PHASE COMPOSITION AND THERMAL PROPERTIES OF FROZEN SALINE SOILS OVER A WIDE RANGE OF NEGATIVE TEMPERATURES

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In spite of intense interest in thermal properties, moisture phase composition, and freezing temperature of saline ground in the last few years, the available data refer, mainly, to the sodium chloride type of salinization. New or improved methods are needed to study frozen saline ground. We developed a procedure for determining the thermal capacity and the enthalpy down to a temperature of \(-125^\circ C\) using a dynamic calorimeter IT-S-400 and a differential scanning calorimeter "Mettler TA2000B". We proposed a combined procedure using the cryoscopic and the contact methods to study the freezing and thawing temperatures and the phase composition of moisture in fine-grained soils. This procedure allows the leveling of an unequal error of the determination using these two methods in various temperature intervals. An estimate of the extent of application of methods of heating up and heating (cooling) at a constant rate to determine the thermal properties, shows that in the temperature interval below the freezing temperature but above the eutectic one, for a salt solution that dominates in soil, the experimental data can be processed with an error not higher than that for non-saline soils.

The dependence of unfrozen water content, freezing-thawing temperature, and thermal properties on the composition of frozen saline fine-grained soils was studied. A decrease in freezing temperature and in heat conductivity and an increase in unfrozen water content is observed from sand to loamy sand to loam to clay, from kaolinite to hydromica to montmorillonite; from sulfates to carbonates to nitrates to chlorides, when the samples are affected by salt solutions with the same cation \(Na^+\); and from sodium to potassium, when the samples are affected by salt solutions with the same anion \(Cl^-\).

The thermal conductivity and the thermal diffusivity of frozen moisture-saturated saline soils are higher than those of thawed ones, when their samples are affected by \(Na_2SO_4\) and \(Na_2CO_3\). When the soil samples are affected by \(NaNO_3\) and \(NaCl\) of particular concentrations, the heat-conducting parameters of thawed soils are close to those of frozen soils, or even somewhat higher. The unfrozen water content in soils of various composition increases with pore solution concentration up to temperatures that correspond to eutectic ones. Two temperature depressions were observed in thermograms for thawing. The first depression is associated with thawing of free moisture, while the second one is observed in the range of temperatures close to the eutectic temperatures of aqueous solutions of these salts (Figure 1a). There are two heat release peaks in the curves for temperature versus heat capacity (Figure 1b). The first peak is determined by freezing of free water. The second peak is observed for a number of saline soils (sand, loam, kaolinite clay) in the range of eutectic temperatures, corresponding to free salt solution. A clearly defined hysteresis of both heat release peaks during cycles of cooling and warming is observed. A heat effect was observed in the cycle of thawing at \(-10^\circ C\) to \(-12^\circ C\), when the ground samples of a particular salinity and moisture content were affected by KCl, and in the cycle of thawing at \(-21^\circ C\) to \(-23^\circ C\) and in the cycle of cooling at \(-29^\circ C\) to \(-39^\circ C\), when the samples were affected by NaCl. The rate of the temperature change was of 0.1 - 2°C/min. A combined study of the temperature dependencies of moisture phase composition, thermograms for thawing, and enthalpies of saline frozen soils supports our hypothesis for the presence of a process, which we associate with formation and disintegration of NaCl cryohydrate, in the range of eutectic temperatures (Figure 1). This effect and this hypothesis was first discussed in our paper in 1988.

D.M. Anderson and A.R. Tice (1971) reported the presence of the second heat release peak at 35-65°C for kaoline and halloysite and three peaks for Li, Ca, and Na forms of montmorillonite.
Figure 1 Representative thermogram for thawing (a) and temperature behavior of heat capacity (b) in a sample of kaoline affected by NaCL solution.