Modifying the Surface of Iron-Oxide Minerals with Organic and Inorganic Modifiers

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Abstract: The article describes the possibility of modifying iron-oxide minerals having iron oxides content over 96% mass with sodium ethylsiliconate, with the purpose of using them as ion-exchangers. The modifiers adsorption with iron oxides surface has been studied in order to determine the mechanism of adsorbate and adsorbent interreaction and the influence of iron atoms coordination valence state on sorption of sodium alkylsiliconates from water solutions. The electrokinetic properties of fortified iron-oxide minerals surface has been studied. There has been educed the mechanism of sodium ethylsiliconate's interaction with iron oxides surface, pre-hydroxylated by means of molecular layering technology. It was found out, that hydroxyl groups of the oxides surface are the basic type of reaction sites, by which their surface is modified. To modify the iron-oxide minerals and achieve the high degree of graft it is necessary to activate the minerals' surface with ions of ferric iron; after that they are modified with sodium ethylsiliconate and the received product is heat-treated. The coverage ratio of iron-oxide minerals surface with sodium ethylsiliconate molecules has been evaluated; the surface density of modifier graft and the thickness of grafted layer have been determined.

Key words: Iron-oxide minerals · Modifying · Mechanism · Surface activation · Hydroxyl groups · Ferric iron · Sodium ethylsiliconate · Surface structure · Graft density · Properties

INTRODUCTION

Due to high radio-protective, mechanical and thermal characteristics of iron oxides it is of considerable practical interest to use the iron-oxide mineral carrying base to obtain selective ion-exchangers, educing radionuclides from water medium [1, 2]. It is commonly known that [3] thermodynamic constants of Cs^+- Na^+ exchange are high, so for modifying iron-oxide minerals there were used sodium alkylsiliconates, containing natrium groups.

In this research the defining role in "surface-supported substance" system is played by the applied modifier. The fixation of liquid-phase chemical compounds on the surface of the carrier was done with the purpose of receiving a material, the ion-exchange properties of which are preeminently determined by the nature of the fixed compound.

The simplest variant of modifying is the adsorption of organic polymers by the surface of mineral carrier [4-9]. On this account there were studied sorption characteristics of iron oxides with various coordination valence states of iron atoms to sodium alkylsiliconates from water solutions. As the basic carriers there were used fortified iron-oxide minerals, namely magnetite (Fe_3O_4 – 97,2% mass.), hematite (Fe_2O_3 – 96,8% mass.) and martite ($Fe_2O_3 \cdot nH_2O$ – 98,2% mass.).

Modifying the solid surfaces from water solutions has some unique advantages, related to modifier's molecules orientation effect towards the sorbent's surface due to electrostatic interaction with its charged active sites (or chemical interaction) [10]. The controlled alteration of such orientation, for example, by regulating the solution's pH allows achieving the highest activation of sorbent's inorganic surface.

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The research of modifiers adsorption by iron oxides surface was aimed at determining the mechanism of adsorbate and adsorbent interreaction and the influence of iron atoms coordination valence state on sorption of sodium alkylsiliconates from water solutions.

Studying the electrokinetic properties of fortified iron-oxide minerals surface is of the utmost interest, as the charge of the surface can have influence on the interaction of the base mineral with the ions of the solution, i.e. on their adsorption.
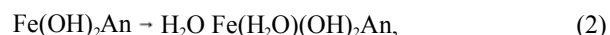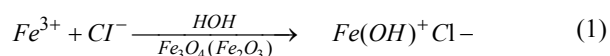
The Main Part: The electrokinetic potential of iron-oxide minerals in the distilled water is negative (Figure 1). It lowers along with lowering the pH of the medium (at adding HCl), changing from negative value to the positive potential at pH <4. So, the charge of the minerals' surface is determined by concentration of H^+ and OH^- ions. Therefore, H^+ and OH^- ions are potential-determining. As we can see in Figure 1 the dependence of [dzeta]-potential on pH of the medium is the most strongly pronounced for magnetite (Fe_3O_4). The surface charge of iron oxides rises within the row: martite ($Fe_2O_3 \cdot n \cdot H_2O$) → hematite ($Fe_2O_3$) → magnetite ($Fe_3O_4$).

Adsorption isotherms (G) of sodium ethylsiliconate (SES) by finely-dispersed iron oxides from water solutions within the researched concentration range are positive: with a rise of the modifier's equilibrium concentration in the solution the adsorption amount rises as well (Figure 2).

The higher adsorption of SES by martite seems to be conditioned by its higher surface [dzeta]-potential, in comparison with magnetite. In this case the interaction of sodium ethylsiliconate with iron oxides surface is conditioned both by electrostatic forces (physical adsorption) and by chemosorption through iron-oxides minerals surface hydroxyl groups, which are the basic type of reaction sites for modifying. In this case martite has an advantage due to its hydroxylated surface.

Adsorption isotherms, shown in Figure 2(a) indicate the polymolecular nature of SES adsorption with iron oxides, but determining the monolayer capacity on the base of these isotherms appears to be difficult as there are no well-defined plateaus at the initial sections of isotherms. And the found adsorption limit values G=70-80 mg/g appear to be considerably overevaluated in comparison with the anticipated value of G. To determine the true value of G there was studied the dependence of iron-oxide minerals electrokinetic potential on SES adsorption (Figure 2b). As we can Figure 2 [dzeta]-potential lowers along the whole range of SES

concentrations and doesn't have pronounced kinkings. So, to determine the SES adsorption in the monolayer, the iron-oxide minerals crystal lattice was completed with ions, same with the dispersion phase [11]. For this purpose there were used Fe^{3+} ions, which, being absorbed from the solution, can complete the iron oxides crystal lattice, altering the general ionic equilibrium in the solution. At this, on the surface of the solid phase the following process is going on:

$$Fe^{3+} + Cl^- \xrightarrow[Fe_3O_4(Fe_2O_3)]{HOH} \quad Fe(OH)^+ Cl- \qquad (1)$$

$$Fe(OH)_2An \rightarrow H_2O\ Fe(H_2O)(OH)_2An, \qquad (2)$$

where An– anion.

Here the ion of iron is coordinated with the corresponding ion of the mineral's solid phase crystal lattice. The appearance of the mentioned compound on it corresponds to the process of its forced hydration with hydroxyls, being part of this compound [12]. Such method of carrier's activation is described in literature as molecular layering technology [13-15], when a semi-volatile, but easy hydrolysable compound is used as a modifier.

Simultaneously with hydrating the surface by the described mechanism, another process is realized in the dispersion. The active complexing ion Fe^{3+}, placed in the dispersion medium, can saturate part of coordination spheres with corresponding ligands. If counter-ion doesn't have sufficient donor properties and there are no other complexing ligands, which is observed in the case under consideration, then the molecules of the solvent are coordinated, which results in forming solvate complexes – aquacomplexes $Fe(H_2O)_x^{3+}$ [16]. Being valency-unsatisfied, but coordinatively saturated, these aquacomplexes add the above mentioned hydroxyl-anionic ligands, forming compounds of the type $Fe(H_2O)_x(OH)_2^+An^-$.

To determine the optimal concentration of Fe^{3+} there was studied their adsorption from water solutions by iron-oxide minerals surface. As we can see in Figure 3, adsorption isotherm is of monomolecular character. The highest adsorption of Fe^{3+} ions is observed on magnetite, which seems to be conditioned by its higher [dzeta]–potential.

It was established that for magnetite the monolayer formation corresponds to adsorption 4,52 mg-eq/g Fe^{3+} and for hematite and martite 3,87 mg-eq/g and 3,51 mg-eq/g respectively. As a result of modification the surface of iron-oxide minerals acquires the additional
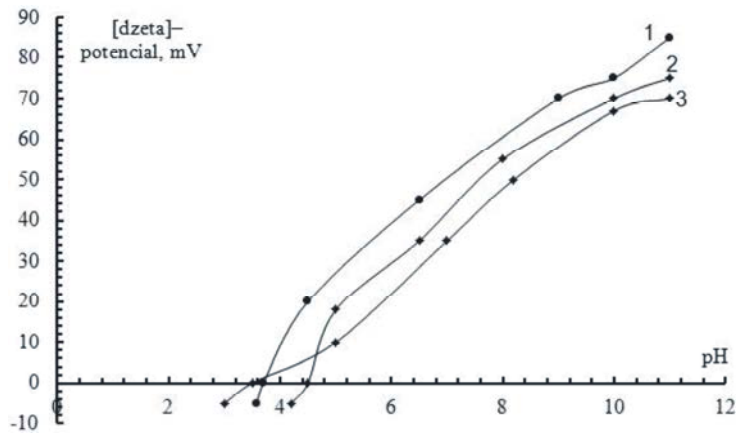
Fig. 1: Alteration of [dzeta]– potential of iron oxides depending on the water solution pH: 1 – for magnetite; 2 – for hematite; 3 – for martite
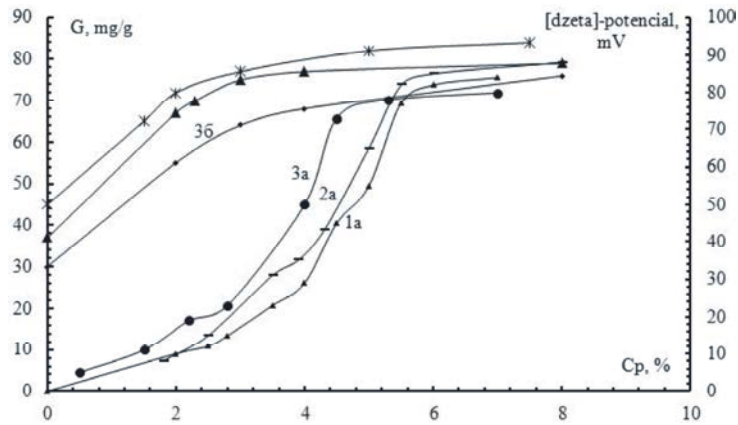

Fig. 2: Adsorption isotherms of SES from water solutions by iron oxides (a) and alteration of [dzeta]-potential of iron oxides (b) depending on the SES concentration:
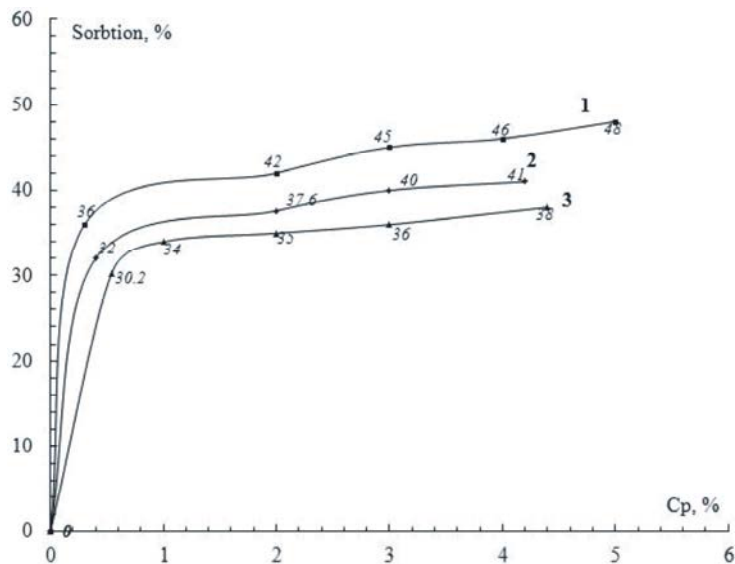1 -magnetite, 2 - hematite, 3 - martite

Fig. 3: Sorption of Fe^{3+} ions from water solution by iron-oxide minerals:
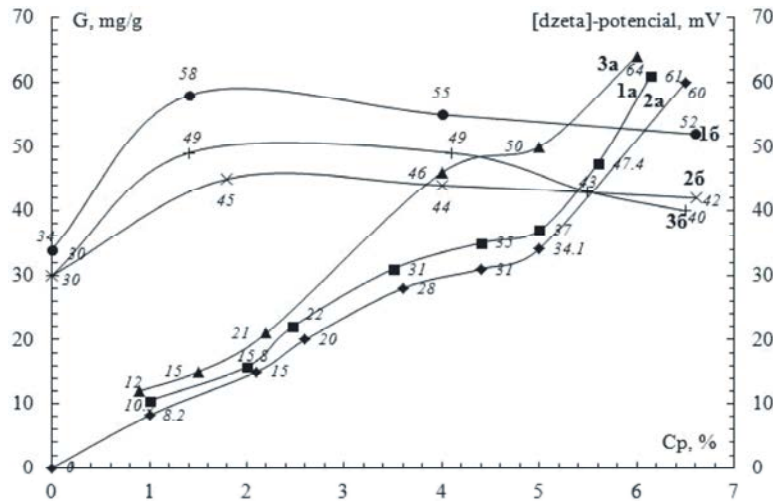1 - magnetite, 2 - hematite, 3 - martite

Fig. 4: Adsorption isotherms of SES by iron-oxide minerals, activated with Fe^{3+} ions (a) and alteration of their [dzeta]–potential (b):

1 - magnetite, 2 - hematite, 3 – martite

active sites represented by $Fe(OH)_2^+$, which increases (in modulus) [dzeta]–potential of magnetite to –33,2 mV, hematite to -30,5 mV and martite to –27,0 mV (Figure 4b).

In Figures 2 and 4 (curve 2a) we can see that the initial section of SES adsorption isotherm on hematite (curve 2a) is more concaved, than for SES adsorption on the other forms of iron oxides. That can be indicative of the competitive interaction of water and SES molecules with hematite surface, due to its lower [dzeta]–potential (compared with magnetite) and small quantity of hydroxyls (compared with martite). Increasing the concentration of SES (Figure 4) causes the decrease of iron-oxide minerals electrokinetic potential, at SES concentration in the monolayer 13,1 mg/g for magnetite, 12,5 mg/g for hematite and 16,5 mg/g for martite. So it is obvious that the salient point on the influence curve [dzeta]=f(Cp.) (Figure 4) corresponds to completion of SES adsorbed monolayer forming on the surface of iron oxides.

At sodium ethylsiliconate's interaction with iron-oxide minerals an essential role is played by surface structure and particles shape. In works by N.N. Kruglitsky [17] it was stated by electron microscope studies that the particles of iron oxides are characterized by irregular shape with rough planes and high tendency to form aggregates. The rough surface of iron-oxide minerals particles contributes to the anchor-type adhesion mechanism of oligomerous films with iron-oxide carrier [18].

By methods of infrared spectroscopy on the surface of iron-oxide minerals there were found hydroxyl groups, supplying the surface with basic properties (Figure 5a).

The analysis of infrared spectra shows the presence of magnetite bands in the range 3480-3400 cm^{-1}, which according to data [19] refers to valence vibrations of crystallization water (band 3480 cm^{-1}), as well as FeOH-groups and adsorption water (band 3400 cm^{-1}).

The adsorption in the range 1050-1100 cm^{-1}, according to the data [20] corresponds to vibrations of water molecules, coordinately-linked with the surface. These bands are observed both on hematite and on martite. On hematite and martite there are observed absorption bands in the range 3420 and 3360 cm^{-1}, which corresponds to valence vibrations of HOH groups. Besides, on martite there are observed absorption bands in the range 3540-3550 cm^{-1}, which corresponds to double groupings of OH-groups, having hydrogen bonds. The bands 3500 cm^{-1} correspond to valence vibrations of crystallization water. The presence of the band 1640 cm^{-1} on all three forms of oxides corresponds to deformation vibrations of HOH. On martite there is also recorded the presence of specific bands in the range 2720 cm^{-1} (isolated OH-groups) and 1627cm^{-1} (adsorption water).

The reason for appearing in iron oxides infrared spectra several bands, referring to free hydroxyl groups of the surface, consists in the fact that the oxygen of OH-group can be in contact with several metal atoms. The metal atoms are nearest neighbors of OH-groups, so their quantity must have determining influence on IH-groups vibration frequency.

It should be borne in mind that the surface of iron-oxide minerals is usually covered with a polymolecular layer of physically-adsorbed water, which almost always hampers the modifying. So, the standard
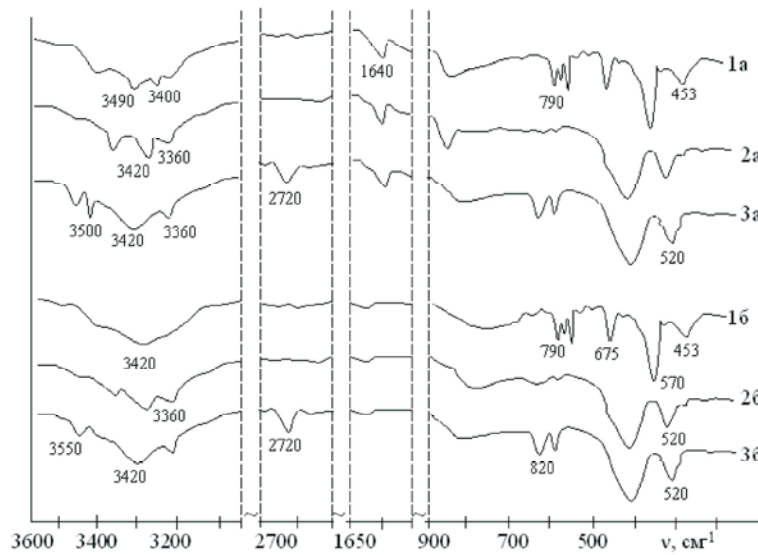
Fig. 5: The infrared spectra of the initial iron-oxide minerals (a) and iron-oxide minerals after their heat treatment at 180°C (a): 1 - magnetite; 2 - hematite; 3 – martite

process, preceding modification, consists in removing the physically adsorbed water, for which purpose the iron-oxide minerals undergo heat treatment at 180°C. The analysis of infrared spectra shows (Figure 5b), that at heating original substances the molecular water is removed, which is proved by intensity reduction with the rise of temperature of liquid water OH-groups valence vibrations band at 3400 cm^{-1}, crystallization water is removed (leveling of absorption bands in the range 3480 cm^{-1} on magnetite and hematite, vanishing of the band 3500 cm^{-1} on martite) and adsorption water is removed (vanishing of the band 1627 cm^{-1} on martite and reduction of intensity of the band 1640 cm^{-1}).

The possibility of covalent consolidating of organic modifiers on iron-oxide minerals is preeminently conditioned by the presence of hydroxyl groups FeOH on their surface. The key role is played by hydroxyl groups on the surface of minerals, rather than those located deep in the structure. The groups Fe-O-Fe are far less reactive. Hydroxyl groups are considerably more active and easily enter into reactions, as the proton of hydroxyl group is weak-acidic and can enter into exchange reactions.

The presented data about the state of iron-oxide minerals surface and the results of sodium ethylsiliconate adsorption allow describing the mechanism of minerals modifying in more detail.

The presence of unsubstituted and substituted with natrium silanol groups in a molecule of sodium ethylsiliconate allows assuming the following types of these compounds' interaction with the iron oxides surface:

- The interaction of SES with iron oxides' surface hydroxyl groups by the scheme:

$$(3)$$
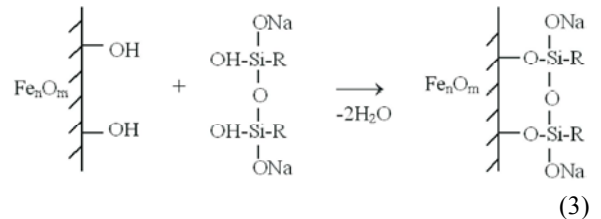
- In case of pre-activation of iron oxides surface with Fe^{3+} ions, interaction due to free silanol groups:

$$(4)$$
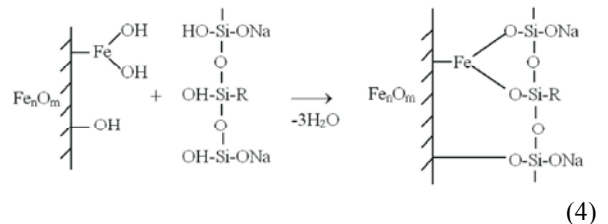
- Formation of hydrogen bonds between ÎÍ-groups of poly-siloxane chain and oxygen atoms of iron oxides surface, which results in relatively high binding strength of modifier with iron-oxide carrier:
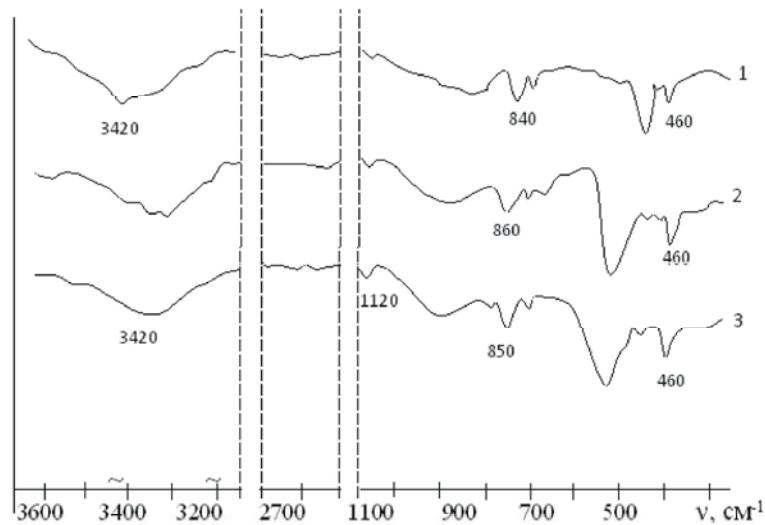

$$(5)$$
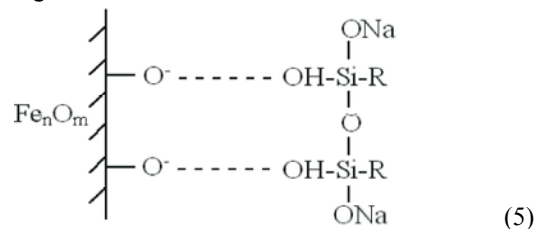
Fig. 6: Infrared spectra of iron-oxide minerals, modified with SES at temperature 150 °C: 1 – magnetite; 2 – hematite; 3 – martite

Even at indoor temperature, though slowly, on the surface of modified iron-oxide minerals there take place reactions of sodium ethylsiliconate polycondensation, which results in molecular weight increment. At this, these reactions go on due to both silanol and silanolate groups. The long-chain molecules, formed in these reactions (3-5), can screen large areas of iron oxides surface:

(6)
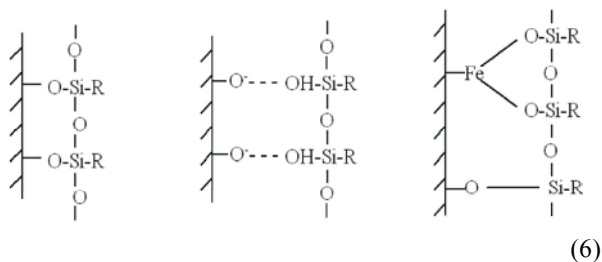
The rise in temperature contributes to increase of these reactions rate. As under normal conditions the polycondensation processes go on slowly, which can be conditioned by the inhibitory influence of alkali, it seems appropriate to develop methods, which would allow accelerating this process. The possible ways of solving this problem can be either raising the temperature of modifier covering formation process, or introducing additives, accelerating the cross-linking processes.

During the heat treatment of sodium ethylsiliconate, sorbed on the surface of iron-oxide minerals at temperature 150-160°C (to consolidate the modifier on the surface of the mineral), the silanol groups, formed at oligomer oxidation, are condensated, which is accompanied by crosslinking of polysiloxane chains into a single polymer network (a space network). The above-mentioned processes contribute to strengthening the bond of sodium ethylsiliconate with the surface of iron-oxide minerals.

The execution of the above-considered modifying mechanisms (schemes 3-6) is proved by reduction in the infrared spectrum of the absorption band intensity of SES-modified dehydrated magnetite in the range 453 cm^{-1} (Figure 6), which corresponds to the valency vibrations of Fe-O··Fe groups.

The considerable reduction of intensity of absorption bands 520 cm^{-1} on martite and hematite (identified as Fe$_2$O$_3$) and bands 570 cm^{-1} and 790-675 cm^{-1} on magnetite (corresponds to Fe$_3$O$_4$), also bears evidence of SES interaction with negatively charged (O$^-$) sites of the iron-oxide minerals surface.

The leveling of absorption bands in the range 3540-3550 cm^{-1} on martite and in the range 3420, 3360 cm^{-1} on hematite, as well as intensity reduction of band 3480 cm^{-1} on all forms of iron-oxide minerals gives evidence of the chemical interaction between the minerals surface's hydroxyl groups FeOH and silanol groups of Si-OH modifier and of polycondensation, which results in space-network structure formation. The latter is confirmed by wide or resolved bands in the range 1000-1120 cm^{-1} (antisymmetric vibrations of Si-O-Si bonds), found in the spectra of SES-modified iron-oxide minerals after their heat treatment in oxygen at 150ºC (Figure 6). A virtually total disappearance of 2720 cm^{-1} band and bands 820 and 860 cm^{-1} in the infrared spectrum of modified martite also gives evidence of the modifier's chemical interaction through isolated hydroxyl groups of the martite surface.

Table 1: The quantitative description of iron-oxide minerals' modified covering

Base	The surface density of modifier graft, mM/g	The thickness of modifier grafted layer, 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

The appearance of band in the absorption area 860 and 825 cm^{-1} on all modified forms of iron-oxide minerals indicates the formation of Si-O-Na metasilicate chains [SiO_3] [21] on their surface and the appearance of band 460 cm^{-1} corresponds to sodium cations.

To evaluate the coverage ratio of iron-oxide minerals surface with SES molecules there was determined the surface density of modifier graft and the thickness of grafted layer. The findings are presented in the table.

In accordance with the obtained data about adsorption character and the subsequent transformations in the adsorption layer, it was accepted, that in the adsorption interaction with iron-oxide minerals surface only one silanol group is involved and the other are involved polycondensation processes of SES molecules cross-linking.

So, the thickness of SES grafted layer increases in the row hematite→martite→magnetite, which confirms the results of the earlier research concerning the intensity of these iron-oxide systems' interaction with sodium ethylsiliconate.

CONCLUSION

So, on the basis of carried-out research, there was theoretically justified and experimentally confirmed the possibility of receiving a hydrolytically stable system of bonds with the surface of iron-oxide minerals at modifying them with organic and inorganic modifiers. The iron-oxides crystal lattice is completed with Fe^{3+} ions by molecular layering technology. As a result, the surface of iron-oxide base acquires the additional active sites represented by $Fe(OH)_2^+$, which contributes to chemosorption interaction of modifier molecules with hydroxyl groups of iron-oxides surface due to forming of bonds $\equiv Si - O - Fe^+$. The reaction of organosiloxanes with the inorganic surface includes several stages: hydrolysis of stable functional groups, condensation of organosiloxane into oligomerous compounds, which interact with hydroxyl groups of iron-oxide minerals surface, forming chemical bonds at heating.

CONCLUSIONS

- There is described the possibility of modifying iron-oxide minerals having iron oxides content over 96% mass with sodium ethylsiliconate (SES), with the purpose of using them as ion-exchangers for decontaminating radioactive solutions.
- In the neutral water medium the electrokinetic potential of iron-oxide minerals is negative and rises within the row magnetite → hematite → martite.
- There are identified the interaction mechanisms of sodium alkylsiliconates with iron oxides surface, pre-hydroxylated by means of molecular layering technology.
- It was stated that hydroxyl groups of oxides surface are the basic type of reaction sites, by which their surface is modified.
- To modify iron-oxide minerals and achieve the high degree of graft it is necessary to activate the minerals' surface with ions of Fe^{3+} and then with sodium ethylsiliconate after which the product is heat-treated. The thickness of the modifier's grafted layer is 5,44 nm on magnetite, 5,17 nm on hematite and 5,37 nm on martite.

ACKNOWLEDGEMENTS

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