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2015 IOP Conf. Ser.: Mater. Sci. Eng. 71 012038

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Creation of functional solid-state composites based on black peat

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Abstract. The paper presents investigations of composite materials based on black peats of Barabinskoe and Taganskoe deposits of the Tomsk region and carboxymethyl cellulose, both modified with iron (III) and copper (II) chloride solutions. In order to improve hydrophobic properties of compositions, optimum salt concentrations are detected. Water sorption and desorption isotherms are obtained for modified specimens. It is suggested to employ synthesized solid-state compositions as insulators in the capacity of both humidity controller and indoor-contaminant absorber.

1. Introduction

Peat based compositions are widely used as heat insulation and exterior walls [1,2] in construction material production and also as sorbents and geochemical barriers in zones of contaminant accumulation [3,4]. Naumova *et al* [5-8] stated the improvement of hydrophobic properties of iron-containing peat compositions, and showed their effective use in sorption of various ions, radionuclides, and other contaminants from man-made solutions. A high sorption capacity of peat allows the effective use of modifiers of diverse natures when controlling the quality characteristics of materials. For the process development of peat-based composites and their effective use, it is necessary to establish a correlation between technological properties and the field of utilization of these materials, their composition, structure, and production conditions.

The aim of this work is to ascertain physicochemical parameters of creating solid-state composites based on black peats at introduction of inorganic modifiers.

The subject of research is black peat from Barabinskoe and Taganskoe deposits of the Tomsk region. Iron (III) and copper (II) chloride solutions are selected as modifying agents.

2. Materials and methods

Metal-containing peat composites were prepared by iron (III) and copper (II) chloride treatment of peat with 0.25 mmol/l concentration in static conditions with intensive shaking for 7-10 days up to maximum saturation. Control of the amount of iron ions before and after modification was carried out



using complexometry. Metal content in the peat phase was detected by this difference. Modified specimens were washed with distilled water up to a complete elimination of relevant ions. To prevent leaching, composites were granulated with carboxymethyl cellulose and processed in a drying chamber at 105 °C. Bulking of the solid occurred due to sorption (swelling) of liquid produced by the original and modified specimens, was detected using the technique described in the work of Markhol [9]. At first, to calculate the amount of the modifier, acid-base properties of peats (complete exchange capacity, ionization constant, pK) were investigated by potentiometry [9]. Sorption activity of peats in relation to iron (III) and copper (II) ions was calculated by distribution coefficients D obtained by the method described in [9]. The structure and the qualitative and quantitative composition of specimens were studied with QUANTAX 70 energy dispersive spectroscopy on the scanning electron microscope Hitachi TM-300. Water vapour adsorption was studied using the gravimetrical static method described in the work [10].

3. Results and discussion

Table 1 presents results of investigation of acid-base properties of black peats.

Table 1. Values of swelling and complete exchange capacity of acid and basic groups and ionization constant of original black peats.

Peat types	*CEC ^{H⁺} (mmol/g)	*pK _a	CEC ^{OH⁻} (mmol/g)	pK _b	*W(%)
Barabinskoe deposit	5.40	9.40	2.10	12.50	80.10
Taganskoe deposit	4.90	10.80	1.30	12.30	79.10

Note: CEC is complete exchange capacity; pK is ionization constant; W is swelling.

From this Table, specimens under research are high-capacity amphoteric electrolytes, while in their acid-base and swelling properties they are not essentially different. Later on, the amount of the modifier was calculated using values of the complete exchange capacity.

Figure 1 illustrates the peat structure from Barabinskoe deposit and Fe (III) ion distribution in it. Fe (III) ions as shown in this Figure are uniformly distributed in the bulk of the peat-based composite. The average content of iron in modified specimens ranges between 3.8 and 5 %. Compressive strength of these specimens is (8-11) MPa.

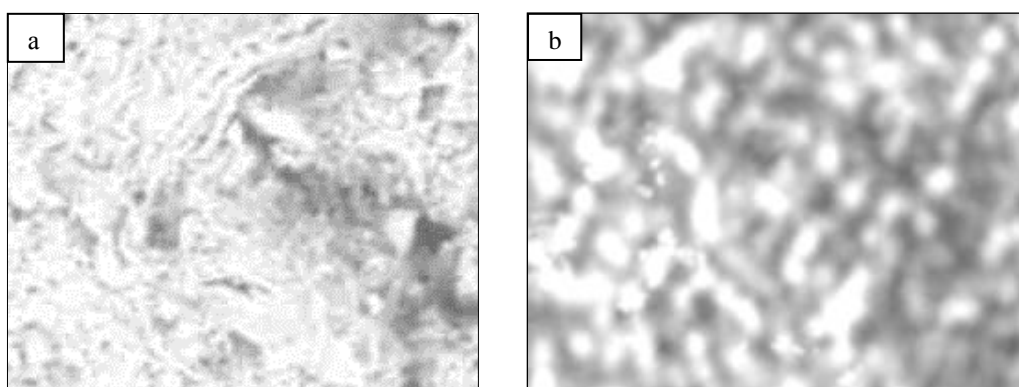


Figure 1. SEM images of peat structure and the elemental analysis of: a – original peat; b – peat modified with iron (III) ions.

Table 2 presents the dependence between distribution coefficients, relative humidity of peats and $C(FeCl_3)$. According to this Table, swelling of modified specimens is considerably lower than that of the original ones. At the same time, minimum of water absorption was observed in peats modified with $FeCl_3$ and $CuCl_2$ solutions with 0,25 mmol/l concentration, and specimens obtained after drying

were of hard consistency, with no hydration upon repeated contact with water. Data obtained prove those described in the work of Lych [11] who observed internal restructuring processes in the peat phase at absorption of polyvalent metal ions with certain concentrations. This is due to clustering of associates leading to the primary and secondary structure formations, and a change of water holding capacity and strength properties of the peat-based composite.

Table 2. Distribution coefficients and relative humidity of peats depending on C_{FeCl_3} at pH = 1.5 and C_{CuCl_2} at pH = 4.3.

Peat types	C_{FeCl_3} (mmol/l)	*W (%)	*D (ml/g)	C_{CuCl_2} (mmol/g)	*W (%)	D (ml/g)
Barabinskoe deposit	0.50	69.7±0.6	49.2±2,4	0.5	79.6±0,7	48.5±2,1
	0.25	52.2±0.3	61.1±2.7	0.25	62.4±0,6	59.8±2,0
	0.10	75.1±0.5	51.1±2,8	0.1	72.3±0,6	47.9±1,9
Taganskoe deposit	0.50	56.6±0.3	44.8±2,1	0.5	73.1±0,6	49.7±2,3
	0.25	48.7±0.3	26.1±1.5	0.25	56.8±0,5	24.2±1,4
	0.10	74.6±0.6	52.9±3,1	0.1	68.8±0,5	51.8±2,3

Note: D is distribution coefficient; W is relative humidity.

Taking into account high values of distribution coefficients, one can state that the composite material will be the efficient contaminant absorber.

To study the moisture exchange in the peat-based composition, isotherms of sorption (1) and desorption (2) were constructed for water vapour in peat specimens taken from Taganskoe deposit. Experimental data are shown in Figure 2.

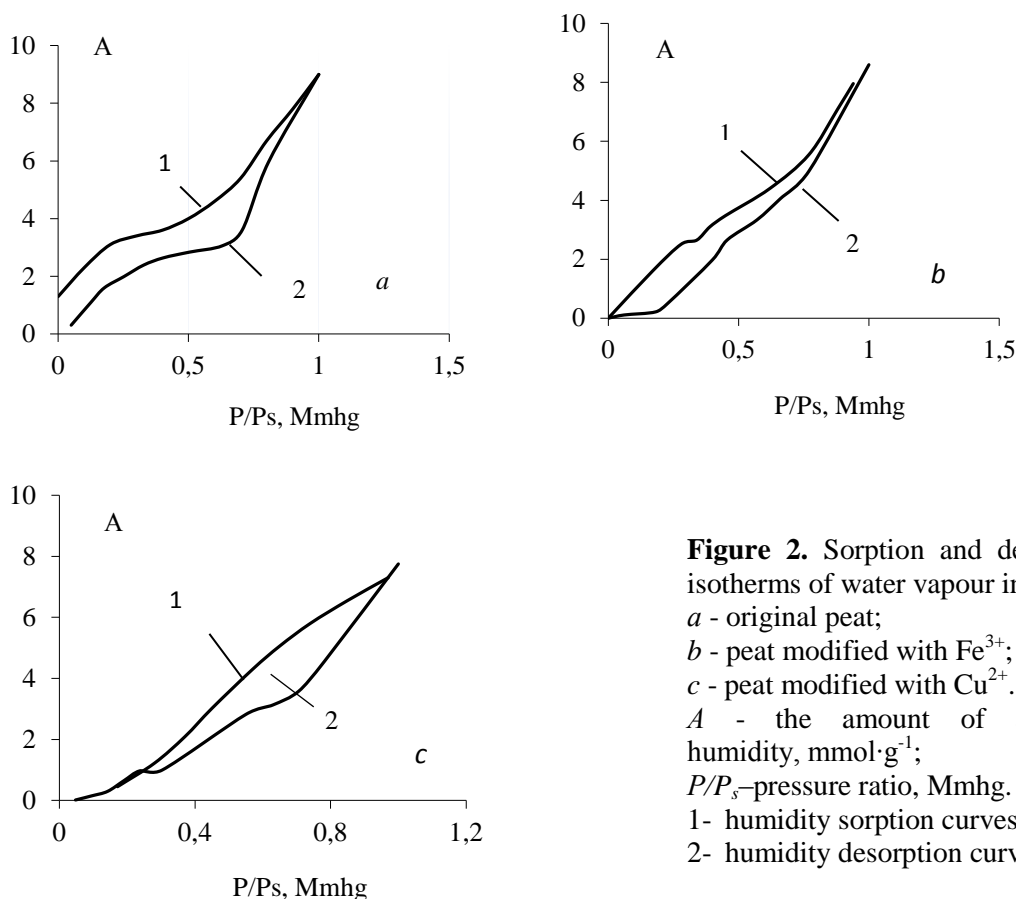


Figure 2. Sorption and desorption isotherms of water vapour in:
a - original peat;
b - peat modified with Fe^{3+} ;
c - peat modified with Cu^{2+} .
A - the amount of absorbed humidity, $\text{mmol}\cdot\text{g}^{-1}$;
P/P_s - pressure ratio, MmHg.
 1- humidity sorption curves,
 2- humidity desorption curves.

As characterized by Figure 2, in case of original peat the sorption isotherm falls under sigmoidal type II according to Brunauer's classification. At low pressure ratios, this isotherm is convex relative to X-axis, lies higher the adsorption isotherm, and does not return to a zero position within the whole interval of pressure ratio that proves a strong interaction between primary portions of water and the surface. At the same time, adsorption exhibits its irreversible character and sorption and desorption isotherm types indicate different-size pores presenting in the composite material. As for modification, it considerably changes isotherm types: they fall under type III (J-shaped) and show hysteresis extending up to the pressure ratio of 0 and 0.15 mm Hg for iron and copper respectively. The initial section of the sorption isotherm indicates the degree of water repellency of both specimens. The latter is connected with blocking of active centres on the peat surface due to their interaction with absorbed ions. At that, porosity calculation showed that all modified specimens possess basically large pores.

4. Conclusions

1. Solid-state compositions are suggested based on black peats of Barabinskoe and Taganskoe deposits of the Tomsk region as well as carboxymethylcellulose modified with iron (III) and copper (II) chloride solutions. It is shown that treatment with iron (III) and copper (II) chloride of 0.25 mmol/l concentrations reduces the moisture absorption by composites.
2. The laws of moisture exchange were established as a result of moisture sorption isotherms describing modified peat specimens.
3. Results obtained show the prospectivity of creation of efficient construction materials based on solid-state peat-based compositions that can be used as new generation heat insulators capable to function both as humidity controller and indoor contaminant absorber.

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