphide, ashes, limestones, mixtures of magnesium hydroxide and carbonate with sulphate and chloride of calcium and barium.

Reactive materials that induce adsorptive reactions (including ion exchange) are best known in the groundwater remediation industry. For best utilization, the reactive materials that lead to advanced decontamination must accomplish a number of essential conditions especially to be hydrophobic, insoluble and easily to use. Good results for treatment of uranium contaminated waters are obtained for appropriate reactive materials such as grainy activated carbon, phosphates compounds (apatite), zeolites and clays type materials (montmorillonite based).Reactive materials that induce precipitation reactions of uranium from mine waters are compounds of divalent iron, limestone, limes, or other calcium carbonates [8].

The paper aim is related with the testing and characterization of some reactive materials identified as proper for permeable reactive barriers, which can be used in decontamination of water from Banat mine area. Batch discontinuous phases contacting has been used for species equilibrium distribution whereas for dynamics species retentions the phases contacting with solid in fixed bed give the results appropriate to the case of BPR.

Experimental part

For laboratory experiments with batch phases contacting and with column fixed bed phases contacting was used mine water from Banat area. The following composition characterizes this water type: U - 1.72mg/L, Mo - 0.26mg/L, Na - 205mg/L, K - 6.25mg/L, Ca - 29.31mg/L, Mg - 21.1mg/L, Al - 1.74mg/L, Fe - 0.3mg/L, $HCO3^-$ - 731mg/L. Other important water parameters are *p*H = 8.4, Eh = 233mV, electrical conductivity μ=1015μS.

The batch contacting phases tests were used to determine the distribution coefficient, K_d, for different types of solid active material and to determine the mean contaminant rate removal. When we have experimental batch equilibrium data , the below relation is used for distribution coefficient of contaminant between solid and liquid [9]. Here c_i represents the initial concentration of contaminants in solution, c_f shown the equilibrium concentration of contaminants in the final liquid solution, m gives the mass of solid active material whereas V shown the volume of solution.

$$Kd = ((c_i-c_f) / m) / c_f / V) \qquad (1)$$

The tests consisted in: measuring the volume (V) of solution containing a known contaminant concentration (c_i); mixing the solution with active solid material weighing m grams; stiring the system for a time characterizing the equilibrium touching; phases separation by filtration and measuring of the contaminant concentration from filtered solution (c_f). The major benefit of this method is that it allows rapid determination of reactive capacity to retain the contaminant. The method is used only for selecting the most suitable reactive materials used, without allowing the data extrapolation in continuous system because the water pass through the column with a certain flow rate which determines the amount of fixed species in BPR. More directly this amount is dependent process reaction rate and phases time contact.

Active materials tested were two types of activated carbon (AC 20 G - Purolite type and MN - P - IPC Ploiesti type), natural zeolite from the Mirsid and Slanic Prahova areas, apatite and organic iron based microgranules (zero-valent iron). The working conditions were:the solid-liquid ratio 1:50; temperature- 20-25^{0}C; electromagnetic stirring with constant rotation speed and suspended solid; phases contacting time - 60 min.

Phase's separation was made by filtration using ceramic filters type Büchner with support filter paper SARTORIS 390. Analytical methods used to establish the liquid phase composition (see K_d expression) depends on the analyzed elements. It was used atomic absorption by mean of an atomic absorption spectrophotometer VARIAN spectrAA-880, colorimetry using the colorimeter UV-VIS CECILIA 1011 type, volumetric and gravimetric analysis. Ph measures were performed with a WTW *p*H electrode Sen Tix 41 coupled to a pH-meter InoLab. The redox potential measures was done with a combination redox electrode INGOLD coupled to a *p*H/mV meter METTLER DELTA 340. State of electrical conductivity was obtained with an electrode coupled to an analyzer type Consort C832 Belgium.

Column experiments were made to simulate more realistic the dynamic conditions that occur in an active (reactive) barrier and to quantify the contaminants retention on reactive material from barrier. The process factors specific for retention of uranium on the studied reactive materials are [10] flow rate of mine water through the column which fix the contact time between water and reactive material, the granulation of reactive material which give the contacting solid bed and the uranium content of water feeding the fixed bed column (in our case this process factor has fixed at a constant value).

Taking into account some data [3, 5, 12] which consider that the kinetics of uranium immobilization reactions from mine waters presents a low rate , the feeding flow from the previous experience was chosen as 0.5 BEV/h (BEV-filling equivalent volume). With the aim to have a higher surface area the reactive materials granulation used in the experiments was, for all solids cases, less than 0.2 mm.

Study of process variables on the mine waters decontamination has been achieved using a glass column of 720mm long and 70mm diameter, with a multi-layers filling. A 2000 mL fixed bed volume of reactive materials (zero-valent iron, treated Slanic Prahova zeolite, activated carbon type AG and apatite) gives the active part of the working column. To ensure the mine water flow through the filling layers and to avoid reactive materials mixing was done the layers separation by sand layers of 0.8 - 1mm granulation. At the bottom of the column was added a permeable layer of gravel and sand. For zero-valent iron, zeolite and apatite, because of low particle granulation (less than 0.2 mm) was made a mixture with sand of 0.8 - 1 mm granulation in a percentage of 30%.

Mine water feeding was done by the free flow, adjusted at the exit of the column to kept a 0.5 BEV / h flow rate. Samples, for analysis of liquid phase composition, were collected every 24 h.

Results and disscusion

Our used solids to be reactive with respect to the water contaminant has been treated following specific procedures, below presented.

Granular activated carbon for uranium polluted water decontamination

To increase the decontamination characteristics of granular activated carbon an impregnation with iron ions has used. The following techniques has been used for iron

Table 1
IRON IMPRINTED ACTIVATED CARBON PROPERTIES

Impregnation method	Specific surface m^2/g	Toral volume of pores cm^3/g	Volume of micropores cm^3/g	pH	Iron content mgFe/g carbon
a	778	0.724	0.295	6.8	36.2
b	762	0.726	0.296	6.9	78.8
c	832	0.752	0.321	7.5	20.9
d	772	0.690	0.301	6.1	87.3
e	836	0.783	0.31	5.4	31.6
f	863	0.781	0.325	5.5	30.9

impregnation [11-13]; table 1 gives the characteristics of interest of each iron activated active carbon solids.

Ion exchange: acid washing of carbon followed by mixing with $FeCl_3$ and then drying in nitrogen atmosphere at 800^0C ;

Iron hydroxide precipitation: acid washing of carbon, mixing with $FeCl_3$, increasing *p*H to 11 with sodium hydroxide and filtering or after mixing with $FeCl_3$, separation, immersion in 0.1 N NaOH solution followed by filtration, washing and drying;

Organic complexion with iron: after acid washing and drying, carbon is mixed with a solution of an organic compound of iron, and the wet product is drying to 800^0 (d);

Zero -valent iron method: after acid washing and thermal treatment, carbon is mixing with $FeCl_3$, is reduced by wet chemical reaction and filtered or mixed with $FeSO_4$ solution in nitrogen atmosphere, followed by oxidation with air at controlled *p*H.

Iron impregnation leads to increase selectivity of activated carbon for uranium and therefore its capacity related to uranium, without altering the specific surface (> 760 m^2/g to 260 m^2/g of metal oxides), which is reflected in the high uranium retention capacity.

Tables 2 and 3 presents the activated carbon Purolite AC 20G and activated carbon type MN - P used in experiments.

Apatite [$Ca_{10}(Po_4)_6(OH)_2$] for uranium water decontamination

This material represents a group of phosphate minerals with metallic ions immobilization properties by adsorption, precipitation or co-precipitation, leading to compounds with an extremely low solubility: $Ca(UO_2)_2(PO_4)_2 \times 10H_2O$ having log K_{ps} = - 49. There are used a wide variety of natural phosphate and those obtained from the burning of bones or synthesis. Special properties presents apatite II resulted from the processing of fish bones. It has the composition: $Ca_{10-x}Na_x(PO_4)_{6-x}(CO_3)_x(OH)_2$ where x <1. Apatite II is completely carbonated, so no fluorine, is microporous and amorphous with nano-crystals. Apatite II can hold uranium over 20% of its weight. Apatite II structure is presented in tigure 3. Apatite characteristics used in experiments are presented in table 4.

Table 2
PUROLITE AC 20G ACTIVATED CARBON CHARACTERISTICS

Physical characteristic :	
Shape	Cylindrical grains with black colour
Humidity content	max 2%
Total surface	900 – 1000 m^2 / g dry product
Grain Effective size	0.6 – 2.4 mm 0.9 – 1.10 mm
Uniformity coefficient	1.7 – 1.8
Bulk density	480 g/ L
Density in water	1.4 g/mL

Table 3
ACTIVATED CARBON TYPE MN-P CHARACTERISTICS
APATITE CHEMICAL ANALYSIS

Physical characteristic :	
Bulk density	0.331 g/cm^3
Benzene equilibrium adsorption capacity (32mg/L)	38.37 %/g
Friability – mixed in ball mill	3.15%
Ash content	3.18%
Specific surface	1007.7 m^2/g

Table 4
APATITE CHEMICAL ANALYSIS

Element	**Concentration, %**
CaO	47
P_2O_5	44.38
Al_2O_3	0.32
Fe_2O_3	0.34
SiO_2	1.7
MgO	1.53
K_2O	0.007
Na_2O	0.93
TiO_2	0.007
Humidity	0.45
Granulometry	100% <0.2mm

Table 5
SLANIC PRAHOVA ZEOLITE CHEMICAL ANALYSIS

Element	Concentration, %
SiO_2	57.5
Al_2O_3	12.25
Fe_2O_3	2.14
CaO	3.65
MgO	1.16
K_2O	3.8
Na_2O	0.88
TiO_2	0.17
Humidity	4.8
Granulometry	100% <0,2mm

Table 6
MIRSID ZEOLITE CHEMICAL ANALYSIS

Element	Concentration, %
SiO_2	62.24
Al_2O_3	12.39
Fe_2O_3	1.003
CaO	3.09
MgO	0.59
K_2O	3.55
Na_2O	0.64
TiO_2	0.16
Humidity	6.13
Granulometry	100% <0.2mm

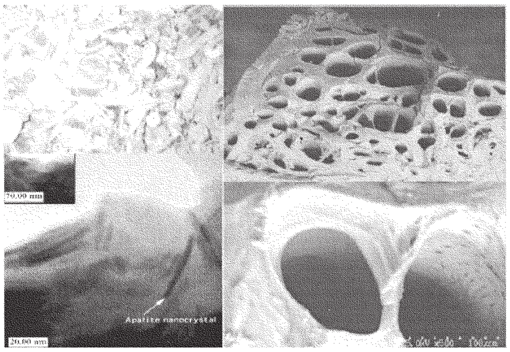

Fig. 3. Apatite II structure

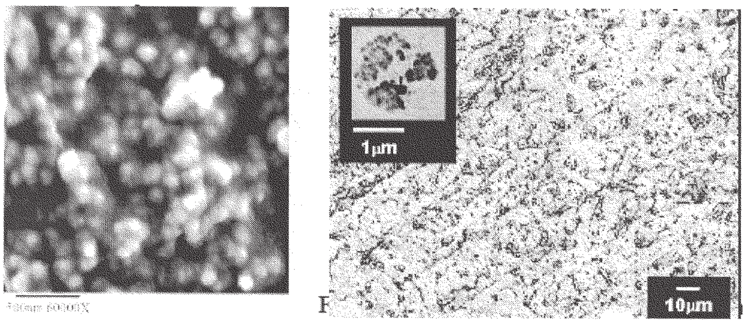

Fig. 4. Zero-valent iron structure

Zeolites represent a wide class of porous alumino-silicates compounds.

A crystalline structure characterizes these materials. The used stoichiometric formula is $M_{x/m}[(AlO_2)x(SiO_2)y]zH_2O$ where M is a cation of m valence, z is the number of water molecules per unit cell, and x and y are integers such that y/x is equal to or greater than 1. The properties contributing to their use for polluted water decontamination are ion exchange capacity, high specific surface and high hydrothermal stability. Large specific area is assigned to the porous structure. The Mirsid Slanic Prahova natural zeolite characteristics are listed in tables 5 and 6.

Zero-valent iron solids for uranium water mine decontamination

This material is the most used for building of reactive permeable barriers. Nano-structured zero-valent iron synthesis lead to obtaining a product with a large specific surface and increased reactivity against granular iron. This leads to extend the treatment for a wide range of pollutants and reducing the generation of hazardous products. The nano-particles ability to react as a strong reducer increases the range of pollutants that can be treated. Nano-particles of zero-valent iron has a diameter ranging between 100 and 200 nm (fig. 4), and the used material characteristics used are presented in table 7.

Table 7
ZERO-VALENT IRON CHARACTERISTICS MERCK

Characteristic	
Iron content	99 %
Density	6.7-7.2 g/cm^3
Apparent density	2.7-2.9g/cm^3
Granulometry	100% <0.2mm
Ion Exchange capacity	1.5meq/g
Specific surface	0.0482 m^2/g

Our first experimental results, obtained after performing the batch contacting tests for uranium immobilization from mine water on reactive materials, show the distribution coefficient k_d. Figure 5 shows that k_d decreases as follows: k_d for activated carbon AC 20G (CA-AG) > k_d for apatite (F.O)>k_d of activated carbon MN - P (CA-MN - P) > k_d for zero-valent iron (FeZV)>k_d for Slanic Prahova natural zeolite (Z-SP)>k_d for Mirsid natural zeolite (ZM).

For column experiments the dynamics of U, HCO_3^-, Fe, Ca, Mg concentration and also of *p*H , of redox potential and of electrical conductivity[13, 14] in the column effluent has been registered. Firstly here we report the case of uranium concentration dynamics. This dynamics relieves that at the beginning the uranium content decrease is low, then becomes faster and after 120 hours of operation uranium concentration decreases below the detection limit of the dosage method (0.048mg/L). Figure 6 shows that the same low uranium concentration value is found after 720 h of operation; that demonstrates the efficiency of the chosen method,

Looking to figure 7 we observe that the dynamics of carbonate concentration decreases in the beginning, returns to the initial concentration value and after 216 h of operation the content of HCO_3^-, decreases again.

For all cases of column experiments it was observed that iron ions from initial solution of concentration near to 0.3 mg/L, appears in the effluent at very small concentration (under 0.001 mg/L) This fact shows that the iron ions solution are immobilized on the column and there are no passage in the effluent of iron soluble compounds. So this immobilization and also the interaction of iron from solids with liquid media create in time inside of solid phases of one physical structure which interact with retained uranium compounds, and other species.

Cationic concentration of calcium and magnesium increased after the first volume, probably due to the solubilisation of the soluble compounds from the sand, then

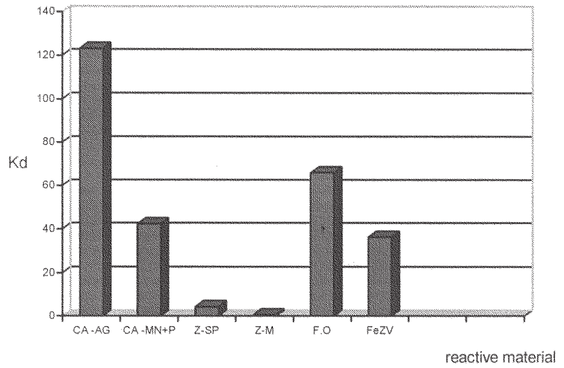

Fig. 5. Distribution coefficient vs.reactive material

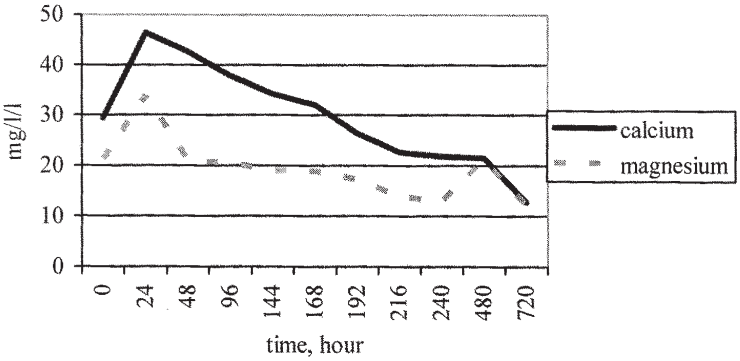

Fig. 8. Calcium and magnesium concentration vs. contact phases time

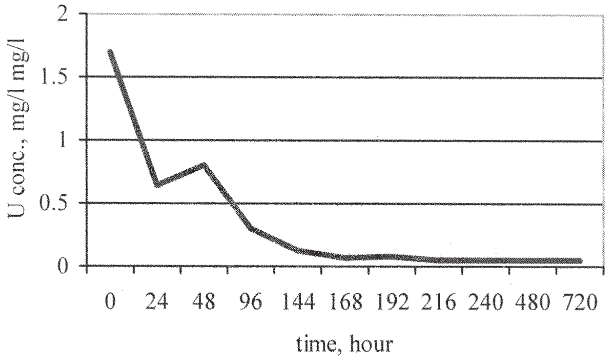

Fig. 6. Uranium concentration vs.contact phases time

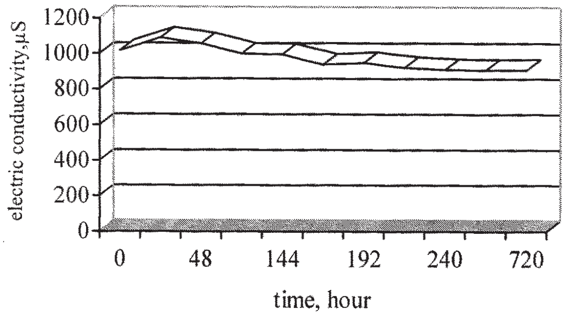

Fig. 9. Electric conductivity variation vs. phases contact time

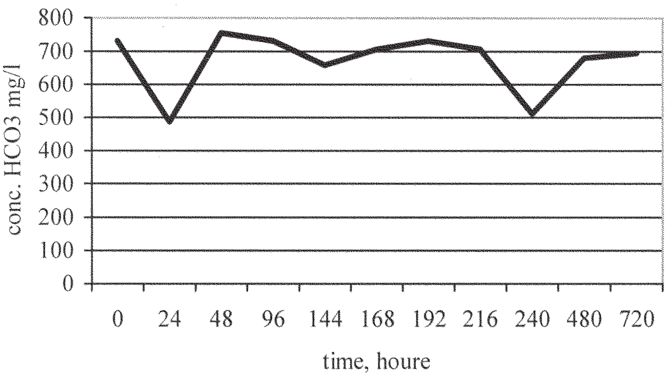

Fig. 7. Carbonate concentration vs.contact phases time

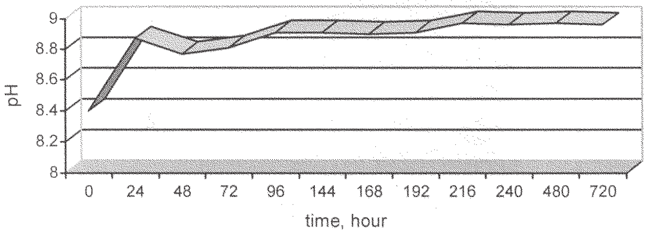

Fig. 10. pH variation on contact phases time

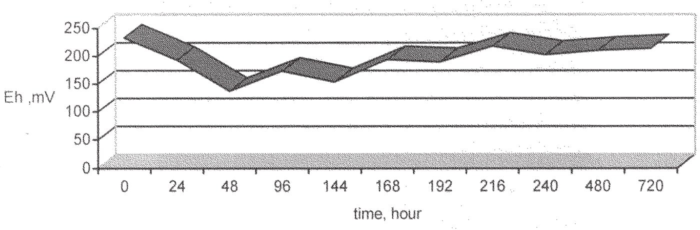

Fig. 11. Redox potential variation vs.contact phases time

is showed a constant decrease as a result of the insoluble compounds formation or as their adsorption,(fig. 8).

Calcium and magnesium content variation is approached by electrical conductivity determinations of the solutions that have a similar behaviour, which is normal because the electrical conductivity values are represented by ions concentration from solution,(fig. 9).

As seen in figure 10, after 24 h the *p*H increase from 8.4, as it is in the initial sample to 8.87 after which the value remains practically constant with a slight increase trend. Regarding redox-Eh potential, Figure 11, is found that in the first volume is a decrease of its value from 233 mV, in initial mine water, to 137mV and then, in the following volume to increase frequently with the tendency to return to the initial value, demonstrates an equilibrium of the occurred oxido-reduction processes.

Conclusions

For achieving a permeable reactive barrier to remove the contaminants from mine waters is necessary to perform laboratory scale treating tests. Laboratory tests are needful for the appropriate reactive material identification, to determine the contaminants mechanism and removal rate, to determine the influence of secondary reactions and to obtain the process parameters. The main experimental conclusions are as follows:

- there were performed two types of experiments using mine water from Banat mining area; these are based on discontinuous batch phases contacting and column fixed bed phases contacting;
- for selection of optimal reactive materials the experiments with discontinuous phases contacting give the k_d values; its decrease in the order k_d for activated carbon AC 20G> k_d for apatite> k_d for activated carbon MN - P> k_d for zero-valent iron> k_d for Slanic Prahova natural zeolite >k_d for Mirsid natural zeolite;
- process parameters that influence the uranium retention on the studied reactive materials in dynamic behaviour are the flow rate of mine water passing through the column (0.5 BEV/h inn reported data) by fixing the value of contact time between water and reactive

material, the grain of the reactive material by content and by dimension (under 0.2 mm) who give the value of solid specific area;

- uranium concentration from taken samples decreases below the detection limit of the dosage method (0.048mg/L); the same low value is found after 720 h of operation which demonstrates the efficiency of the chosen method;
- laboratory tests performed to study the ionic composition of mine waters provide information regarding precipitate formation in the reactive material caused by redox potential and pH conditions changing. Speed of precipitate formation may also influence the operation mode and maintenance requirements of contaminants removal systems;
- chemical processes of retention on the studied reactive materials are the reductive precipitation for zero-valent iron and adsorption on the apatite surfaces, activated carbon and natural zeolites;

From the obtained experimental data can be concluded that the reactive materials selection has been well accomplished regarding the uranium mine waters decontamination. These data represent the basis for the design parameters used to determine the residence time of the contaminant inside the reactive material and from here the thickness of a BPR

BPR offers a low cost alternative to classical methods of ex-situ treatment with advanced decontamination. Effects of environmental impact and health from uranium mining areas are immediately and for long term.

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Manuscript received: 3.03.2009