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Research Article

Hybrid Composite Materials for Immobilization of Radionuclides in Liquid Radioactive Waste

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Abstract

The biphasic hybrid composite materials for immobilization and fixation of radionuclides of the Liquid Radioactive Waste (LRW) of the research water-water reactor KIR WWR-K have been studied. It was found that the hybrid compositions have a high synergistic effect regard to the sorption of radionuclides, especially $^{137}\text{Cs}^+$ and $^{134}\text{Cs}^+$. The distribution coefficient of cesium radionuclides in the composite materials are 2 times higher in comparison with the those sorption activity in the mineral matrix. It has been established that the sorption of radionuclides by two-phase hybrid compositions is carried out by a combination of three mechanisms. Firstly, due to the electrostatic binding reaction between the functional groups of sorbents and metal ions stabilized by the system of coordination bonds with electron-donating nitrogen and oxygen atoms of the amino and carbonyl groups of the polymer matrix. Secondly, as a result of ion exchange between counterions of the mineral matrix and radionuclides ions in the environmental solution.

Finally, due to the superequimolar absorption of radionuclides as a result of deformation of the crystal lattice of mineral fillers of the polymer matrix of bentonite and copper ferrocyanide, which increases their pore size. It has been shown that biphasic hybrid composite materials have an increased mechanical and radiation resistance while retaining elasticity even at high doses of electron irradiation, at which in despite on a noticeable decrease the value of deformation there is no significant decline in their compressive strength. The obtained information on the mechanism of binding of biphasic hybrid composite materials with various metal ions makes it possible to synthesize new classes of materials for selective sorption of certain types of radionuclides in the body of mineral and polymer matrices. This will allow us to use these materials as a highly effective sorption materials with a synergetic effect for the detection, identification, immobilization and fixation of LRW radionuclides.

Introduction

Modern trends in the area of radioactive waste stabilization are intended to developing the technologies for disposal of any radioactive materials in the environmentally safe and acceptable way [1]. Various methods are considered to be effective in radioactive waste management, but the choice of reprocessing technology always depends on several factors such as activity, composition, physical characteristics of waste, disposal requirements, available conditioning methods and storage options. Various methods of isotope separation from the liquid phase are used for liquid radioactive waste management, for example, simple evaporation, sorption and ion exchange methods, pyro- and hydro-metallurgical methods, liquid extraction, chemical precipitation, extraction chromatography and membrane methods [2,3]. Among these methods the most perspective are those that change the characteristics of wastes in the ways that allow them to be processed according to the methods with less technical and economic requirements and guarantee higher safety. These requirements are met in case of composite materials application, where radioactive contamination is chemically bound on a stable carrier (for example, a mineral filler) stabilized in a strong and sealed matrix. Such waste stabilization based on the chemical and physical mechanisms of radionuclide immobilization provides stable, sealed and safe conditions for the storage and disposal of radioactive waste with limited impact on humans and the environment [4,5]. To fulfill the tasks of preventing the spread of easily migrating forms of widespread radionuclides (especially $^{134}\text{Cs}^+$, $^{137}\text{Cs}^+$, $^{85,90}\text{Sr}^{+2}$, $^{90}\text{Y}^{+3}$, $^{57,60}\text{Co}^{+2}$) in liquid media, it is necessary to use materials that combine the following technical and operational parameters: high values of thermal and radiation stability, mechanical strength, sorption capacity, selectivity, resistance to acids, alkalis and organic solvents. An equally important attribute is controllability and pragmatism of the process of radionuclides sorption and fixation in the volume of a natural or synthetic matrix. The matrix material shall have acceptable physical parameters, such as low specific gravity, small size, structural flexibility and formability, which is especially important when they are used as structural backfill materials and create artificial barriers in the construction of engineering structures. The function of backfill materials is to form an impermeable zone around radioactive waste, since nuclear waste shall be kept separate from the environment. Backfill materials shall have swelling properties, since the swelling properties lead to development of impermeability in backfill materials [6,7].

It should be noted that there are practically no materials that satisfy to all the requirements for radiation safety of the environment as well as at the places of their direct production that is at nuclear power plants. The only way to achieve these requirements is to develop a technology for synthesis of new classes of composite materials consisting of both natural and organic synthetic polymeric materials including industrial waste [8-11]. It is well known that both clay and ferrocyanide complexes of Transition-Valent Metals (TVM) are currently the most studied classes of natural and synthetic sorbents for immobilization of radionuclides from LRW, and are also widely used in practice as barrier materials to prevent the spread of RN in environment [12-16]. Many different classes of polymers have been explored as potentially active starting materials for radioactive waste immobilization and fixation, such as polyesters, epoxies, elastomers, polysiloxanes, crown ethers or even modified sulfur polymers [17,18]. In this paper, we propose a new class of biphasic hybrid composite materials consisting of Intercalated Complexes (ICC) of the natural mineral bentonite with TVM ferrocyanides (phase I), which are incorporated into the bulk of the polymer matrix (phase II). To date there are no reports of direct encapsulation of radioactive waste into biphasic hybrid compositions in which the polymer network is the main carrier matrix, in the volume of which intercalated complexes of clay-ferrocyanide PVM are distributed.

The purpose of the study is to assess the probability of immobilization of LRW radionuclides from the research



pressurized water reactor WWR-K at the Institute of Nuclear Physics (Almaty) with three adsorption materials in a single frame - natural bentonite sorbent, its intercalated complex with copper ferrocyanides and Percolated Complex (PCC) polymer matrix - ICC. Compatibility of the polymer base with various mineral fillers and their intercalated complexes with ferrocyanides contributes to functionalization of the hybrid composition due to synergistic effects in combination with improvement of technical and operational parameters for creating engineering structures during design and construction of the storage facilities for low- and medium-level LRW.

Experimental Section

Materials

Monomers of Acrylic Acid (AAc), Acrylamide (AAm) and crosslinking agent N,N'-Methylene-Bis-Acrylamide (MBAAm), initiators ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (PSA) and sodium metabisulfite $\text{Na}_2\text{S}_2\text{O}_3$ (SMB) from Sigma-Aldrich (USA) of chemically pure grade were used with no additional purification. Bentonite of the JSC "Ilsky Zavod Utyazhelitel" (Russia) TU-2164-003-00136716-2015 was used after washing with distilled water and drying to constant weight at a temperature of 70 °C. Copper vitriol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and potassium ferrocyanide $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ of chemically pure grade were used with no further purification.

Preparation of composite materials

ICC was synthesized by mixing the aqueous solutions of CuSO_4 (0.1M) and $\text{K}_4[\text{Fe}(\text{CN})_6]$ (0.1M) in a ratio of 2:1 in the volume of bentonite swollen in water under vigorous stirring on a magnetic stirrer. After washing and filtering the suspension the ICC solid residue was dried at 60 °C to constant weight. Synthesis of PCC consisted of the following stages: 5g of a sample of ICC swollen in water, 5g of AAm, 5ml of AAc and the calculated amount of MBA (5ml of 0.1M, which corresponds to the degree of crosslinking of the polymer gel of 0.72 mol. % or 0.01 wt.% in relation to the acrylamide monomer) were added under stirring. Total volume of the reaction system was 100ml. At the final stage of stirring 0.5ml of APS and 0.5ml of SMB were added to the reaction mixture at concentrations of 0.1M, respectively. After thorough mixing the reaction mixture was poured onto rectangular and cylindrical substrates made of organic material and placed in an oven at a temperature of 60 °C, where the in-situ polymerization process took place for 6 hours, after which the samples were cooled to room temperature for a day. After removing the samples from the substrates, they were repeatedly washed and dried in a thermostat to a constant weight at $t < 50$ °C to prevent thermal degradation of the polymer matrix.

Instruments and measurements

The experiments on sorption of LRW radionuclides by a natural mineral and its percolated analogue were performed under static conditions by periodical mixing of the sorbent samples placed in 21ml of LRW for 24 and 72 hours. Then the liquid and solid phases were separated in a separating funnel to prevent the sorption of RN on a paper filter. In the resulting filtrate, the specific activity of RN was determined and the degree of binding (purification) θ and the distribution coefficient K_d of radionuclides between the liquid and solid phases were calculated according to the equations (1) and (2), respectively [19].

$$\theta = \frac{A_0 - A_{eq}}{A_{eq}} \cdot 100\% \quad (1)$$

$$K_d = \frac{A_0 - A_{eq}}{A_{eq}} \cdot \frac{V}{m_s} \quad (2)$$

where A_0 and A_{eq} are the initial and equilibrium specific activity of RN before and after sorption, respectively; V is the volume of the liquid phase, ml; m_s is the sorbent mass, g.

For elemental analysis of leachates and water samples (if necessary, diluted with deionized water) the following methods were used [20,21]:

- inductively coupled plasma mass spectrometry (ICP MS) on the ELAN-9000 quadrupole mass spectrometer (PerkinElmer SCIEX), the provisions of [22,23] were taken into account;
- inductively coupled plasma optical emission spectrometry (OES-ICP) on the OPTIMA-8000 double-view OE spectrometer (PerkinElmer Inc.), the provisions of [24] were taken into account.

Scanning Electron Microscopy (SEM) was performed using a Hitachi model TM 4000 Plus microscope equipped with an X-ray fluorescence Energy Dispersive Analysis (EDS) attachment with a crystal detector. The samples were studied under low vacuum in the back-scattered electron mode. The mechanical properties of the samples of hydrogel materials were analyzed on a texture analyzer TA XTplus Stable Micro Systems (England) with software. The principle of the texture analyzer operation is that the sample is subjected to controlled forces during compression using a probe. The resistance of the material to these forces is measured by the torque sensor.

Results and discussion

Establishment of the structure of hybrid compositions

Previously, the authors of [23] synthesized hybrid composites by in-situ polymerization of a mixture of bentonite and acrylamide and acrylic acid monomers in the presence of modifiers such as starch [24] with MBAAm as a crosslinking agent. The work was mainly related to determination of the swelling parameters of polymer compositions in water and their sorption characteristics in respect to the heavy and nonferrous metals ions. One of the interesting class of intercalated compounds with high collector properties with respect to mono- and bivalent alkali and alkaline earth metals, in particular, cesium and strontium radionuclides, is represented by ferrocyanide complexes of transition metals with a layered crystal structure [25,26]. Copper ferrocyanide was used as a ferrocyanide intercalated complex, the structure of which is considered as a solid solution between isomorphous compounds $\text{K}_2\text{Cu}[\text{Fe}(\text{CN})_6]$ and $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ in a ratio of 1:1 [19,34].

We have recently studied [27] the mechanism of percolated structures formation in the bulk of hybrid compositions synthesized by in-situ polymerization by direct mixing of a solution of Acrylic Acid (AAc) and Acrylamide (AAm) monomers in the presence of a crosslinking agent MBA and an intercalated mineral filler - bentonite with potassium hexacyanoferrate $\text{K}_4[\text{Fe}(\text{CN})_6]$ (PHF) and Copper Ferrocyanide (FCCu) of the hypothetical composition $\text{K}_{(4-x)}\text{Cu}_x[\text{Fe}(\text{CN})_6]$. It was found that introduction of a solid solution of the $\text{K}_{(4-x)}\text{Cu}_x[\text{Fe}(\text{CN})_6]$ complex into the structure of bentonite leads to a change in chemical composition of the layered silicate, in particular, the content of potassium and iron ions increases and copper ions appear, which were absent in the original inorganic ion exchanger. The content of aluminum and silicon oxides noticeably decreases, which may be caused by the reaction of their isomorphous replacement by metal ions of ferrocyanide complexes due to the processes of physical adsorption and ion exchange between the mobile ions of the BT and FCCu crystal lattice. Figure 1 shows the data of scanning electron microscopy of bentonite, ICC and PCC with an increase in resolution of the samples by 600 times. It can be seen that the particles of potassium ferrocyanide (a) are the well-formed crystalline formations. The intercalated particles of a mixed $\text{K}_{(4-x)}\text{Cu}_x[\text{Fe}(\text{CN})_6]$ (b) solid solution are placed on the surface of the bentonite layered structure in the form of fine-grained inclusions. Percolation of ICCs into the volume of the polymer matrix shows their placement between layers of a slightly cross-linked network (c). According to the SEM data, it can be concluded that the hybrid composite material is a distributed ICC microcomposition in the volume of a polymer matrix, the morphological structure of which repeats the contour of a layered mineral. In addition, it can be seen that the micro-structure of the primary silicate particle with inhomogeneous regions is more widespread towards the interior of the PCC than near the interface of the bulk polymer-inorganic intercalated particle {BT: $\text{K}_{(4-x)}\text{Cu}_x[\text{Fe}(\text{CN})_6]$ }. Deep penetration of the polymer into the interlayer galleries is also observed, along with increased intercrystalline cavities inside the primary particle of {BT: $\text{K}_{(4-x)}\text{Cu}_x[\text{Fe}(\text{CN})_6]$ }. The layers seem to be well separated both inside and at the boundaries of the primary inorganic complex particle and the polymer layers, that is, in the process of in-situ polymerization the mixtures of AAm and AAc monomers in the presence of a crosslinking agent MBA completely penetrate into the interlayer space of the ICC with formation of a percolated composite material, thus resembling the structure of interpenetrating networks.

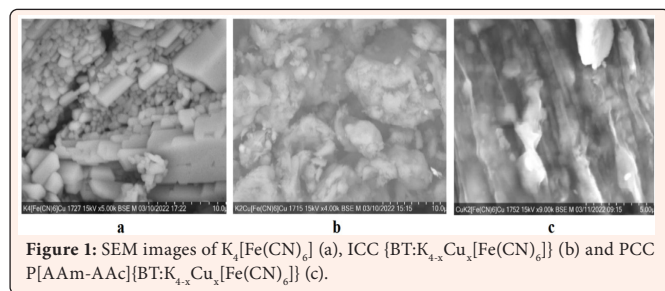


Figure 1: SEM images of $K_4[Fe(CN)_6]$ (a), ICC $\{BT:K_{4-x}Cu_x[Fe(CN)_6]\}$ (b) and PCC $P[AAm-AAc]\{BT:K_{4-x}Cu_x[Fe(CN)_6]\}$ (c).

It is also seen from the SEM data that incorporation of mineral fillers, including ICC, into the polymer matrix can be associated with an increase in the macro- or micro-defectiveness of the structure due to the disorder of macromolecules in the layer adjacent to the surface of solid inorganic particles. There is a clear development of the heterogeneous structure of the biphasic hybrid polymer composition. Under these conditions, a significant change should be expected in the deformation-strength parameters of the composition, which is discussed below.

Sorption properties of hybrid compositions

It is known from the literature [28] that the adsorption centers of clay minerals in relation to ions of alkali and alkaline earth metals are negatively charged aluminosilicate surfaces of sheets, consisting of a sequence of tetrahedral and octahedral silica and alumina chains, respectively, in a ratio of 2:1, between which there are free sodium, calcium and magnesium ions capable of ion exchange with ions of cesium, strontium and other transient metals from the environment. At the same time, the bonds between the layers are extremely weak, so that water and other polar substances can penetrate between the aluminosilicate layers of the natural mineral, as a result of which the bentonite swells, while maintaining a colloidal-dispersed state. Previously in many studies [28-30], it was noted that the optimal pH value of the medium for the effective sorption of cesium and strontium is an alkaline medium, which is associated with a change in the properties of both the adsorbate and the adsorbent. The reason for this is the fact that in an alkaline medium Sr^{2+} transforms into the less soluble form $SrOH^+$ and the negative charge of the interlayer surface of the adsorbent also increases which ultimately leads to an increase in intensity of the adsorption interaction of the solid phase with strontium cations, although this dependence is insignificant for cesium.

In [31] the mechanism of intercalation of iron hydroxocomplexes into the matrix of the porous structure of cobalt and nickel ferrocyanide was reviewed. It has been established that, as a rule, molecules of different sizes and geometry can intercalate into the same layered matrix, that is, there is no molecular sieve effect at the stage of layered materials modification, which determines a wide range of radionuclides absorbed by them of various valences and forms of occurrence in aqueous solutions. The authors of [25,26] studied the methods for selective precipitation of cesium radionuclides with ferrocyanides of various metals characterized by the highest selectivity in separation of cesium from solutions of complex composition. It was shown in [32] that the surface-modified ferrocyanide sorbents based on glauconite and clinoptilolite aluminosilicates exceed the specificity and sorption capacity of the original mineral sorbents. Interaction of metal ions with hydrogels based on acrylamide and its copolymers with acrylic acid occurs mainly due to electrostatic forces between the negatively charged functional groups of the macromolecular chain and cations of the external environment, as well as formation of coordination bonds between lone electron pairs of heteroatoms of the polymer ligand and free vacant orbitals of metals. Due to its structure, the copolymer of acrylic acid and acrylamide can form all four types of structures with metal ions [33]. Carboxyl-type complexes are formed due to electrostatic interactions with carboxylate groups of the polymer chain and metal ions, which can be additionally stabilized by donor-acceptor interactions with carbonyl oxygen. The second type of interaction refers to the complexes of the acrylamide type, where metal ions are coordinated both with carbonyl oxygen atoms and with the primary nitrogen atom of the acrylamide group. The remaining two types of structures represent a combination of the two previous ones, where not only primary, but also secondary and tertiary amino groups can participate in coordination with cations, coupled with electrostatic contacts with any negatively charged functional groups of different basicity, for example, highly charged sulfo-groups or phosphor-groups in the composition of (co)polymers.

Figure 2 shows the dependence of the change in the swelling coefficient (1,2), the pH of the medium (1', 2') and the degree of binding (θ) (1', 2') of stable cesium and

strontium isotopes and the pH of the medium (1', 2') on the concentration of metal chlorides in the solution. It can be seen that the hybrid composition is characterized by a high swelling coefficient in distilled water, which undergoes contraction (compression) by more than 100 times from 650 g/g to 2.5-6.3 g/g as the concentration of Cs^+ (1) и Sr^{2+} increases in the external solution. The onset of contraction of the swelling coefficient of the percolated complex $P[AAm-AAc]\{BT:K_{4-x}Cu_x[Fe(CN)_6]\}$ for Sr^{2+} is observed at its concentration of $5 \cdot 10^{-5}$ mol/l, while for Cs^+ the contraction region is $[Cs^+]=10^{-4}$ mol/l. Consequently, with the growth of the charge of cations, their interaction with the outer and interlayer surfaces of the hybrid composition occurs more intensively with their penetration into the volume of the percolated matrix with the growth of the concentration of metal ions in the environment. Sorption of metal ions is accompanied by a decrease in the pH of the medium from 8 to 4 units pH, which indicates a significant role in the sorption interaction of the main acrylamide-acrylate skeleton of the polymer matrix, inside which intercalated complex of $\{BT:K_{(4-x)}Cu_x[Fe(CN)_6]\}$ are percolated. The maximum binding of Cs^+ and Sr^{2+} falls on their concentration, at which the beginning of PCC contraction is observed, that is, 10^{-4} and $5 \cdot 10^{-5}$ mol/l, respectively, which corresponds to the points of saturation of the hybrid composition sorption centers with the sorbed cations.

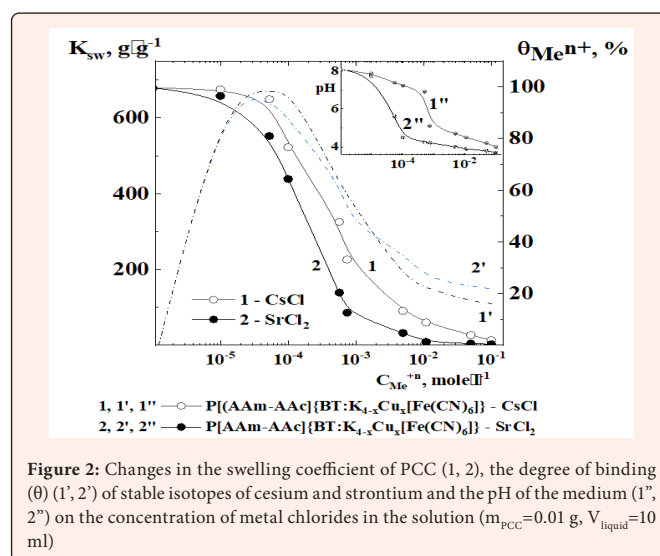


Figure 2: Changes in the swelling coefficient of PCC (1, 2), the degree of binding (θ) (1', 2') of stable isotopes of cesium and strontium and the pH of the medium (1'', 2'') on the concentration of metal chlorides in the solution ($m_{PCC}=0.01$ g, $V_{liquid}=10$ ml)

We can present the following mechanism of metal ions binding with the components of hybrid composition: (a) complexation with carboxyl groups of the polymer matrix with the release of protons, which explains the decrease in the pH of the medium, especially in the case of binding with Sr^{2+} ; (b) ion exchange interaction between sodium and calcium ions of a natural mineral and cesium and strontium ions in an external solution, respectively; (c) reactions of isomorphous substitution of potassium cations in the complex intercalated with Cs^+ and Sr^{2+} ions (Figure 3). There is also an incorporation into the cubic structure of copper ferrocyanide particles intercalated into clay, especially cesium ions, which is associated with the correspondence of the dehydrated Cs^+ diameter with the size of the entrance windows of transition metal ferrocyanides and the minimum solubility of cesium and strontium forms of ferrocyanide complexes [34]. This study was performed as a model system for further discussion of the results of radionuclide sorption from real liquid radioactive waste produced by the research reactor WWR-K. Figure 4 shows the data on sorption of ^{134}Cs , ^{137}Cs , ^{57}Co , ^{60}Co radionuclides from LRW obtained as a result of analysis of their radiation activity before and after sorption by the percolated composite. It can be seen that a significant increase in the sorption of radionuclides is observed with the growth of hybrid compositions mass from 0.01 g to 0.05 g and their contact time from 24 h (Figure 4a) to 72 h (Figure 4b) with LRW. It can be seen from (Table 1) that, at the same values of mass of the samples of natural mineral and the percolated complex, there is a significant difference in the sorption activity with respect to certain radionuclides. The natural mineral bentonite shows a high sorption activity with respect to ^{57}Co , ^{60}Co and ^{85}Sr ions, while PCC $P[AAm-AAc]\{BT:K_{4-x}Cu_x[Fe(CN)_6]\}$ preferentially sorbs ^{134}Cs and ^{137}Cs . The values of the distribution coefficient for radionuclides also differ significantly, especially for ^{134}Cs and ^{137}Cs isotopes. The distribution coefficients of these isotopes between the hybrid matrix and the liquid medium are two orders of magnitude higher than those for the clay mineral. The same can be noted for $^{57}Co^{2+}$, $^{60}Co^{2+}$ and $^{85}Sr^{2+}$ isotopes, those distribution coefficient is one order of magnitude higher than for the hybrid composition.

Table 1: Values of purification degree (θ) and distribution coefficient (K_d) of radionuclides.

Sorbent	m_{nan} Γ	^{134}Cs		^{137}Cs		^{60}Co		^{57}Co		^{85}Sr	
		θ %	$K_d \times 10^{-3}, \text{cm}^3 \times \text{g}^{-1}$	θ , %	$K_d \times 10^{-3}, \text{cm}^3 \times \text{g}^{-1}$	θ , %	$K_d \times 10^{-3}, \text{cm}^3 \times \text{g}^{-1}$	θ , %	$K_d \times 10^{-3}, \text{cm}^3 \times \text{g}^{-1}$	θ , %	$K_d \times 10^{-3}, \text{cm}^3 \times \text{g}^{-1}$
BT	0.01	12.0	0.285	0	-	88.6	16.39	86.4	13.38	24.9	0.697
	0.1	40.9	0.145	27.0	0.077	86.4	1.329	84.4	1.139	33.0	0.103
PCC	0.01	98.0	103.94	97.0	66.86	72.6	5.55	70.1	4.923	0	-
	0.1	99.5	23.96	98.9	33.19	82.5	1.305	81.4	1.119	11.7	0.025

where:

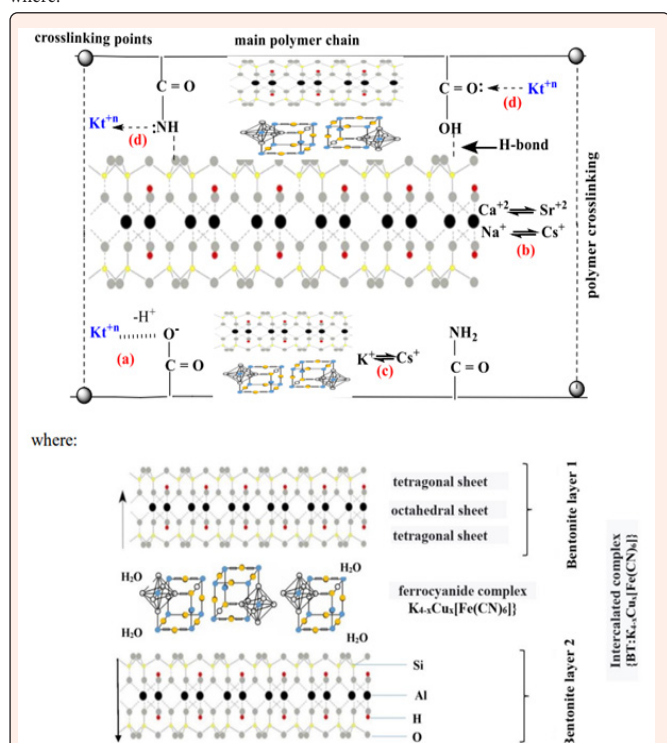


Figure 3: Schematic diagram of the sorption of cesium and strontium ions by percolated complexes $\text{P}[\text{AAm-AAc}]\{\text{BT:K}_{x-1}\text{Cu}_x[\text{Fe}(\text{CN})_6]\}$

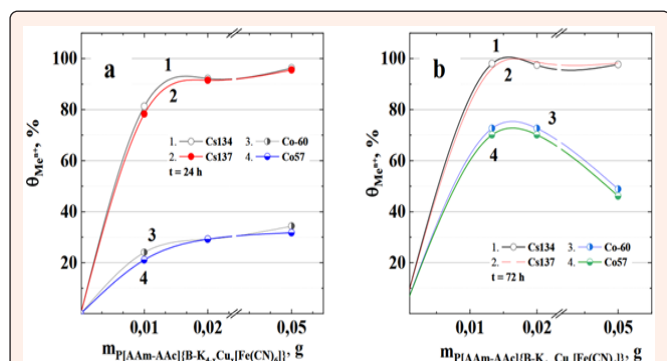


Figure 4: Dependence of the degree of binding of LRW radionuclides on mass of hybrid compositions $\text{P}[\text{AAm-AAc}]\{\text{BT:K}_{x-1}\text{Cu}_x[\text{Fe}(\text{CN})_6]\}$ and the time of their contact: a-24 h, b-72 h.

Previously [34-36], it was shown that mixed copper ferrocyanides are characterized by a unique selectivity with respect to cesium ions due to the ion exchange of monovalent potassium ions and molecular sorption of cesium on copper ferrocyanide due to the defective structure of the latter. In addition, it has been established that the cation exchange reaction of the outer sphere of ferrocyanides proceeds without transition of $[\text{Fe}(\text{CN})_6]^{4-}$ into solution. This can explain such high values of sorption of cesium radionuclides by PCC, since it contains copper ferrocyanide. Therefore, the high sorption activity of PCC compared to bentonite is associated with the presence of three adsorption centers: negatively charged aluminosilicate backbones of bentonite clay, copper ferrocyanide and carboxyl-acrylamide groups of the polymer matrix, as shown in Figure 3. It is noteworthy that with the growth of the sample mass there is a noticeable decrease in the sorption of transition-valent metals, in particular ^{57}Co and ^{60}Co , capable of forming both ionic bonds with negatively charged groups of the mineral and polymer matrix, ion exchange with their counterions, molecular sorption with the ferrocyanide lattice and coordination between the nitrogen atoms of the primary amine and the carbonyl oxygen of the acrylate group of the hybrid composition (Figure 3d). All these three types of interaction contribute to the contraction of the swollen PCC, which leads to a decrease in the area of the PCC-LRW contact surface and a decrease in its permeability due to network compression. The resulting hybrid compositions have a well-developed porous surface, which contributes to the accelerated penetration into their volume of hydrated ions in the composition of LRW (Figure 5). The data on chemical analysis of elements in the LRW composition before and after sorption on bentonite and PCC indicate that there is an ion exchange reaction between the liquid medium and sorbents of stable (non-radioactive) ions. Table 2 presents data on the change in concentration of some active ions in the composition of LRW capable to ion exchange with counterions of both the mineral and the composite matrix. It can be seen that upon contact of LRW with a mineral and composite sorbent, the liquid phase after sorption is enriched with potassium ions, and especially with mobile sodium ions, which indicates the reaction of their replacement from the crystal lattice of solid sorbents by Ca^{2+} , Zn^{2+} , $^{57}\text{Co}^{2+}$, $^{60}\text{Co}^{2+}$, $^{137}\text{Cs}^+$, $^{134}\text{Cs}^+$ and $^{85}\text{Sr}^{2+}$. Table 3 provides the results of chemical analysis for the components of the model LRW solution prepared from metal chlorides at a concentration of 10^{-4} mol/l of each of the salts. It can be seen that stable isotopes of four elements are concentrated in the matrix of the hybrid composition. The relatively low accumulation coefficient $K^{\text{Na},\text{f}}$ of cesium and strontium compared to cobalt and yttrium is defined by the fact that in the process of bentonite clay modification in order to obtain intercalated complexes $[\text{BT:K}_{x-1}\text{Cu}_x[\text{Fe}(\text{CN})_6]]$ cesium and strontium salts were introduced as labels into the ICC mineral component swollen in water to analyze the possibility of controlling the ion-exchange processes of these ions with their radioactive isotopes from LRW.

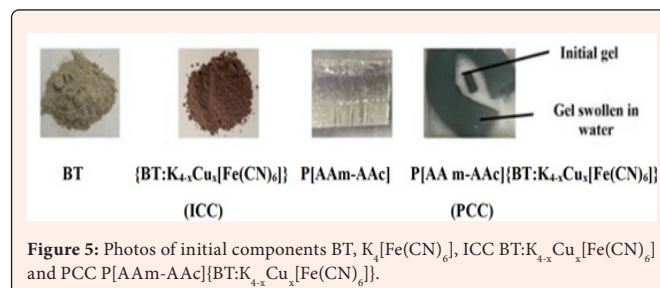


Figure 5: Photos of initial components BT, $\text{K}_{x-1}[\text{Cu}_x[\text{Fe}(\text{CN})_6]]$, ICC $\text{BT:K}_{x-1}\text{Cu}_x[\text{Fe}(\text{CN})_6]$ and PCC $\text{P}[\text{AAm-AAc}]\{\text{BT:K}_{x-1}\text{Cu}_x[\text{Fe}(\text{CN})_6]\}$.

Table 2: Change in the concentration of some active LRW ions before and after sorption by bentonite and hybrid matrix ($m_s=0.1$ g).

Ions	$C_{in}, mg \times l^{-1}$	Bentonite	$P[AAm-AAc]\{BT:K_{4-x}Cu_x[Fe(CN)_6]\}$
Na ⁺	400	1720	3150
K ⁺	80	98.6	80.4
Ca ⁺²	220	35.1	175
Mg ⁺²	23	14.6	28.3
Zn ⁺²	0.00047	0.00012	0.00032
Mn ⁺²	0.00036	0.00018	0.000166

Table 3: Results of chemical analysis of dry PCC samples before and after sorption of model solutions of radionuclides. $C_{Me}^{+n} = 10^{-4} mol \cdot l^{-1}$. RN – radionuclide.

Sample Code	Cs	Sr	Co	Y
	%			
$P[AAm-AAc]\{BT:K_{4-x}Cu_x[Fe(CN)_6]\}$ initial	0.026	0.027	5.9×10^{-4}	1.53×10^{-3}
$P[AAm-AAc]\{BT:K_{4-x}Cu_x[Fe(CN)_6]\}$ after sorption	0.156	0.74	0.055	0.0746
$K^{RN} a.f = [RN]:[RN]_0$	6	27.4	93.2	48.76

The results of mapping (Figure 6) of SEM data with the XRF attachment of energy-dispersive analysis showed that there are reactions of K⁺ ions substitution by Cs⁺ ions and ion exchange with mobile sodium ions on ICC particles, which corresponds to a section of the mineral matrix, while Co⁺² and Y⁺³ are concentrated in the polymer matrix. It can also be stated that there is intermatrix migration of mono- and polyvalent ions between the mineral and polymer parts of the hybrid composite material. It should be noted that it is rather difficult to characterize running of all possible ion-exchange and sorption processes that take place during impregnation of radionuclides to the bulk of natural and hybrid sorbents due to their different radiation activity and half-life of radionuclides. According to the data of changes in concentration of the main chemically active components before and after sorption, it can be concluded that in the process of sorption of radionuclides by sorbents of different nature, there are three mechanisms of interaction described above, in particular, electrostatic binding between the functional groups of sorbents and metal ions, stabilized by a system of coordination bonds with electron-donating nitrogen and oxygen atoms of amino and carbonyl groups of the polymer matrix, ion ex-change between the counterions of the solid matrix and ions of radionuclides and superequimolar ab-sorption as a result of deformation of the crystal lattice of fillers of the polymer matrix of bentonite and copper ferrocyanide with vacancies in the positions corresponding to ions $[Fe(CN)_6]^{-4}$ respectively [35,36]. In this article, we do not use the term exchange capacity (EC), because for highly swelling hydrogels, sensitive to environmental conditions (pH, ionic strength of the solution, etc.) and the multi-component nature of hydrogels, it is not possible to give an exact adequate value of the statistical exchange capacity of hybrid compositions. For establishment of EC, it is necessary to perform the detailed studies taking into account many factors, which is the subject of subsequent research. The question of radiation resistance of the hybrid composition components during sorption of radionuclides arises. It is known that inorganic materials (ferrocyanide of transition-valent metals) and clay minerals correspond to many requirements for their use at extremely high levels of radiation activity [14,37].

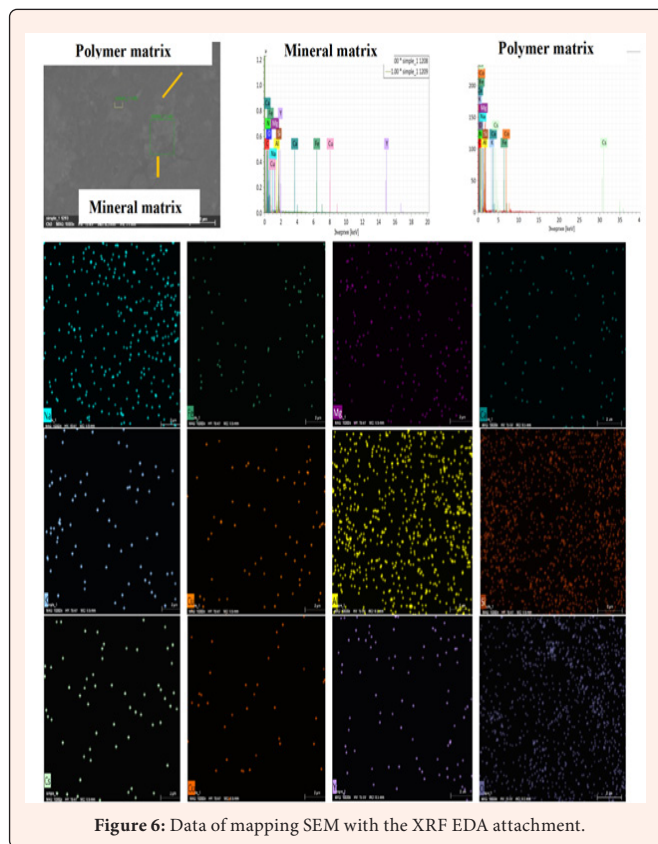


Figure 6: Data of mapping SEM with the XRF EDA attachment.

Mechanical properties

Materials containing radioactive elements are exposed to specific environmental conditions (for example, temperature, pressure) and ionizing radiation [2-4]. The latter is able to significantly modify the properties of materials due to strong energy effects at the molecular level, which lead to changes in the structure, molecular-phase composition, formation of new bonds due to radiation breaking and cross-linking of destroyed polymer chains, etc. It is impossible to unambiguously predict the influence of ionizing radiation on the structure and properties of composite materials, especially in the case of a polymer matrix frame. In this regard the mechanical properties of hybrid compositions were studied in a radiation environment using the example of effect of electron beams, generated by the electron accelerator equipment. Earlier [38] we showed that in the process of stretching, at relatively large deformations, close to the sample rupture, a situation is realized in hybrid polymer compositions, when polymer is detached from the surface of inorganic filler with formation of voids-vacuoles, oriented along the load direction. Therefore, it can be assumed that the main factor, characterizing the deformation strength of the composite is the adhesion strength at the interface between the mineral filler and the polymer matrix. With high adhesion energy of interaction, dispersion of mineral particles, thickness of the interphase layer, crosslinking density of the polymer matrix, the strength of the material should increase, otherwise, it should decrease. In the studied hybrid compositions, the first case is observed, that is filling with mineral particles resulted in an increase in the material strength. At the initial part of stretching ($\epsilon \leq 200$ %), a wave-like change in

shear stress was observed with appearance of a plateau in PCC which did not occur in the case of polymer gel P[AA-AK]. This may be connected with rearrangement of the internal structure of the percolated complex P[AAm-AAc]{BT:K_{4-x}Cu_x[Fe(CN)₆]} during stretching, when the agglomerates of solid fillers are stretched along the polymer chains, which is determined by the force of adhesion between the polymer chains and mineral particles at the interface boundary. At the same time, polymer chains are naturally intertwined with each other, between the nodes of which there are micro-particles of mineral filler. This can also be interpreted from the point of view of percolation of polymer chains through the layers of inorganic filler.

Figure 7 shows the deformation curves of uniaxial compression of hybrid composition P [AAm-AAc]{BT:K_{4-x}Cu_x[Fe(CN)₆]} samples at different doses of irradiation. It can be seen that with the growth of the radiation dose from 5 to 25 kGy there is a decrease in the degree of samples deformation from 60% to 53% with insignificant change in the compression stress with restoration of the original shape, that is, the hybrid compositions possess and retain their highly elastic properties within the specified load value (1 kg·cm⁻² or 98.066 kPa). An increase in the load from 1.0 to 10 kg·cm⁻² (980.66 kPa) in the cyclic mode (5 cycles) also did not lead to destruction of cylindrical samples of hybrid compositions, which indicates that the deformation behavior is typical for covalently cross-linked polymer hydrogels. Therefore, deformation of hybrid compositions is irreversible due to preservation of chemical bonds, even if destruction of macromolecular chains of the polymer matrix is possible during electron irradiation. The destruction of the polymer frame is not catastrophic, since at the place of break of the linear sections connections between the nodes of the crosslinks, new crosslinks are formed, but with a smaller molecular weight, which can only lead to an increase in the strength of hybrid composition with a slight loss of elasticity.

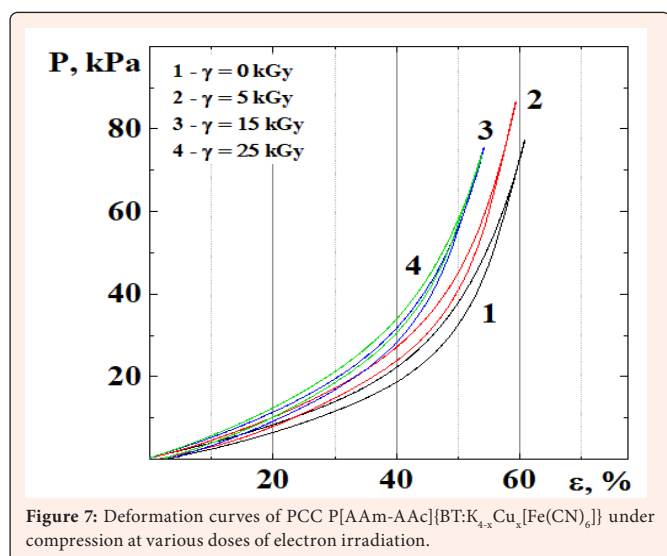


Figure 7: Deformation curves of PCC P[AAm-AAc]{BT:K_{4-x}Cu_x[Fe(CN)₆]} under compression at various doses of electron irradiation.

Conclusion

Thus, from the presented data, it can be concluded that biphasic hybrid composite materials represent a promising class of sorption-active materials for immobilization and fixation of LRW radionuclides. Hybrid compositions are characterized by a high synergistic effect in relation to sorption of radionuclides, especially for ¹³⁷Cs⁺ and ¹³⁴Cs⁺, which distribution coefficients are 2 orders of magnitude higher than the sorption activity of the mineral matrix. It is established that sorption of radionuclides by biphasic hybrid compositions occurs due to the electrostatic bonding reaction between functional groups of sorbents and metal ions, stabilized by a system of coordination bonds with electron-donating atoms of nitrogen and oxygen of amino- and carbonyl groups of the polymer matrix, ion exchange between counterions of the solid matrix and ions of radionuclides and super-equimolar absorption as a result of deformation of the crystal lattice of polymer matrix fillers of bentonite and copper ferrocyanide, which increases the size of pores of their crystal lattice. It is shown that biphasic hybrid composite materials are characterized by a high mechanical and radiation resistance with preservation of elasticity even at high doses of electron irradiation, during which a significant decrease in their strength parameters is not observed despite a noticeable decrease in deformation. The obtained information about the

mechanism of binding of biphasic hybrid composite materials with various metal ions makes it possible to synthesize new classes of materials for selective sorption of certain types of radionuclides based on the dynamics of sorption on the interphase surface of mineral and polymer matrices directly in their volume, which will enable us to use these materials as highly effective sorption materials with synergetic effect for detection, identification, immobilization and fixation of LRW radionuclides. The work was carried out in a frame of the Scientific and Technical Program of the Ministry of Education and Science of the Republic of Kazakhstan for 2021-2023 on the topic "Applied research based on a nuclear reactor in the field of radioactive waste management, production of radioisotopes and radiation materials science" (state registration number 0121RK00777).

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