



Soviet-era science, translated into English

NON-THERMOACTIVE WATER IN FINELY DISPERSED ROCKS

PERMAFROST STUDIES

1970

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-197001.65300>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

UDC 551.491.6

PERMAFROST STUDIES

A. A. ANANYAN

NON-THERMOACTIVE WATER IN FINELY DISPERSED ROCKS

(Presented by Academician V. I. Smirnov, February 19, 1970)

In the water-rock system, the orienting influence of active centers on the surface of rock particles on the translational motion of the water molecules closest to them distorts the structure of water ⁽¹⁾. A certain ordering of the structure of the nearest layers of water occurs relative to the active centers on the surface of rock particles, and heat of wetting is released. The orienting action is transmitted by an "relay" mechanism ⁽²⁾ to subsequent layers of water, attenuating with increasing distance from the surface of the solid rock particles.

Distortion of the structure of water is a kinetic obstacle that makes it difficult for molecules to group into the structure of ice ⁽³⁾. Therefore, at the freezing temperature of a rock, only that quantity of water crystallizes whose molecules are least oriented by the influence of the surface.

With further lowering of temperature, the influence of the intermolecular orientational effect between neighboring water molecules increases in the unfrozen water; ever new quantities of molecules are grouped into the structure of ice. Some amount of water with molecules most strongly oriented by the surface of the rock particles does not crystallize at all. It is possible that the significant orienting influence of the active centers of the rock on the nearest water molecules leads to bending of the hydrogen bonds or even to some deformation of the molecules themselves.

As an example, data for a heavy loam are presented. Some physical properties are given below. From the adsorption of water vapor ⁽⁴⁾, the specific surface area was determined to be 133 m²/g; the weight amount of water was then recalculated into an averaged number of molecular layers of water. Investigation of the mineralogical composition showed that in the fraction < 0.005 mm, montmorillonite predominates with an admixture of hydromica.

Fraction diameter, mm	1-0.5	0.5-0.25	0.25-1.0	0.1-0.05	0.05-0.01	0.01-0.005	< 0.005
Granulometric composition, %	0.6	2.3	2.5	12.5	42.4	12.8	26.9

The results of calorimetric determinations of the amount of unfrozen water (W_{unf} , %) as a function of temperature (t°) and total moisture content (W , %), as well as the recalculation of the weight moisture content into the averaged number of molecular layers (n), are given in Table 1.

The increase in the content of unfrozen water in the sample with a moisture content of 62% compared with the second sample is due to the presence of thin layers of unfrozen water on the surface of the numerous ice crystals formed⁽⁵⁾. Therefore, in the second sample the main phase transitions of water into ice practically end in the temperature interval from -3.2 to -6.4° , whereas in the first sample they end at about -20.6° , evidently owing to thin interlayers of unfrozen water on the ice crystals.

Calorimetric studies have practically not established phase transitions of water into ice upon further lowering of the temperature (small changes in the amount of unfrozen water may be attributed to the accuracy of the experiment).

The data in Table 1 show that, after the main phase transitions of water into ice, about two molecular layers of water remain in the noncrystallized state. Therefore, unfrozen water in finely dispersed rocks may be divided into a thermoactive part, which can crystallize, and a nonthermoactive part, whose molecules cannot group into the structure of ice. At low temperatures such water is apparently in a glassy state.

Table 1

$W_1 = 62\%; n_1 = 16.9$		$W_2 = 13.5\%; n_2 = 3.7$			
t°	$W, \%$	n	t°	$W, \%$	n
-0.5	14.9	4.1	-0.6	12.9	3.2
-1.2	13.4	3.7	-1.2	10.4	2.8
-3.2	11.6	3.2	-3.2	8.6	2.3
-6.5	9.5	2.6	-6.4	7.4	2.0
-10.8	8.3	2.3	-11.2	6.8	1.9
-20.6	7.8	2.1	-21.4	6.7	1.8

$W_1 =$	$W_2 =$				
62%; $n_1 =$	13.5%; $n_2 =$				
16.9	3.7				
-44.0	6.8	1.9	-43.0	7.0	1.9
-60.0	6.4	1.7	-60.0	6.2	1.7

The presence of noncrystallized water in a glassy state on porous glass, at a degree of filling of 1.6 molecular layers of water, was established by Litvan ⁽⁶⁾; similar results were also obtained by Antonio ⁽⁷⁾.

What are the other physical properties of the first layers of water near the surface of particles of finely dispersed rocks? It is known that in clays water is completely removed at temperatures above 200°. Most investigators consider the density of water at the surface of clay particles to be significantly greater than unity ⁽⁸⁾. According to Kemper ⁽⁹⁾, the limiting values of viscosity in the clay-water system, obtained for the first molecular layers, exceeded the viscosity of bulk water by several times.

The question arises: to what category should such water be assigned? Its high boiling temperature, high density, increased viscosity, and absence of phase transitions into ice make it possible to regard it as an analogue of "anomalous" water, which, according to B. V. Deryagin and coauthors ⁽¹⁰⁾, was first isolated by them in capillaries in this country, and later confirmed by Lippincott et al. ⁽¹¹⁾.

Moscow State University
named after M. V. Lomonosov

Received
16 II 1970

REFERENCES

1. A. A. Ananyan, *Collection of Scientific Reports of Higher Education Institutions, Geological-Geographical Sciences*, No. 2 (1959).
2. G. I. Distler, S. A. Kobzyreva, *Investigations in the Field of Surface Phenomena*, "Nauka," 1967.
3. A. A. Ananyan, *Collection. Permafrost Studies*, vol. 7, Moscow, 1967.
4. B. R. Puri, K. Murari, *Soil Sci.*, 97, No. 5, 344 (1964).
5. N. H. Fletcher, *Phill. Mag.*, 7, No. 74, 255 (1962).
6. G. C. Litvan, *Canad. J. Chem.*, 44, 2617 (1966).

7. A. A. Antonio, *J. Phys. Chem.*, 68, 2754 (1964).
8. A. A. Rode, *Fundamentals of the Theory of Soil Moisture*, Leningrad, 1965.
9. W. D. Kemper, *Soil Sci. Soc. Am. Proc.*, 25, No. 4, 255 (1961).
10. B. V. Deryagin, N. V. Churaev et al., *Izv. AN SSSR, ser. khim.*, 1967, No. 10.
11. E. R. Lippencott, R. R. Stromberg et al., *Science*, 164, No. 3887, 1482 (1969).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.