Reduction of technology risk at NPP during radioactive waste management

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Abstract. The authors developed a technology for disposing of liquid radioactive waste, which ensures the reduction of their exposure dose rate (MED) by concentrating radionuclides from liquid radioactive waste (LRW) inside the iron oxide matrix of radiation protective sorbents (ion exchangers). Due to the high density, iron oxide ion exchangers provide an effective radiation protective shield against photon radiation with an energy of up to 1.5 MeV. This will reduce the radiation background of “spent” sorbents. The possibility of obtaining a hydrolytically stable system of bonds with the surface of iron oxide minerals when they are modified with organic and inorganic modifiers is theoretically substantiated and experimentally confirmed. It was established that the hydroxyl groups of the surface of oxides are the main type of reaction centers along which their surface is modified. Modified iron oxide ion exchangers have high chemical and radiation resistance, thermal stability, mechanical strength and mass transfer rate. The conditioning technology of spent ion exchangers into cement matrices allows creating an engineering barrier providing effective radiation protection and safe isolation of radionuclides.

1. Introduction

When using nuclear power plants and the operation of experimental reactors at all stages of the nuclear cycle, especially during the reprocessing of spent nuclear fuel, liquid radioactive waste (LRW) is generated. At the same time, the waste of the enterprises for the extraction of ore and processing of uranium contains mainly natural radionuclides (natural uranium and its decay products), and in the waste of NPPs and during the regeneration of irradiated flumes - artificial radionuclides (fission products and transuranic elements), which have high activity. Liquid radioactive waste (LRW) of a nuclear power plant of medium activity level is mainly represented by radionuclides of uranium fission products - 137Cs, 134Cs, 90Sr, 40K, 232Th, 226Ra, and 60Co. Liquid waste during the operation of the RBMK reactor produces about 100 thousand m3 per year [1,2].

Taking into account the pace of development of nuclear energy, it can be assumed that over the current decade, the activity of radioactive waste accumulated as a result of the operation of nuclear power plants will be over $10^{19}$ Bq. Obviously, storing liquid waste in tanks is unreliable and expensive. At the same time, various proposed programs for the disposal, long-term storage and disposal of radioactive waste are still at the research and development stage [1,2].

At most NPPs, low-level LRW is simply merged into nearby reservoirs, while radionuclides accumulate and concentrate in bottom sediments and aquatic organisms, thus entering food chains, the final links of which can be higher animals and humans.
Currently, the strategy of cleaning liquid waste from the nuclear industry, as well as water basins from radionuclides, is based on the lifetime of the radionuclides, concentration, physicochemical properties, vastness of polluted areas, as well as other factors. LRW reprocessing is aimed at solving two main tasks: cleaning the bulk of the waste from radionuclides and concentrating the latter in a minimal amount [3-5].

For the collection, processing, and long-term localization of radioactive waste, a centralized system has been created, including territorial special plants and disposal facilities (PZRO) [4,5]. However, for RBMK NPP-type reactors, accounting for incoming waste for long-term storage, assessment of the quality of their preparation and disposal at most PFOR do not meet modern scientific and technical requirements. The problem of the disposal of LRW is inextricably linked to the problem of the disposal of waste sorption materials, which, after use, are a source of secondary radioactive radiation. During the processing, storage and transportation of radioactive waste, additional irradiation of the maintenance personnel of nuclear power plants occurs. In this regard, there is a need to develop new scientific and technical approaches not just for the disposal of solid radioactive waste, but for transferring them from the class of increased radioactivity to low-level or even non-radioactive objects [1].

2. Relevance, scientific significance of the issue
One of the promising ways of conditioning, reprocessing and disposal of liquid radioactive waste to reduce their exposure dose rate (MED), in our opinion, is the conversion of low-level liquid radioactive waste (SRW) by concentrating radionuclides from liquid radioactive waste inside the iron oxide matrix sorbents (ion exchangers). Sorbents obtained on the basis of iron oxide systems can be widely used in various fields of modern engineering and technology due to the presence of a complex of specialized properties [6-14].

The development of such sorbents has the greatest relevance for nuclear power engineering. The ion exchangers based on ion exchange resins and activated carbons used for the treatment of wastewater from nuclear power plants have low strength and thermal characteristics. In addition, they do not have a radiation protective effect, and after mining they become sources of radioactive radiation, which causes problems of their disposal and disposal. In this direction, the most promising and technological modified iron oxide ion exchangers. Due to their high density, they provide an effective radiation protective shield from photon radiation with an energy of up to 1.5 MeV. This will reduce the radiation background of “spent” sorbents.

When developing sorbents, the authors used an approach based on the fact that the applied modifier plays a determining role in the “substance on the carrier” system. In order to obtain material, the sorption properties of which are mainly determined by the nature of the fixed compound, the authors fixed the chemical compounds in the liquid phase on the surface of the iron oxide carrier [15-24].

Enriched iron oxide minerals represented by magnetite (Fe₃O₄ - 97.2% wt.), Hematite (Fe₂O₃ - 96.8% wt.) And martite (Fe₂O₃ • nH₂O - 98.2% wt.) Were used as the main carrier. Effective modifiers of iron oxide sorbents are sodium polyethylsiliconates (TECN).

3. Results and discussion
The fixing of the modifier on the surface of iron oxides occurs due to the reaction of TECN with hydroxyl groups of the surface of oxides. The methods of infrared (IR) spectroscopy on the surface of iron oxide minerals revealed the presence of hydroxyl groups, which tell the surface the main character (Figure 1).
Analysis of infrared spectra shows the presence of magnetite bands in the region of 3480-3400 cm⁻¹, which, according to [19], refer to stretching vibrations of water of crystallization (3480 cm⁻¹ band), as well as FeOH groups and adsorption water (3400 cm⁻¹ band).

The absorption in the region of 1050-1100 cm⁻¹ according to the data of [20] corresponds to the vibrations of water molecules coordinated to the surface. The presence of these bands is noted both on hematite and martite. On hematite and martite, there are absorption bands in the region of 3420 and 3360 cm⁻¹, which corresponds to the stretching vibrations of the HON groups. On the martite, in addition, the absorption bands in the region of 3540-3550 cm⁻¹ are noted, which corresponds to the paired groups of OH groups, between which there is a hydrogen bond. The 3500 cm⁻¹ band corresponds to the stretching vibrations of water of crystallization. The presence of a band at 1640 cm⁻¹ on all three forms of iron oxides corresponds to the deformation vibrations of NON. The presence of specific bands in the region of 2720 cm⁻¹ (isolated OH groups) and 1627 cm⁻¹ (adsorption water) are also noted on martite.

The reason for the appearance in the IR spectra of iron oxides of several bands belonging to the free hydroxyl groups of the surface is that the oxygen of the OH group can be in contact with several metal atoms. The metal atoms are the nearest neighbors of the OH group, so their number should have a decisive influence on the frequency of vibrations of OH groups.

The possibility of covalent fixing of organic modifiers on iron oxide minerals is mainly due to the presence of hydroxyl groups FeOH on their surface. Moreover, hydroxogroups of the surface of minerals are of primary importance, and not contained deep in the structure. Fe-O-Fe groups are much less reactive. Hydroxyl groups are much more active and easier to react, since the proton of the hydroxyl group has a weakly acidic character, and is capable of entering into exchange reactions.

During the subsequent heat treatment of the modified iron oxide systems, a polycondensation reaction occurs between the silanol groups of PESN and the hydroxyl groups of FeₙOₙm, accompanied
by crosslinking of the polysiloxane chains together into a single modification grid, as a result of which the modifier is attached to the surface of the iron oxide.

The presence in the molecule of ethylsiliconate sodium unsubstituted and sodium-substituted silanol groups suggests the following interaction with the surface of iron oxides fig.2:

![Figure 2. Surface of iron oxides.](image)

Table 1. Quantitative characterization of the modification shell of iron oxide minerals.

| Matrix    | Surface density of grafting modifier, mmol/g | Thickness of the grafted layer of modifier, nm |
|-----------|---------------------------------------------|-----------------------------------------------|
| Magnetite | $0.874 \times 10^{-3}$                      | 5.44                                          |
| Hematite  | $0.762 \times 10^{-3}$                      | 5.17                                          |
| Martite   | $0.778 \times 10^{-3}$                      | 5.37                                          |

Thus, the thickness of the grafted ESN layer increases in the hematite – martite – magnetite series, which confirms previous studies on the intensity of the interaction of these iron oxide systems with sodium ethyl silicate.

Using chemical analysis and flame photometry, it has been established that during the sorption of radionuclides from aqueous media on modified iron oxides, the Na$^+$ ion is exchanged with the polysiloxane shell of the adsorbent surface for Rn$^{+n}$ cations according to the scheme fig. 3.

Iron oxide ion exchangers are designed to concentrate a wide range of radionuclides: 137Cs, 134Cs, 90Sr, 40K, 232Th, 226Ra, 60Co and, in their ion-exchange properties, are superior to sorbents based on ion-exchange resins (KU 2-8 (Russia), Amberlit (Rand H), Ionak (ICC) (USA), Vofatit (Germany), etc.) — full dynamic exchange capacity (PDOE): for β-emitters - 6.9 meq/g, for γ-emitters - 7.1 meq/g. When this is the multiplicity of protection against photon radiation is 5 times higher than that of traditional ion exchangers [4,5].
Figure 3. the scheme of exchanging of Na⁺ ion with the polysiloxane shell of the adsorbent surface for Rn + n cations, where Rnⁿ⁺ is a radionuclide.

Used modified iron oxide ion exchangers have high chemical and radiation resistance, thermal stability, mechanical strength and mass transfer rate.

Spent ion exchangers are pressed with subsequent disposal by incorporation into cement blocks. Concrete composites obtained using this technology have the following characteristics (Table 2).

Table 2. Characteristics of radiation protective concrete composites.

| Characteristic                          | Indicator                           |
|----------------------------------------|-------------------------------------|
| Compressive strength                   | 350-400 kg/cm²                      |
| Density of material is                  | 2650 - 2750 kg/m³                    |
| Water absorption                       | 10 - 15 mass %                       |
| Power loss exposure dose                | 15-17 times                          |
| Leachability of 137Cs                  | to 10-4 (g/cm²)/day                 |
| Alpha pollution material surfaces      | up to 2 (dis/cm)/min.               |

4. Conclusion
The possibility of obtaining a hydrolytically stable system of bonds with the surface of iron oxide minerals when they are modified with organic and inorganic modifiers is theoretically substantiated and experimentally confirmed. It has been established that the hydroxyl groups of the surface of oxides are the main type of reaction centers along which their surface is modified.

Modified iron oxide ion exchangers have high chemical and radiation resistance, thermal stability, mechanical strength and mass transfer rate.

The conditioning technology of spent ion exchangers into cement matrices allows creating an engineering barrier providing effective radiation protection and safe isolation of radionuclides.

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