Uranium Immobilization on Reactive Material Using RPB

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Abstract: The paper present the researches on the characterization and probation reactive materials identified as optimal for permeable reactive barriers (RPB) accomplishment, which can be used in mine water decontamination. Experimental studies using mine waters from the Banat-Romania area, in discontinuous system, led to the selection of optimal reactive materials, depending on the distribution coefficient, K_d, namely: activated carbon type AC 20 G > apatite > activated carbon tip MN + P > zero-valent iron > indigenous natural zeolite from the Slanic Prahova area > indigenous natural zeolite from the Mirsid area. These materials were used for experiments in the continuously system for a multilayer column and the established process parameters - the flow rate of mine water through the column (0.5 BEV/h) and therefore the contact time between phases, grain of reactive material (<0.2 mm) and feeding uranium content (1.72 mg / l), lead to high immobilization of uranium (<0.048mg / l after 120 hours). Chemical mechanisms for uranium recovery on the selected materials are appropriate for low uranium content in mine waters. Laboratory tests performed on the column have followed besides uranium immobilization on reactive material, variation and concentration of carbonate ions, iron, calcium, magnesium and variation of pH, redox potential and electrical conductivity of mines water. These data provide information on the possibility of precipitates formation in the reactive material, which may affect the operating manner and maintenance requirements for systems to remove inorganic contaminants from permeable reactive barriers. Utilization of these types of materials for permeable reactive barriers, lead to high decontamination of mine water from uranium mining activities, according to environmental quality standards.

Keywords: permeable reactive barriers (BRP), uranium, decontamination, mine water

1. Introduction

Permeable reactive barriers (BPR) is a technology for polluted waters decontamination based on underground location in the stream path of radioactive contaminated water, of a reactive material which transforms dissolved contaminants in a form friendly to the environment (either by degradation products less harmful, either by immobilization) so that downstream concentration will be permitted by the regulations in force [1,2]. International researches [3] on a wide range of materials used for uranium mine waters decontamination by BRP are the adsorption or substitution and precipitation. Reactive materials tested with satisfactory results for permeable reactive barriers of adsorption or substitution are: activated carbon, ion-exchange resins, iron (III) oxides and oxi-hydroxides, magnetite, peat, humate, lignite, coal, phosphate, titanium oxide and zeolite. The optimum reactive materials for the precipitation reactive barriers are: biodegradation microorganisms, iron (II) carbonate, iron (II) hydroxide and iron (II) sulphide, ashes, lime stone, zero-valent metals and mixtures of magnesium hydroxide and carbonate with sulphate and calcium chloride and barium chloride.

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: to be hydrophobic, insoluble and easily to use. Good results for the uranium decontamination are obtained for the appropriate reactive material : grainy activated carbon, phosphates compounds (apatite), zeolites and clays type materials (montmorillonite). Reactive materials that induce precipitation reactions of uranium from mine waters are: zero-valent iron, compounds of divalent iron, lime stone, lime, or other calcium carbonate. The widest application has zero-valent iron [4].

The work being presented research on the characterization and testing (in the discontinuous and continuous system) reactive materials identified as optimum for permeable reactive barriers performed, which can be used in decontamination of water from the Banat-Romania mine area.

2. Experimental

For laboratory experiments in the discontinuous behaviour and on columns was used mine water from the Banat-Romania area with the following physico-chemical characteristics: 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, pH - 8.4; Eh - 233mV, conductivity - 1015µS.

The discontinuous tests were used to determine the distribution coefficient, K_d, for different types of reactive material and to determine the speed of contaminant removal. Coefficient distribution is defined as the ratio between the amount of contaminant adsorbed on the solid and the amount of contaminant left in solution at equilibrium and is calculated with the Relation 1 [5]:

$$K_d = \frac{c_i - c_f}{m} \cdot \frac{V}{c_f} \qquad (1)$$

Where, c_i = initial concentration of contaminants in solution, c_f = concentration of contaminants in the final solution, m = mass of solid reagent material, V = volume of solution (density of waste water can be considered 1g/cm³). Reactive materials tested were: two types of activated carbon: Type AC 20 G - Purolite and type MN + P - IPC Ploiesti; natural zeolite from the Mirsid and Slanic Prahova areas; apatite; zero-valent iron. The working conditions were: the solid-liquid: 1:50, temperature: ambient; electromagnetic stirring with constant speed, operating time during 60 min.

Phase's homogenization was made with a magnetic stirrer, type IKA RH-KT/C and their separation was made by filtration using ceramic filters type Büchner with support filter paper SARTORIS 390, attached to a vacuum pump type KNP NEUBERGER LaboPort. Analytical methods used depends on the analyzed elements: atomic absorption - using an atomic absorption spectrophotometer VARIAN spectrAA-880 with appropriate lamps, colourimetry - using colorimeter type UV-VIS CECILIA 1011, volumetric and gravimetric analysis. pH measures were performed with a WTW pH electrode Sen Tix 41 coupled to a pH-meter InoLab and red-ox potential measures was done with a combination red-ox electrode INGOLD coupled to a pH/mV meter METTLER DELTA 340. Electrical conductivity was measured with an electrode coupled to an analyzer type Consort C832 Belgium.

Taking into account the kinetics of uranium immobilization reactions from mine waters is slow, the feeding flow from the previous experience and was chosen as 0.5 BEV/h (BEV-filling equivalent volume). Reactive materials granulation used in the experiments was for zero-valent iron, zeolite and apatite, less than 0.2 mm, in aim to have a higher surface area.

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 (2000ml) of reactive materials like zero-valent iron, treated Slanic Prahova zeolite, activated carbon type AG and apatite. 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, and on the bottom of the column was added a permeable layer of gravel and sand.

For zero-valent iron, zeolite and apatite, because of granulation < 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, the flow is adjusted at the exit of the column and kept at 0.5 BEV / h. Samples were collected every 24 hours.

3. Results and discussion

Experimental results obtained after performing the discontinuous tests for uranium immobilization from mine water on reactive materials, show the distribution coefficient k_d values, Fig. 1, which decreases as follows: activated carbon AC 20G (CA-AG) > apatite (F.O)> activated carbon MN + P (CA-MN + P) > zero-valent iron (FeZV)> Slanic Prahova natural zeolite (Z-SP)> Mirsid natural zeolite (ZM).
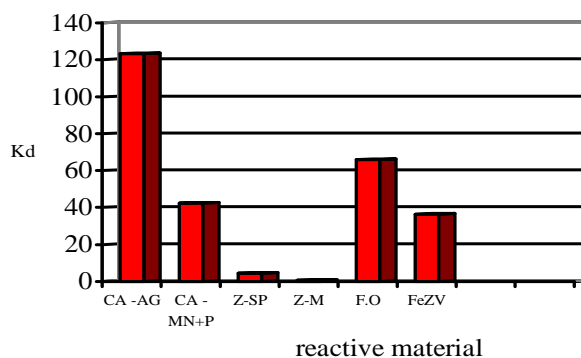

Figure 1. Distribution coefficient against reactive material

Experiments achieved in the column, have followed the uranium concentration variation U, HCO_3^-carbonate, Fe, Ca, Mg, the pH, red-ox potential and electrical conductivity [6, 7]. The study of uranium concentration variation relieve that at the beginning the uranium content decrease is slow, then becomes faster, that after 120 hours of operation uranium concentration decrease below the detection limit of the dosage method (0.048mg/L). The same low value is found after 720 hours of operation which demonstrates the efficiency of the chosen method, Fig. 2.

Regarding the variation of carbonate concentration is found that after decreasing in the beginning, than the value returns to the initial concentration value, but after 216 hours of operation the content of HCO_3^-, decrease again, Fig. 3.

The iron content from initial solution is quite small, 0.3 mg/L, and after the first volumes of water past the content decrease below 0.001 mg/L, which shows that the iron in solution is immobilized on the column and there are no passage in the solution of iron soluble compounds that might form as a result of the large amount of zero-valent iron.
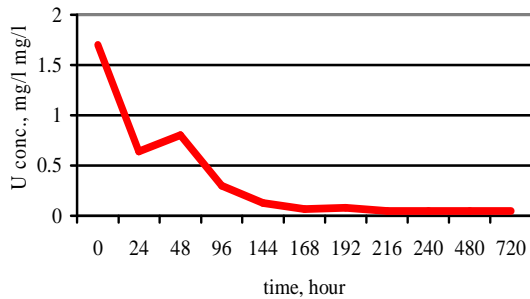
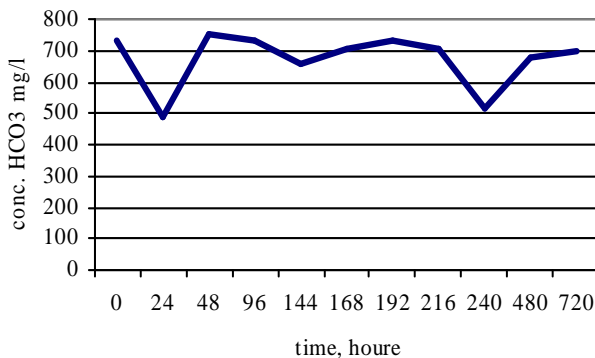Figure 2. Uranium concentration against contact phases time

Figure 3. Carbonate concentration against contact phases time

Cationic concentration of calcium and magnesium increased after the first volume, probably due to the solubilization of the soluble compounds from the sand, than is showed a constant decrease as a result of the insoluble compounds formation or as their adsorption, figure 4.
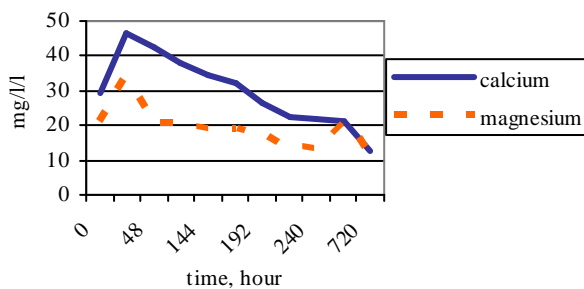

Figure 4. Calcium and magnesium concentration against contact phases time

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, Figure 5.
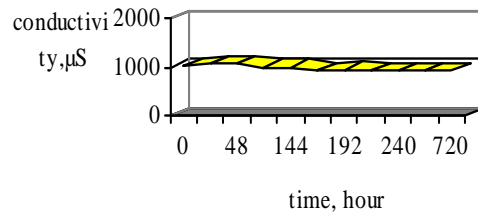

Figure 5. Electric conductivity variation against phases contact time

As seen in Fig, 6, after 24 hours the pH 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 red-ox-Eh potential, Fig. 7, is found that in the first volume is a decrease of its value from 233 mV, in initial mine water, to 137mV and than, in the following volume to increase frequently with the tendency to return to the initial value, demonstrate an equilibrium of the occurred oxido-reduction processes.
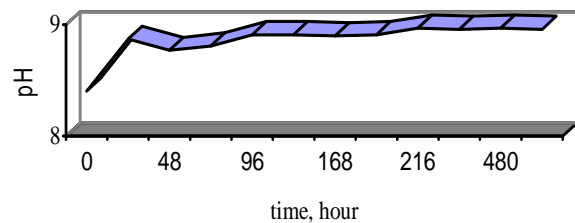

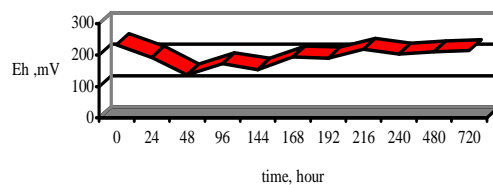Figure 6. pH variation on contact phases time

Figure 7. Red-ox potential variation against contact phases time

4. Conclusions

For achieved 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:

1) were performed two types of experiments using mine water from Banat-Romania mining area: in the discontinuous static behaviour and in dynamical system on the column;

2) for the selection of optimal reactive materials the experiment was performed in a discontinuous system in experimental conditions identical for each type of reactive material, determining the values of the distribution coefficient K_d; from experimental data results that the K_d values decrease in the following order: activated carbon AC 20G> apatite> activated carbon MN + P> zero-valent iron> Slanic Prahova natural zeolite>Mirsid natural zeolite;

3) process parameters that influence the uranium retention on the studied reactive materials in dynamic behaviour are: the flow of mine water passing through the column, the contact time between water and reactive material, grain of the reactive material, under 0.2 mm to have a specific area as large as possible and the feeding uranium content, which is constant, 0.5 BEV / h;

4) 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 hours of operation which demonstrates the efficiency of the chosen method;

5) laboratory tests performed to study the ionic composition of mine waters provides information regarding precipitate formation in the reactive material caused by red-ox potential and pH conditions changing. Speed of precipitate formation may also influence the operation mode and maintenance requirements of contaminants removal systems;

6) chemical processes of retention on the studied reactive material are: reductive precipitation for zero-valent iron and adsorption on the apatite surfaces, on the activated carbon and natural zeolites;

From the obtained experimental data can be concluded that the reactive materials selection has been good accomplished concerning scope uranium mine waters decontamination. These data represent the basis for the design parameters used to determine the stationary time of the contaminant on the reactive material and the thickness of the treatment area.

Upon the whole, permeable reactive barrier 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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