USE OF MACROMOLECULAR COMPOUNDS TO CONTROL INTERNAL MASS TRANSFER IN A GRANULAR MATERIAL

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UDC 662.641.542.47:553.97

Experimental data are presented on the effects of water-soluble macromolecular compounds (MMC) on the internal mass transfer in quartz sand and peat under nonisothermal conditions.

Disperse materials can be divided into two basic goups on the basis of deformation properties: materials in which the dispersed phase does not change in geometry on mass transfer (such as sand), and materials for which there is an ongoing change in structure in water transport (peat, clay, and soil). In a deformable system, it is difficult to identify those phenomena in the general process of water transfer produced by the modifying compounds, the more so since these materials are very sensitive to MMC and electrolytes.

The actions of MMC in regulating the structures of dispersed systems have been considered in detail many times [1-4]. However, there are virtually no papers on the effects of compounds on the internal mass transfer in natural dispersed materials, although the characteristics of the water transfer and the rheological properties are equally responsible for producing the structure and properties of the material on dewatering in a rheologically complex dispersed system.

Previous studies [5-8] have shown that it is possible to control the water transport in a peat system by means of polymers. Here we examine the trends in the internal nonisothermal mass transfer in disperse materials modified by MMC of various chemical natures.

The experiments were performed on an upgraded apparatus [9, 10] providing a linear temperature distribution in the material. The materials were peat and quartz sand washed with hydrochloric acid. The modifiers were hydrolyzed polyacrylonitrile HPAN, the K-4 preparation composed of anionic MMC (AMMC); VPK-101, an MMC of cationic type (CMMC); polyvinyl alohol PVA, which is an MMC of nonionic type NMMC; etc. [11]. These were used as aqueous solutions of 0.1-1% concentration in amounts of $1 \cdot 10^{-4}$-5%, on the basis of the dry material. The acidity was adjusted by the addition of HCl or NaOH.

The values of the thermal gradient coefficient δ were determined by graphical differentiation of the curves for the final stationary water distribution. The experiments were repeated three times.

It has been shown [9, 10, 12, 13] that the thermal gradient coefficient for an open-pore material is mainly a function of the porosity, water content, and temperature. Not much is known about the role of surface phenomena in thermal water transport in natural systems, although it has been shown [14-22] that the anamalous properties of the dispersion medium at the phase boundaries may make a contribution to the mass transfer.

The results of Fig. 1 show that the nature of the MMC determines the details of the thermal water transport in sand. The pore-space parameters of sand are unchanged during the mass transfer, so the variation in δ are mainly due to changes in the properties of the dispersion medium and in the surface phenomena produced by the MMC. The relationships indicate a general trend in the effects of MMC on the transport in sand, which is that all types of MMC at concentrations less than the critical value C_c decrease δ, whereas for $C > C_c$ they increase it. The value of C_c is dependent on the chemical properties of the MMC, and, as has already been shown [6], corresponds to the amount necessary to produce monosorption. This is maximal for CMMC and minimal for NMMC.

Peat Institute, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 43, No. 6, pp. 976-982, December, 1982. Original article submitted January 4, 1982.

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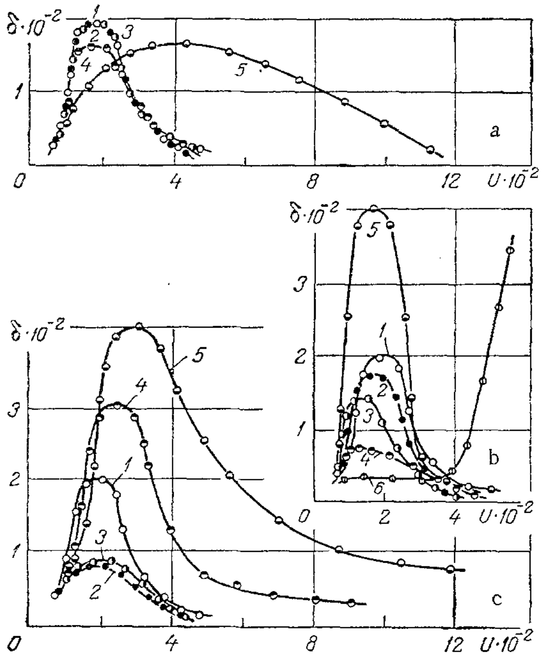

Fig. 1. Effects of water content U (kg/kg) in quartz sand (ρ = 1650 kg/m^3) and of MMC concentration on the variation in δ (deg^{-1}): a) PVA: 1) 0%; 2) 0.001; 3) 0.01; 4) 0.1; 5) 1.0; b) VPK-101: 1) 0%; 2) 0.001; 3) 0.01; 4) 0.1; 5) 0.2; 6) 1.0; c) K-4: 1) 0%; 2) 0.001; 3) 0.01; 4) 0.1; 5) 0.5.

TABLE 1. Effects of MMC on the Amount of Bound Water in Peat (desorption isotherm, T = 293°K)

MMC	MMC concentration as percent of dry peat	Equilibrium water content of peak (kg/kg) for a relative water vapor pressure φ = 0.98
Control	0	1,192
	0,1	1,404
	0,5	1,498
	1,0	1,689
Carboxymethylcellulose	0,1	1,405
	0,5	1,608
	1,0	1,972
VPK-101	0,01	1,140
	0,5	1,810
PVA	1,0	1,162

Figure 1 shows that the nature of the MMC has a very marked effect on the water transport in the range of water contents corresponding to the hygroscopic state. An MMC producing ions has much more effect on the water transport than a nonionic one, primarily because of the behavior of the ionic MMC in water, and also because of the type of interaction with the surface of the solid [1, 2, 5, 6]. The water in a disperse material in the hygroscopic state is bound by adsorption, so any change in the amount of adsorbed water produced by the MMC will affect the position and magnitude of the maximum in δ. This can be used in a method of determining the amount of bound water [12]. According to [12], the boundary between water bound by adsorption and free capillary or osmotic water corresponds to the water content at which there is a maximum in δ.

Figure 1 shows that the maximum δ for AMMC is displaced towards higher water contents relative to the control, while for CMMC it is displaced towards the low side. When NMMC are used ($C < C_c$), the maximum in δ is unaltered (Fig. 1). This indicates that in a system with

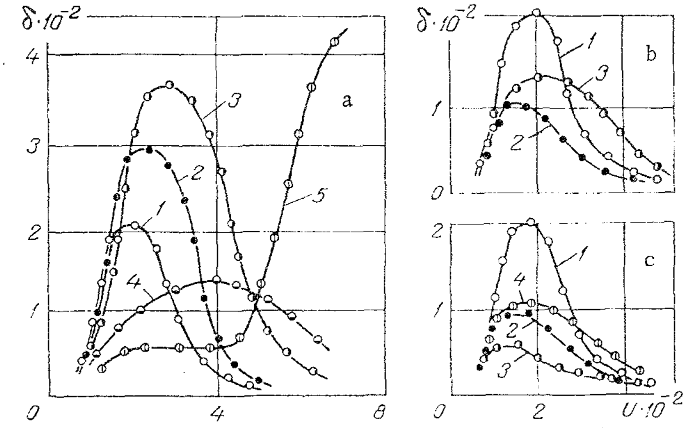

Fig. 2. Effects of water content U (kg/kg) in quartz sand (ρ = 1650 kg/m^3) and of pH of aqueous HPAN solutions and its concentration on δ (deg^{-1}): a) pH = 12.5: 1) 0%; 2) 0.01; 3) 0.1; 4) 0.5; 5) 1.0; b) pH = 6.0: 1) 0%; 2) 0.01; 3) 0.1); c) pH = 3.0: 1) 0%; 2) 0.01; 3) 0.1; 4) 1.0.

negatively charged surfaces (quartz sand or peat), the AMMC increases the amount of bound water because of an increase in the negative charge arising from adsorption of the ionized negatively charged AMMC radicals. Table 1 shows this for peat.

The action of CMMC is the opposite. There is a reduction in the amount of bound water for $C < C_c$ because of the reduced surface charge arising from the adsorption of the positively charged CMMC radicals. The subsequent adsorption of the CMMC alters the sign of the surface charge on the quartz and increases the content of bound water and the value of δ (Fig. 1b, curve 5).

Nonionic MMC, in particular PVA, has virtually no effect on the water binding, as is evident from the coincidence between the maxima in δ for $C < C_c$ (Fig. 1a, curves 1-3, data of Table 1, and also [21]).

The surface of a natural ion-exchange material, in particular, sand, contains various active centers. As in the case of silica gels [16], the silanol groups in the quartz sand have weak acid properties, and in a neutral medium this favors cation exchange, which converts the AMMC macromolecules into the isoelectric state. In a conformation respect, the AMMC molecules are transformed to bundles with low charge, which can readily reach the surface of the solid through the barrier represented by the hydration shell. The blocking of the surface of the quartz by the macromolecules when the amounts of AMMC are low reduces the content of bound water somewhat and decreases δ (Fig. 1c, curves 2 and 3). A similar effect can be obtained on reducing the pH of the AMMC solutions (Figs. 2b and c). The concentration ranges corresponding to reduction in δ are then considerably widened.

Adsorption of ionized AMMC increases δ because of the increased surface charge and the production of thicker hydration shells. This is also favored by increasing the pH of the AMMC solutions (Fig. 2).

Figures 1 and 2 show that the effects of MMC occur in a range of water contents considerably exceeding the hygroscopic state. For $C > C_c$ there is osmotic immobilization of the water by the polymer in the pore space of the sand. This is indicated by Table 2, which shows that above a certain concentration the strength of the sand structure after dewatering is increased (the sand runs freely in the initial state). The bound structures in the sand are produced by cohesion structuring consequent on the MMC macromolecules filling the pore space for $C > C_c$.

The main trends in the effects of MMC on isothermal mass transfer in peat are as for quartz sand. A peat system has a more highly developed network of active centers and a porous structure, which eliminate the effects from low MMC concentrations (Fig. 3). The os-

TABLE 2. Effects of MMC Concentration on the Strength of Drying Structures in Sand

MMC	MMC concentration, %	Limiting compression stress, MPa
Control	0	0
HPAN	0,001	0
	0,01	0
	0,1	0,008
	1,0	0,33
VPK-101	0,001	0
	0,01	0
	0,1	0
	0,2	0,02
	0,5	0,07
PVA	0,001	0
	0,01	0
	0,1	0,07
	1,0	0,24

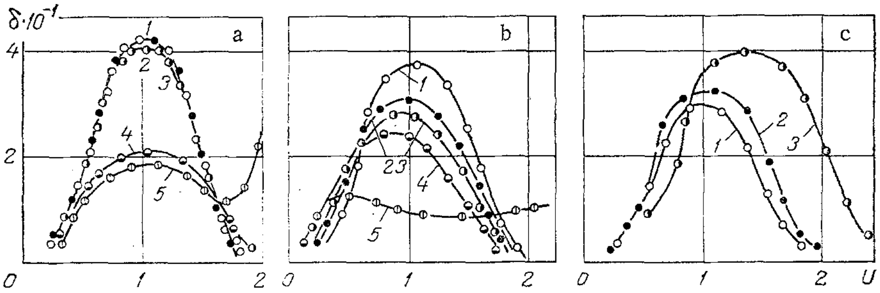

Fig. 3. Effects of water content U (kg/kg) in peat (ρ = 210 kg/m^3) and MMC concentration on δ (deg^{-1}): a) PVA: 1) 0%; 2) 0.05; 3) 0.2; 4) 1.0; 5) 2.0; b) VPK-101: 1) 0%; 2) 0.05; 3) 0.2; 4) 1.0; 5) 5.0; c) HPAN: 1) 0%; 2) 0.08; 3) 1.0.

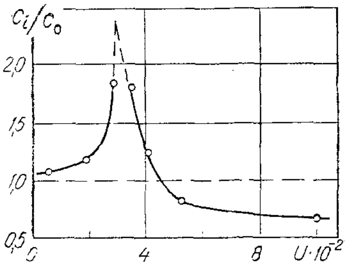

Fig. 4. Variation in relative concentration C_i/C_0 for HPAN on water content U (kg/kg) for quartz sand (stationary state).

motic water absorption is also less pronounced at high MMC concentrations, which is due to the semicolloidal and macromolecular nature of the organic components of peat [22], which are similar in properties to MMC.

It has been found that a 0.1% concentration of AMMC or above produces a redistribution of the MMC in quartz sand (Fig. 4), with the maximum C displaced towards larger water contents in the material than that for the maximum in δ. At 0.01% or less of the K-4 preparation in sand, changes in the concentrations of the MMC in the material are not observed or are at the limits of analysis [23]. This behavior of MMC may explain the formation of a minimum δ at high PVA concentrations (curve 5 of Fig. 3a).

These experimental data thus indicate that MMC can be used to control nonisothermal mass transfer in disperse materials and can provide a sound basis for choosing modifying compounds.

NOTATION

δ is the thermal gradient coefficient; C, concentration; C_c, critical concentration; U, water content; U_{mh}, maximum hygroscopic water content; ρ, density of dry substance.

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INERT-GAS ENERGY-ACCOMMODATION COEFFICIENTS ON TUNGSTEN

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UDC 533.06

Measurements have been made of the energy-accommodation coefficients for inert gases on the thermally cleaned and partially controllable surface of tungsten at about 300°K under conditions of oil-free pumping.

It is necessary to specify the boundary conditions in order to solve problems on heat transfer in low-density gases in the presence of solid surfaces. These boundary conditions contain physical quantities dependent on the interaction of the gas molecules with the surface at the microscopic level. Energy-accommodation coefficients (EAC) provide important information on the microscopic processes at such surfaces [1].

It is shown from theory and experiment [2] that energy accommodation may play a decisive part in heat transfer at very low gas pressures, when the mean free path of the molecules is much larger than the characteristic geometrical dimensions of the problem.

These accommodation coefficients are dependent on various physicochemical factors related to the nature and state of the gas and surface. The variety of factors hinders theoretical examination of the accommodation. When the scope for theory is restricted, information from experiment has to provide a basis for defining limits in gasdynamic processes, and it can also assist in improving theoretical models.

There is now extensive experimental evidence on EAC for gases on metals. In recent years, experiments have been performed at a high level [3-6]. However, most experimental studies have a major disadvantage arising from lack of control on the state of the surface. As a rule, authors give only the temperature at which the surface was cleaned by thermal desorption, together with information on the vacuum.

We have measured EAC for inert gases on tungsten by a nonstationary heated-filament method. The extent of removal of contaminants was determined by the thermal flash method, and also from the change in emissivity. Recrystallization during the heat treatment was detected by x-ray examination.

The methods of determining the EAC have been used before and are described in detail in [7, 8]. Figure 1 shows the apparatus. The following are the basic parameters: limiting vacuum in the measurement chamber during pumping $\sim 2 \cdot 10^{-9}$ mm Hg, rate of pressure rise in the chamber due to gas desorption from the walls and leaks at the level of 10^{-8} mm Hg per hour, pressure sensitivity of the capacitance micromanometer about 10^6 Hz/mm Hg, and heating temperature of the high-vacuum part of the equipment not less than 250°C.

We used highly purified He, Ne, Ar, Kr, and Xe. Measurements were made on filaments made from group A tungsten: diameter 50 μm, length 300 mm. The surface was cleaned from traces of oxides and graphite lubricant (aquadag), and also from adsorbed gases by heating

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Gor'kii Urals University, Sverdlovsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 43, No. 6, pp. 983-988, December, 1982. Original article submitted October 1, 1981.

0022-0841/82/4306-1394$07.50