

typical that can be explained by the raising part of low-molecular paraffin hydrocarbons (Fig. 4, *e*). The rise of a part of tar components in the composition of oil deposit increases the degree of amorphism in the ATPD structure.

For the paraffin hydrocarbons of oil deposit of 122 well of Upper-Salat deposit the similar tendency of crystal structure change at oil stream temperature decrease is observed (Fig. 4, *f-h*). The raised content of tar components in deposit composition increases the amorphism degree in ATPD structure.

Thus, the studied oils differ significantly in alkanets composition, content of tar and aromatic components that defines the peculiarities of deposit formation in them. For the oil of 122 well with high content of solid

paraffins, but distinguished by higher concentration of tar components, the process of sludge formation is observed starting from the temperature +50 °C. In the oil of 118 well deposit formation occurs even at +70 °C.

Oil stream temperature decrease results in increase of a part of dendritic type of paraffin hydrocarbons crystallization and amorphism degree in oil deposit structure. The deposit formed from the oil of 118 well at 60...70 °C, is characterized by a higher content of high-molecular paraffins and slight tar component concentration, low solubility in organic solvents. By the physical properties it is distinguished by higher fragility. The deposit, formed at 30...50 °C, contains the considerable quantity of tar components and it is more soluble in organic solvents.

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INFLUENCE OF REDOX CONDITIONS AND MECHANICAL ACTION ON CHANGE IN PEAT HUMIC ACID COMPOSITION

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Mechanical action on humic acids is shown to result in change of their composition accompanying decrease in aromaticity degree and increase in oxygen-containing fragments. Mechanical treatment of peat in oxidizing conditions increases the efficiency of extracting water-soluble components and humic acids to the maximum. Structural parameters and functional composition of humic acid molecules change at peat treatment in the redox conditions depending on the conditions.

Humic acids (HA) are the main components of peats in quantity and biological activity and correspond to high-molecular polymer compounds, stiff and insoluble in water [1, 2]. The solution of fundamental task of their investigation is added up to application of extraction, chemical, physicochemical and enzymatic methods. Using mechanochemical transformations in solid phase for developing complex macromolecules of HA is a perspective method of their deeper investigation [3, 4].

The fundamental investigation on solid-phase mechanochemical HA transformations gives the signifi-

cant technological advantages to the production of bio-active substances on basis of the investigated reactions.

Previously, the preliminary data, indicating the possibility of selective mechanochemical reactions of macromolecules decomposition into definite types of bindings and production preparations from peats with primary content of substances of certain classes – carbohydrates, phenols, lipids, HA were obtained [3, 5]. Due to the system of analytical methods the composition and properties of HA, polysaccharides, polyphenols and lipids from peats, mechanoactivated in the presence of alkaline and enzymatic agents, were investigated.

The aim of the given paper is to study peat HA composition after their mechanical treatment and at peat treatment in oxidizing and reductive conditions.

Objects and methods of investigations

High-moor pine-cotton-grass peat of high decomposition degree (55 %) of the Bakchar swamp and low-moor peat of «Klyukvennoe» deposit (Tomsk region) were used as the objects of investigation.

Mechanochemical treatment of peat and HA was carried out at a planetary-type mill APF-4 with discrete mode of operation (the development of the SD RAS Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk). The acceleration of effecting spheres of stainless steel with the diameter of 10mm was 200 m/s², processing time was 2 min at temperature 20 °C.

The organic compounds were extracted from peat by the classical complex scheme, described in G.L. Stadnikov's paper on raw plant materials [6]. Water-soluble components - polysaccharides and polyphenols ($t=95^{\circ}\text{C}$), bitumens (CH_3Cl), HA and fulvic acids (FA) (0,1N NaOH and 10 % HCl) were extracted sequentially from the initial and treated samples.

Peat treatment together with 0,5 % of peroxydisulphate $\text{K}_2\text{S}_2\text{O}_8$ and 0,5 % Zn was carried out to ascertain the influence of oxidizing and reductive conditions on mechanochemical transformations of organic compounds.

The elemental composition of HA and FA was determined at the analyzer «Carlo Erba Strumentazione» model 1106 (Italy).

To obtain the information about structural fragments content in HA the method of NMR¹³C-spectroscopy was used [7]. Spectra registration was carried out at radiospectrometer NMR of «Bruker» (Germany), having operating frequency by carbon 125 MHz, using the technique of Fourier transform with accumulation. Accumulation time changed from some hours to a day. The investigated HA samples were dissolved in 0,5 N of deuterated alkali. To eliminate Overhauser nuclear effect the recording of NMR¹³C spectra was carried out with protons suppression in INVGATE mode. Tetramethylsilane was used as an external standard. Spectra were taken with 4 sec lag between the pulses. Besides NMR spectra registration they were integrated, that allowed us to determine relative content of carbon magnetic cores, belonging to one or another group of atoms.

Functional structure of HA was analyzed by the method of IR-spectroscopy. Registration of HA spectra was carried out at IR-Fourier spectrometer «Nikolet 5700» with Raman module («Thermo Electron» corporation, USA) in tablets with KBr at the ratio 1:300 respectively in the range of frequency values from 400 to 4000 cm^{-1} with compensation of adsorbed water signals. For quantitative estimation of absorption bands intensity the method of base lines and relative optical densities is used [8].

Results and their discussion

To determine the stability of fragments of HA macromolecules at mechanical action the treatment of HA of high-moor pine-cotton-grass peat was carried out.

The results of investigations of HA mechanic treatment influence on their composition are presented in Table 1–3. The data of elemental analysis (Table 1) show that after HA dispersion at mechanoactivator the atomic ratio H/C and O/C increase. This indicates the decrease of aromaticity degree and increase of oxygen containing fragments in HA molecule.

Table 1. Elemental composition of high-moor pine-cotton-grass peat HA

HA sample	Elemental composition, rel. %				Ratio		
	C	H	N	O	H/C	O/C	C/N
Initial	55,6	5,6	2,9	35,8	1,22	0,48	22,4
Mechanically treated	53,4	6,6	3,1	36,9	1,50	0,52	20,1

According to the results of the analysis of HA fragment composition by the method of NMR¹³C – spectroscopy (Table 2) we may judge about significant decrease of HA aromaticity degree after their mechanic treatment. This shows that chemical transformations occur not only in peripheric part of macromolecule, but also in aromatic frame. The absence of agents supporting selecting radical reactions at HA mechanic treatment results in growth of oxygen containing fragments. The ratios of oxygen containing alkyl fragments $\text{C}_{\text{al}}\text{O}$ to alkyl ones – C_{al} and oxygen containing aromatic groups $\text{C}_{\text{ar}}\text{O}$ to carbon aromatic atoms C_{ar} increase in them in two times in comparison with initial HA. The amount of carboxylate and carbonyl groups increased, but a part of quinoid groups decreased. The ratio of a sum of HA hydrophilic fragments to a sum of hydrophobic (hphl/hphb) increased twice, that may indicate the growth of HA solubility [4, 7].

Table 2. Content of carbon atoms in structural fragments of high-moor pine-cotton-grass peat HA (according to the data of NMR¹³C-spectroscopy)

HA sample	Carbon atoms content in structural fragments, rel. %							
	$\text{C}=\text{O}$ 220...185 ppm	C_{carb} 186...180 ppm	COOH 180...160ppm	$\text{C}_{\text{ar}}\text{O}$ 160...140ppm	C_{ar} 140...106 ppm	$\text{C}_{\text{al}}\text{O}$ 106...58 ppm	C_{al} 54...0 ppm	hphl/hphb*
Initial	0,8	2,1	6,3	6,3	30,4	21,8	31,6	0,61
Mechanically treated	2,1	1,5	8,2	9,5	24,1	33,6	20,8	1,23

* hphl/hphb is the ratio of HA hydrophilic components to hydrophobic ones

The ratios of absorption bands optical densities conforming to hydrophilic and hydrophobic groups and fragments are calculated by the results of IR-spectroscopy (Table 3). It is seen from the data of Table 3 that mechanical treatment of extracted HA decreases total

content of hydroxyl groups (D_{3400}/D_{2920}), phenolic hydroxyls (D_{1270}/D_{2920}) and aromatic fragments (D_{1610}/D_{2920}) in macromolecules [3, 8]. In this case, the part of carbohydrate structures (D_{1070}) and carboxylic groups (D_{1700}) increases.

Table 3. Ratio of absorption bands optical densities at different wavelength for HA of high-moor pine-cotton-grass peat (by the data of IR-spectroscopy)

HA sample	Ratio of optical densities				
	D_{3400}/D_{2920}	D_{1700}/D_{2920}	D_{1610}/D_{2920}	D_{1270}/D_{2920}	D_{1070}/D_{2920}
Initial	1,64	1,45	1,67	1,32	0,77
Mechanically treated	1,05	1,51	1,56	1,17	0,92

To study the influence of oxidizing and reductive conditions on mechanochemical transformations of peat and, in this case, the change of HA composition the treatment of low-moor peat in the presence of 0,5 % Zn and 0,5 % $K_2S_2O_8$ was carried out.

The investigation of mechanical action influence on peat type content in various conditions confirmed the above stated fact [3, 5], that mechanical treatment increases the yield of water-soluble substances – polysaccharides, polyphenols and HA (Fig. 1). Maximal quantity of water-soluble components and HA is extracted at peat treatment in oxidizing conditions (with 0,5 % $K_2S_2O_8$).

The peculiarity of reductive conditions of peat treatment was significant increase of fulvic acids (FA) amount (Fig. 1). In this case, the content of water-soluble substances and HA also increased, but to a lesser extent, than in oxidizing conditions.

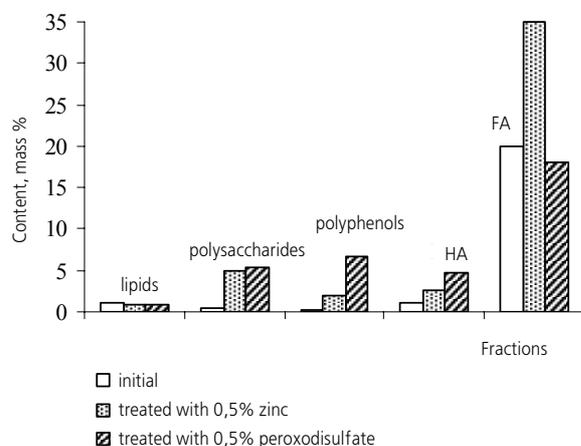


Fig. 1. Change of yields of lipids, polysaccharides, polyphenols, HA and FA of «Klyukvennoe» deposit peat depending on reductive and oxidizing conditions of mechanical treatment

According to the data of fragmentary composition analysis (Table 4) the decrease of carbonyl and quinoid fragments amount in peat HA, mechanically treated with Zn, is noted. But in this case, the part of carbohydrate fragments and substitutes carbon aromatic atoms significantly increased. But peat treatment in oxidizing conditions – with $K_2S_2O_8$ increased insignificantly content of COO-groups quinoid fragments and oxygen

containing fragments $C_{al}O$. In HA macromolecules, extracted from peat, treated in oxidizing and reductive conditions, content of $C_{ar}O$ decreased in 1,5...2 times, that influenced, in its turn, the reduction of hydrophilic and hydrophobic components ratio.

Table 4. Carbon atoms content in structural fragments of «Klyukvennoe» deposit peat HA (by the data of NMR ^{13}C -spectroscopy)

Peat samples	Carbon atoms content in structural fragments, rel. %						
	COO-, CO-, C_{quin} 220...160 ppm	$C_{ar}O$ 160...140 ppm	$C_{ar}C-H$ 140...106 ppm	$C_{ar}O$ 106...58 ppm	CH_3O 58...54 ppm	C_{ar} 54...0 ppm	hphl/hphb
Initial	17,7	13,2	15,9	24,5	4,2	24,5	1,47
Treated without admixtures	15,9	14,5	16,5	23,9	4,0	25,0	1,40
Treated with 0,5 % Zn	8,7	5,6	21,0	32,2	3,9	28,2	1,03
Treated with 0,5 % $K_2S_2O_8$	19,1	8,5	16,2	26,0	4,2	26,7	1,33

The analysis of IR-spectra of HA macromolecules, extracted from peat, allowed showing the differences in their functional structure (Table 5). The results of spectral coefficients calculation with respect to absorption band optical density $C=C$ of aromatic core (D_{1610}) indicate the growth of alkyl substituents amount (D_{2920}), total amount of hydroxyls (D_{3390}), including phenolic and alcohol hydroxyls and carboxylic groups (D_{1230}).

Table 5. Ratio of absorption bands optical densities at different wavelength for HA of high-moor peat of «Klyukvennoe» deposit (by the data of IR-spectroscopy)

Peat samples	Ratio of optical densities							
	D_{1070}/D_{1610}	D_{1170}/D_{1610}	D_{1230}/D_{1610}	D_{1515}/D_{1610}	D_{1720}/D_{1610}	D_{2850}/D_{1610}	D_{2920}/D_{1610}	D_{3390}/D_{1610}
Initial	0,63	0,70	0,75	0,68	0,93	0,78	0,88	1,05
Treated without admixtures	0,69	0,70	0,77	0,69	0,94	0,78	0,89	1,14
Treated with 0,5 % Zn	0,76	0,91	0,83	0,65	1,01	0,99	0,97	1,24
Treated with 0,5 % $K_2S_2O_8$	0,82	0,78	0,84	0,64	1,05	0,90	1,04	1,11

The differences in carbohydrate fragments of HA at peat treatment in various conditions should be noted: in reductive conditions the part of alcohol groups OH (D_{1170}) and in oxidizing ones the part of C-O polysaccharides (D_{1070}) increases. However, the most part of coefficients differ insignificantly. Obviously, HA macromolecules undergo negligible changes at mechanical action on peat.

Fulvic acid (FA) is a low-molecular part of peat humic substances [2]. Qualitative composition of FA functional groups is the same as of HA, but they differ from HA in low carbon content and correspondingly higher oxygen content (Table 6).

Table 6. Ratio of absorption bands optical densities at different wavelength for FA of high-moor peat of «Klyukvennoe» deposit (by the data of IR-spectroscopy)

Peat samples	Ratio of optical densities					
	D_{1070}/D_{1610}	D_{1150}/D_{1610}	D_{1270}/D_{1610}	D_{1720}/D_{1610}	D_{2920}/D_{1610}	D_{3375}/D_{1610}
Treated with 0,5 % Zn	0,97	0,87	0,86	1,37	0,83	1,94
Treated with 0,5 % $K_2S_2O_8$	1,55	–	1,19	1,49	1,40	2,62

On the whole, functional structure of FA macromolecules, extracted from peat at mechanical treatment with Zn and $K_2S_2O_8$, differs greater than for HA. FA molecules, characterized by less molecular weight and part of aromatic fragments, are subjected to larger extent to mechanodestruction than HA molecules. In oxidizing conditions the quantity of carbohydrate CO-groups, alkyl and hydroxyl substituents increases.

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COMPARATIVE CHARACTERISTIC OF HUMIC ACIDS OF PEAT SERIES IN TOMSK REGION

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On the basis of comparative analysis of element composition, infrared spectra and spectra of electron paramagnetic resonance as well as biological activity (according to indicators of reversible erythrocyte aggregation) it is shown that humic acids of different types of peat in Tomsk region differ in biological properties depending on the characteristic of their chemical composition. Humic acids of transitional sedge peat type have a higher biological activity in comparison with other peats, which is explained, first of all, by high content of aromatic polyconjugation system, nitrogen and active acid groups.

Humic acids (HA) as natural high molecular systems have complex composition and represent a wide class of homologues, consisting of compounds, differ in structure, composition, quantity and topography of molecular fragments [1–3]. Peat is the most perspective material for production humic preparations of various functions. It is characterized by high content and wide set of humic substances (HS) of different chemical composition and properties [4]. Chemical and biological properties of HA, extracted from different types of peat are specific depending on the formation of raw ma-

terial and peat-forming plants (of parent matter) and determined by the composition and ratio of individual substances, content of aliphatic and aromatic fragments, functional groups as well as by their heterogeneity and polydispersity [4–6].

The investigations in chemistry of HA have being conducted for many years; however, the questions on defining their biological activity are not solved yet. In papers [7, 8] it was repeatedly stressed on the variety of HA biological activity in peats of different formation (different in floristic composition, ash content, degree