Obtaining modified sorbents based on natural raw materials of Kazakhstan and research of their properties

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ABSTRACT
Kazakhstan takes a leading position in the production of uranium. During the hydrometallurgical processing of uranium-containing raw materials, a significant amount of liquid industrial waste is generated, such as waste solutions that require disposal. One of the most effective methods of cleaning liquid objects contaminated with radionuclides is sorption methods. Synthetic sorbents are not always justified due to their high cost and natural ones due to their low sorption capacity. The production of modified ion-exchange materials based on their combination is an urgent problem in the nuclear industry. The authors considered options for modifying natural aluminosilicate and coal-mineral raw materials of Kazakhstan. For research, zeolite from the previously unexplored Kusmurun deposit and shungite from the Koksu deposit were selected. It is proposed to modify natural sorbents with a tributylphostat and di-2-ethylhexylphosphoric acid mixture in kerosene, a mixture of phosphoric acid and polyacrylamide, technogenic raw materials. The probable mechanism of modification by each of the methods is considered. The sorption properties of the modified sorbents have been studied, and their mechanical strength has been determined.

Keywords: natural sorbents, modification, uranium sorption, mechanical strength.

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Introduction

Recently, more and more attention has been paid to the ecological safety of the republic, in connection with the increased threat of environmental pollution by radionuclides, particularly uranium. When processing uranium-containing raw materials, a significant amount of liquid technogenic wastes are formed. The main method of utilization is sorption, which requires the use of inexpensive sorbents of complex action.

Such sorbents can be obtained based on domestic natural raw materials. The significant disadvantages of natural sorbents include low sorption capacity, which can be increased by developing effective and inexpensive methods for their modification.

Various options for obtaining sorbents with improved sorption and kinetic properties are used. Many of them are based on the introduction of additional functional groups into the sorbent structure, which leads to the formation of new
adsorption centers, increasing the sorption capacity and selectivity of the sorbent. For this purpose, use is made of inorganic materials modified with amidoxime or iminodiacetate groups and, salts of heteropoly acids [1], [2]. Sorbents with amidoxime groups on various carriers have shown high efficiency in the extraction of radionuclides, as well as good kinetic properties [3], [4], [5], [6].

To isolate radionuclides from complex technological solutions, sorbents with diphyryl, aminophosphinate, carbamoylmethyl-phosphinate, and other phosphorus-containing functional groups have been developed, which can produce stable complexes with radionuclides [7], [8], [9], [10].

The most promising sorbents with functional groups fixed on polymer matrices that form complex compounds are materials obtained on the basis of natural minerals and radionuclide extractants. Such "solid-phase extractants" are characterized by good sorption properties [11].

The synthesis of organopolymers occupies a special place in the production of modified sorbents. This is how an organozeolite was synthesized on the basis of natural zeolite-containing tuffs and a water-soluble polymer of polyhexamethylguanidine, epichlorohydrin as a cross-linking agent, which simultaneously exhibits cation-exchange, anion-exchange and bactericidal properties [12]. The sorbent is highly selective to oxygen-containing anions and uranium carbonate complexes.

All described methods were developed using foreign raw materials and expensive modifying reagents, many of them are difficult to implement. Among the works of domestic scientists, the most interesting are examples of modification of zeolite and shungite, previously activated with sulfuric acid, copper (II) and nickel hydroxides, which are given in [13]. The authors discussed modified sorbents' features and general regularities of uranium sorption. It is shown that the use of pre-activated and modified shungite and zeolite for the sorption of uranium makes it possible to increase its extraction in comparison with the use of natural sorbents. However, the laborious process of modification is a limiting factor in the widespread use of sorbents obtained by this method.

Thus, a common disadvantage of the described methods is the complexity of implementation, high cost, and the use of scarce reagents. Therefore, in modern economic conditions, the development of effective and inexpensive sorption materials using cheap local raw materials remains relevant.

Research methodology

The modification of natural sorbents was carried out with organic extractants and, phosphoric acid in combination with polyacrylamide. Zeolite from the Kusmurun deposit and shungite from the Koksu deposit after preliminary flotation was used as natural sorbents [14].

When flotation of shungite, kerosene KO-25, TU 38.401-58-10-01 was used as a collector, as a foaming agent - T-80 - a mixture of derivatives of heterocyclic alcohols: mono- and dihydric alcohols of dioxane and pyran series, TU 20.14.60-029 - 05766801-2016. We also used liquid glass (sodium silicate), state standard GOST 13078-81 and quicklime (calcium oxide), state standard GOST 9179-77.

Modification experiments were carried out as follows: 10 g of a natural sorbent (zeolite or shungite) was poured with a solution of the sum of extractants (di-2ethylhexylphosphoric acid and tributyl phosphate) in kerosene. The resulting compositions were kept for 72 h, dried at room temperature, and then in an oven at 100 °C.

Modification with phosphoric acid and polyacrylamide was carried out under the following conditions: a weighed portion of the natural sorbent in an amount of 10 g was treated with a dilute (1: 4) solution of phosphoric acid, after 12 hours the sorbent was washed to remove excess acid, dried and filled with a solution of polyacrylamide (concentration - 20 g / l), leaving for 12 hours. Then the polyacrylamide solution was poured off, the sorbents were washed with distilled water and dried.

Testing of the sorption capacity of the modified sorbents was carried out under static conditions. Sorption was carried out for 4 hours at room temperature (~ 25°C) at the ratio S: W = 1:5. Desorption was carried out with a solution of 1M sodium carbonate in a static mode at a ratio of S: L = 1: 10.

In the course of the research, the mechanical strength of the modified sorbents was also determined in comparison with the initial ion-exchange materials.

In order to determine the effect of activators on mechanical strength, 6 samples were made in the form of pressed briquettes from pre-modified sorbents. Pressed briquettes were made using a PSU-10 hydraulic press designed for static compression testing of standard samples of building materials. The method for modifying natural
sorbents for the manufacture of pressed briquettes, according to the numbering, is presented in Table 1.

**Table 1 - Methods for modifying natural sorbents**

<table>
<thead>
<tr>
<th></th>
<th>Zeolite</th>
<th>Shungite</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Initial</td>
<td>Initial</td>
</tr>
<tr>
<td>2.</td>
<td>Initial Modified with a mixture of di-2-ethihexylphosphoric acid and tributyl phosphate in kerosene. (Di-2 EGPK + TBP + kerosene)</td>
<td>Modified with a mixture of di-2-ethihexylphosphoric acid and tributyl phosphate in kerosene. (Di-2 EGPK + TBP + kerosene)</td>
</tr>
<tr>
<td>3.</td>
<td>Modified with phosphoric acid and polyacrylamide (H$_3$PO$_4$ + PAA)</td>
<td>Modified with phosphoric acid and polyacrylamide (H$_3$PO$_4$ + PAA)</td>
</tr>
<tr>
<td>4.</td>
<td>Initial</td>
<td>Initial</td>
</tr>
<tr>
<td>5.</td>
<td>Modified with a mixture of di-2-ethihexylphosphoric acid and tributyl phosphate in kerosene. (Di-2 EGPK + TBP + kerosene)</td>
<td>Modified with phosphoric acid and polyacrylamide (H$_3$PO$_4$ + PAA)</td>
</tr>
<tr>
<td>6.</td>
<td>Modified with phosphoric acid and polyacrylamide (H$_3$PO$_4$ + PAA)</td>
<td>Modified with phosphoric acid and polyacrylamide (H$_3$PO$_4$ + PAA)</td>
</tr>
</tbody>
</table>

2 series of experiments were carried out. In the first, the samples were pressed at a 200 kg / dm$^3$, water was used as a binder, and briquettes in the form of a cylinder ($r = 8$, $h = 16$) were obtained, which were carefully dried and compressed until the first crack. Compression speed 0.1 mm / sec.

In the second, the samples were pressed at 300 kg / dm$^3$, liquid glass was used as a binder, the studies were carried out similarly to the previous one.

**Analysis methods**

The quantitative content of uranium in solutions before and after sorption was determined on an Optima 8000DV inductively coupled plasma atomic emission spectrometer (ICP).

IR spectra were obtained on an Avatar 370 FT-IR spectrometer in the spectral range of 4000-400 cm$^{-1}$ from preparations in the form of a tablet prepared by pressing 2 mg of a sample and 200 mg of KBr. Experiment attachment: Transmission E.S.P.

To determine the strength of modified sorbents in comparison with the original used a universal floor testing machine Autograph AG-X 100 kN, Shimadzu GmbH, Japan.

**The discussion of the results**

On the basis of natural raw materials from Kazakhstan, various options for modifying natural minerals have been developed. [15]. The most promising were the methods that included the treatment of natural minerals with organic extractants: di-2 ethylhexylphosphoric acid in combination with tributyl phosphate, phosphoric acid in combination with polyacrylamide. In the course of the research, we used a previously unexplored zeolite from the Kusmurun deposit and shungite from the Koksu deposit after preliminary flotation. We have proposed and tested three options for shungite beneficiation technology. The most promising was the method described in [14]. The product obtained in the flotation process can be classified as shungite concentrate.

IR spectroscopic studies of modified natural sorbents (Figs. 1, 2) showed that when zeolite is modified with a mixture of extractants, the sample contains plagioclase spectra of the albite type Na[AlSi$_3$O$_8$] – 762, 747, 726, 647, 590, 528, 465 cm$^{-1}$. Possibly present: Heulandite Ca[Al$_2$Si$_7$O$_{18}$] ∙ 6 H$_2$O - 3428, 1032, 523, 465 cm$^{-1}$, lamentitis Ca[Al$_2$Si$_2$O$_6$] ∙ 4 H$_2$O - 3572, 1032, 762, 523 cm$^{-1}$, phillipsite K, Ca[Al$_3$Si$_5$O$_{16}$] ∙ 6 H$_2$O – 3428, 1639, 1032, 590 cm$^{-1}$, quartz $\alpha$-SiO$_2$ – 696, 465 cm$^{-1}$, calcite CaCO$_3$ – 1797, 1428, 878, 714 cm$^{-1}$ [16], di-2 ethylhexyl phosphoric acid (C$_{16}$H$_{35}$PO$_4$) - 2960, 2931, 2874, 2861, 1461, 1384 cm$^{-1}$ and tributyl phosphate (C$_{12}$H$_{27}$PO$_4$) - 2960, 2873 cm$^{-1}$ [18].

**Figure 1 – IR spectrum of zeolite modified with a mixture of Di-2 ethylhexylphosphoric acid, tributyl phosphate and kerosene**
When natural sorbents are modified with a mixture of phosphoric acid and polyacrylamide, for example, shungite, as a result of the interaction of the matrix with modifiers, new compounds are formed, in particular, calcium compounds interact with orthophosphoric acid to form dibasic calcium phosphate. In addition, it can be assumed that when natural sorbents are modified with this mixture, a gel-like film of polyacrylamide is formed on the surface of the matrix, which contributes to an increase in the sorption capacity of sorbents. [22].

Thus, it follows from the data obtained that the mechanism of the formation of modified sorbents based on a matrix of zeolite and shungite by a mixture of extractants di-2 ethylhexylphosphoric acid, tributyl phosphate and kerosene and a mixture of phosphoric acid and polyacrylamide have different nature.

The uranium content in waste solutions, as a rule, is 5-15 mg/dm³. In this regard, we have adjusted the productive solution in accordance with the given uranium concentration and studied the sorption process by modified natural materials. The initial uranium concentration was 11.9 mg/dm³. The kinetic dependences of the sorption of uranium in a static mode from the imitate showed that with all the described modified sorbents it is possible to extract uranium by more than 90% already in the first 45-50 minutes.

In the course of the research, the possibility of repeated use of modified sorbents for the extraction of uranium from liquid radioactive waste was also studied, for which the concentration of di-2 ethylhexylphosphoric acid and tributyl phosphate, as well as phosphoric acid and polyacrylamide, was doubled when modifying zeolite and shungite. Sorption and desorption by modified sorbents were carried out in a static mode, alternating the processes of sorption and desorption. The research results are presented in Table 2.

![Figure 2 – IR spectrum of shungite after flotation modified with a mixture of di-2 ethylhexylphosphoric acid, tributyl phosphate and kerosene](image)

Table 2 - Results of experiments on sorption and desorption of uranium

<table>
<thead>
<tr>
<th>Stage</th>
<th>Process</th>
<th>Uranium content, mg/dm³</th>
<th>The degree of extraction %, degree of desorption%</th>
<th>Uranium content, mg/dm³</th>
<th>The degree of extraction %, degree of desorption%</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Sorption</td>
<td>0.79</td>
<td>93.36</td>
<td>0.046</td>
<td>99.6</td>
</tr>
<tr>
<td></td>
<td>Desorption</td>
<td>9.50</td>
<td>85.51</td>
<td>10.62</td>
<td>89.6</td>
</tr>
<tr>
<td>II</td>
<td>Sorption</td>
<td>7.18</td>
<td>39.66</td>
<td>0.06</td>
<td>99.5</td>
</tr>
<tr>
<td></td>
<td>Desorption</td>
<td>0.39</td>
<td>8.68</td>
<td>8.06</td>
<td>67.99</td>
</tr>
<tr>
<td>III</td>
<td>Sorption</td>
<td>7.41</td>
<td>37.73</td>
<td>0.96</td>
<td>91.93</td>
</tr>
<tr>
<td></td>
<td>Desorption</td>
<td>0.30</td>
<td>6.35</td>
<td>3.8</td>
<td>32.09</td>
</tr>
</tbody>
</table>

![Figure 3 – IR spectrum of shungite after flotation modified with a mixture of phosphoric acid and polyacrylamide](image)
It follows from the table that with an increase in the concentration of the modifier, shungite can be used repeatedly. For zeolite, this relationship is not observed.

One of the main factors in sorption is the mechanical strength of the sorbents. We have determined the mechanical strength of the modified sorbents in comparison with the initial ion-exchange materials [23].

The mechanical strength of a material is characterized by its ability to resist various external mechanical influences and is characterized by ultimate strength:
1) when compressed; 2) when stretched; 3) flexural strength and 4) abrasion resistance. We investigated the compressive strength of natural sorbents.

The results obtained are shown in Figure 4, which shows the effect of activators and a binder reagent on the mechanical strength of natural sorbents.

Based on the studies carried out, it can be concluded that the ability of resistance to external mechanical influences (in our case, to compression) during the treatment of zeolite and shungite with phosphoric acid and polyacrylamide increases significantly, and in the case of using a mixture of extractants in kerosene with kerosene it decreases.

It also follows from the figure that the difference in the degree of deformation of the initial sample of zeolite and that modified with a mixture of orthophosphoric acid and polyacrylamide significantly exceeds the similar difference for shungite. At the same time, the decrease in the degree of deformation of a zeolite sample modified with a mixture of extractants in relation to the initial raw material is significantly less than in shungite.

Thus, the optimal options for modifying natural minerals have been determined using the example of zeolite and shungite, and the physicochemical properties of the obtained modified sorbents have been investigated.

It should be noted that the modified sorbents, especially the first two options, have proven themselves well in the testing process. These sorbents can be used for analytical purposes, as well as in low-tonnage production conditions. Their widespread use for the disposal of large volumes of liquid uranium-containing waste is unprofitable. Currently, work in this direction continues. In order to reduce the cost of modified sorbents, studies are being conducted on the possibility of using technogenic raw materials as modifiers, in particular, phosphorus slag, which is a waste of the phosphorus industry and is formed during the electrothermal production of yellow phosphorus. According to the performed physicochemical studies, the main phase of the phosphorus slag - calcium silicate - is represented by the amorphous phase of volostanite. The slag also includes multicomponent glass, small amounts of calcite, ankerite. Phosphorus is present as lazulite.

Analysis of scientific and technical literature in the field of calcium silicate synthesis showed that rational and environmentally friendly options include methods based on the interaction of the initial components in an aqueous medium at elevated temperatures and, in some cases, pressure, i.e. hydrothermal method. The hydrothermal method allows not only the synthesis of hydrosilicates, but also affects their structure and particle morphology. Hydrothermal conditions
simulate the formation of minerals in the earth's interior. Calcium carbonate and sodium chloride are commonly used as the aqueous phase.

During research, it was found that during the hydrothermal treatment of slag in a carbonate medium with an increase in temperature, the amorphous phase is transformed into a crystalline phase, and the morphology of particles also changes: the conglomerates existing in the initial sample gradually change their shape and turn into particles of an acicular structure (Fig. 5, 6). During the hydrothermal treatment of phosphorus slag with sodium chloride, its amorphous structure is retained.

Several options for modifying natural minerals have been developed. An indicator of one or another modification method is the sorption process.

The best option for modifying natural minerals (zeolite or shungite) is mixing a natural sorbent with phosphoric slag activated in a chloride or carbonate medium and processing with a polyacrylamide solution.

The structure of the phosphorus slag activated with sodium chloride solution is partially retained even after it has been modified by natural minerals. This is especially clearly seen on the example of shungite (Fig. 7).

IR spectroscopic analysis of a sample of modified shungite showed the presence of: calcite - CaCO₃ – 1798, 1423, 875, 849, 712 cm⁻¹, quartz - SiO₂ – 1166, 1081, 798, 779, 695, 516, 468, 396, 368 cm⁻¹ [[16], [24]]. The band at a wavenumber of 319 cm⁻¹ falls within the range of bond manifestations Ca – O [25]. There are: wollastonite - CaSiO₃ – 1081, 1060n, 1035, 928n, 909n, 516, 468 cm⁻¹ [16], muscovite - KAl₂[(OH, F)₂| AlSi₃O₁₀] – 1028, 928 cm⁻¹ [16], [26], multicomponent glass - 1035, 928 cm⁻¹ [27]. Stretching vibrations of bonds Si–O–Si - 1035 cm⁻¹, shoulder at 928 cm⁻¹ corresponds to stretching vibrations of terminal bonds Si–O–Si [28], bassanite - Ca[SO₄] · ½ H₂O – 634, 602, 468 cm⁻¹ [29].

When activated with sodium carbonate - in the process of modification, the structure is transformed.

Studies have established that the sorption capacity of modified sorbents increases when dressing natural minerals with phosphorus slag. If the slag modified with slag activated in a chloride medium sorbs both uranium and iron, then in a carbonate medium it is mainly iron. This property can be used to separate them.

Thus, the possibility of using technogenic raw materials - phosphorus slags - as modifiers of natural minerals has been shown.
Conclusions

In the course of research, methods have been developed and tested for modifying natural sorbents, which make it possible to actively extract uranium. The modifiers were a mixture of di-2-ethylphosphoric acid and tributyl phosphate in kerosene, phosphoric acid, polyacrylamide and technogenic raw materials. On the basis of IR spectroscopic studies, a prediction was made regarding the mechanism of interaction of modifiers with the matrix of a natural sorbent. It is shown that the mechanism of the formation of modified sorbents based on a matrix of zeolite and shungite with a mixture of extractants di-2-ethylhexylphosphoric acid and tributyl phosphate in kerosene and a mixture of phosphoric acid and polyacrylamide is of a different nature.

The properties of modified sorbents have been studied, and their sorption capacity and mechanical strength have been assessed. It is shown that the degree of uranium extraction by modified sorbents exceeds 90% already in the first 45-50 minutes.

It was found that when processing both zeolite and shungite with a mixture of phosphoric acid and an acid and polyacrylamide, the mechanical strength of the sample increases, and a mixture of extractants (di-2-ethylhexylphosphoric acid and tributyl phosphate) in kerosene helps to reduce its value.

The possibility of using technogenic raw materials - phosphorus slags - as modifiers of natural minerals is shown.

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Получение модифицированных сорбентов на основе природного сырья Казахстана и исследование их свойств

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АННОТАЦИЯ
При гидрометаллургической переработке урансодержащего сырья образуется значительное количество жидкотехногенных отходов – сбросных растворов, требующих утилизации. Одним из наиболее эффективных приемов очистки загрязненных радионуклидами жидких объектов является использование сорбционных методов. Применение синтетических сорбентов не всегда оправдано ввиду их высокой стоимости, а природных – ввиду низкой сорбционной емкости. Получение модифицированных ионообменных материалов на основе их сочетания является актуальной проблемой атомной промышленности. Авторами рассмотрены варианты модификации природного минерального сырья Казахстана. Для исследований выбраны цеолит не изученного ранее месторождения Космурун и шунгит месторождения Коксу. Предложено модифицировать природные сорбенты смесью трибутилфосфата и ди-2-этилгексилфосфорной кислоты в керосине, смесью фосфорной кислоты и полиакриламида, а также техногенным сырьем. Рассмотрен вероятный механизм модификации каждым из способов. Изучены сорбционные свойства модифицированных сорбентов и определена их механическая прочность.

Ключевые слова: природные сорбенты, модификация, сорбция урана, механическая прочность.

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