Experimental study of freezing point and water phase composition of saline soils contaminated with hydrocarbons

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ABSTRACT
The results of freezing point research are discussed for pure and saline - oil-contaminated soil in this article. Different methods and the latest equipment to obtain the data. These details which were obtained using various equipment were compared. The thawing thermogramms both pure and contaminated saline soils of different particle size distribution were studied. The dominant influence of salinity was revealed.

RÉSUMÉ
Cet article présente les résultats de l’étude du point de congélation pour les sols non-salins et non-contaminés et pour les sols salins, contaminés par le pétrole. Les données ont été obtenues par différentes méthodes et avec un équipement récent. Celles récoltées à l’aide de différents équipements ont été comparées. Les thermogrammes de décongélation des deux types de sols de distributions différentes de taille des particules sont étudiés. L’influence dominante de la salinité est également révélée.

1 INTRODUCTION

The oil industry is highly developed today in many countries and considered to be one of the most dangerous sectors of the economy concerning the effects on the environment. The result of accidents is oil pollution of environment, and also high-mineralized water and water used to maintain reservoir pressure which have aggressive chemical properties. The effects of oil pollution in a permafrost zone may be much more influential functionally and longer in time. The results of observations show that under the conditions of the permafrost zone disintegration of hydrocarbons in the soil has lower speed (Solomonov et al., 2001), so contaminated soils can be a source of secondary pollution (Chuvilin, Miklyaeva, 2005).

The interaction of oil-contaminated soil with the engineering constructions and buildings (infrastructure fields, pipelines) determined the necessity of studies related with the changes of physical, mechanical and thermal properties of soils, including the freezing point. Currently there is not enough of researches on this topic. One of the first studies was conducted in VSEGINGEO and was devoted to the study of the strength properties of contaminated soil (Sheshin et al., 1992). The studying of rheological properties of oil-contaminated soils were engaged at the geocryological department in Moscow State University later (Shevchenko, Shirshova, 2008). It was concluded that the oil pollution does not affect on the nature of rheological processes in the frozen clay. Investigation of soil thermal properties conducted at the geocryological department in Moscow State University revealed that the thermal conductivity of frozen soil decreases with increasing of oil pollution (Motenko et al., 2001).

Experimental studies of the freezing point of oil-contaminated soil were carried by Grechishchev S.E. (2001). The results of his studies demonstrated there is no effect of oil pollution on the freezing point. Biggar in his report (2004) cites the data about decreasing of the freezing temperature for large values of pollution on 0,05 ° C, but notes that the sensitivity of the equipment with which the study was conducted, is not sufficient to make such a conclusion.

Investigation regarding the influence of salinity on soil properties, including the freezing point over the years was engaged by many Russian and foreign researchers. Over the years, they have accumulated a large amount of experimental materials.

Often soil salinization takes place in areas of oil production. Trigger mechanism in this case is highly mineralized technological flows, a significant role has water-soluble chlorides, less - sulfates and carbonates in their composition. Sources of salt are crude oil (fluid reservoir), commercial waste water, the contents of the barns, cleaning fluids and other geochemically active substances used for extraction and oil desalting. The scale and intensity of the impact of saline water on the ground is often more significant than the impact of its own oil and oil products. Accidents on the oil industry led to a marked salinity at all, even a relatively low salt concentrations in the reservoir fluids and wastewater respectively (Solntseva N.P., 1998).

Pollution of areas with salt and oil may have even more influence than the mechanical transformation of the land. There is not enough of data in the literature on the combined action of oil and sodium chloride. However the pollution by salt and oil can influence other than that exerted by each pollutant separately, as oil and saline solution interact with each other and their joint presence in
the pore space causes the flow of specific physical and chemical processes (Nebogina 2009).

In this regard, urgent action has to be taken to explore oil and salt contamination individually and collectively on the properties of the soil. Due to the change in the properties of soil-foundations could lead to a change in temperature regime, the emergence of subsidence and other negative permafrost processes, and ultimately loss bearing capacity and accidents.

The freezing temperature is one of the very important characteristic for the prediction of temperature regime of soils, as well as the calculation of the depth of seasonal thawing. Knowledge of this parameter is necessary to evaluate the permafrost conditions of the territory, as well as to analyze the properties of soil, including thermal characteristics of the ground. The freezing point is primarily determined by parameters of composition and structure of the grounds, as the value of the specific activity of the surface and the intensity of surface forces, the geometry of the capillary-porous system (pore radius distribution), the concentration of ions in the pore solution of salts, as well as the dynamics of the process of freezing (Fundamentals geocryology, 1996).

The aim of the study was an experimental study of the freezing temperature and water phase composition of soils in the laboratory.

2 RESEARCH METHOD

The cryoscopic method is used to determine the freezing point. Supercooling is one of the main reason of error in determining of the freezing point of the wet soil. Significantly more accurate results are obtained by a method foundated on the removal of heating curves, called the method of "the end of melting". According to specialists of cryochemistry (Sergeev, Batyuk, 1978) investigating the behavior of aqueous salt solutions). Its advantage is that the solid phase is not prone to superheating and melting rate increases rapidly with temperature increasing, which contributes to the rapid establishment of thermal equilibrium between the solid and liquid phases.

Research of saline soils confirmed this advantage and determining of phase transition temperature is quite reasonably recommended for the frozen ground with determining of thawing temperature. The soil samples were frozen to a temperature of -30 °C for the experiment. Set speed of freezing provides the massive cryostructure of samples. Thawing cycle is performed in air at room temperature (+25°C). The result of experiment - the temperature change of sample over time - thaw thermogram (Figure 1). Humidity of the tested soil sample is determined by the gravimetric method. The typical form of thawing thermograms and its graphics processing are shown in Fig. 1. The reduction of humidity decreases the value of the total thermal effect that leads to less accuracy of temperature determination. The temperature limit for non-saline soil of the applicability for this method is the value of temperature -1 ... -3°C. This limit for saline soils is shifted to lower temperatures. In the study of saline soil temperature range of pore solution freezing (thawing) increases with the increasing of pore solution concentration, thermogram becomes more flat, causing an increase in error in its graphics processing (Motenko, 1997).

![Figure 1. Thawing thermograms of frozen soil samples: 1 – non-saline, 2 – saline](image)

Cryoscopic method uses release of the latent heat of crystallization (or melting heat absorption) and lowering the freezing temperature (melting) of water in the pores of the soil. The experiment is to ascertain the temperature and humidity of the soil.

3 EQUIPMENT

Different types of equipment were used for research of thawing temperature. We used a system consisting of a thermocouple connected to a recorder device KSP-4 during the early stages of experimental studies. Ni-Cu thermocouple registered the temperature change of soil sample over time. Work junction was placed at the center of the sample and the second junction – in Dewar reservoir where the temperature is maintained 0°C with a mixture of melting ice and water. We fixed a thermocouple value at 0°C at the end of the experiment. The advantage of this method is a continuous record of temperature changes in time and high accuracy of (± 0.05 °C). The disadvantage of this equipment is a limit in temperature range in which to conduct research (-10 ... +10 °C).

For studies of thawing thermoagrams in a wider temperature range (-30 to +20 °C) after determining Tbf on KSP-4 we used for the experiments device IRT-2 (produced by JSC "Eksis" Fig. 2). This device was developed for the temperature measurements with any type of sensor (thermocouple or resistance sensor). It was worked out the method of determining of freezing/thawing temperature on this device (Grechishcheva, Motenko, 2010). The study was conducted on the same samples with Ni-Cu thermocouples that have been used in conjunction with the KSP-4. Comparison of the data obtained by these two devices on the same samples revealed that the conversion of the analog signal to a digital signal with device IRT-2 leads to a loss of accuracy of temperature measurements from ± 0,05 to ± 0,1 °C. However, the instrument IRT-2 allows to obtain more detailed study of thawing thermograms due to the increasing of temperature range of measurements.
It has also been worked out in early studies the method of determining of freezing/thawing temperature on the device for determining the thermal characteristics of soils ITS-\(\lambda C\)-10 (Fig. 3). The temperature measurement are conducted in 3 special points of the heat cell in an experiment of determining of the thermal characteristics. Interval of time for measurements can be set (for example 10 seconds). One of the salient points is the center of the sample, where a temperature sensor is placed. Thus, using a device for measurements of thermal properties ITS-\(\lambda C\)-10 the temperature changes in time of sample center can be obtained. It was built thawing thermograms and the thawing temperature was determined on the basis of these data.

The apparent advantage of this device is the ability to determine the freezing/thawing point in a single experiment with determining of thermal characteristics, i.e. with one sample. This significantly reduces the time required for experiments and minimizes random error in determining that occurs due to heterogeneity of the samples (Grechishcheva, Motenko, 2013; Zykov et al., 2013). The accuracy of the temperature determining is \(\pm 0.15 \, ^\circ C\) in thawing cycle and \(\pm 0.2 \, ^\circ C\) in a cycle of freezing. For the determination of thermal characteristics it is necessary to create a large temperature difference of the sample and the space of experiment (more than 40 \(^\circ C\)), it is impossible to avoid the effect of supercooling. Thus, the thawing temperature of the soil, measured with a device for determination of thermal characteristics ITS-\(\lambda C\)-10 is higher average for 0.2-0.5 \(^\circ C\) than the freezing point.

Later studies of thawing temperature were conducted with the instrument IRS-1 (production of OJSC "Fundamentproject"), specially developed for. In the process of research it was worked out the method of freezing/thawing temperature determination with this device (Motenko, Grechishcheva, 2013). The device IRS-1 uses as a sensitive element a platinum resistance sensors 1×1 mm, that are connected to a converter to a PC (fig. 4).

The advantage of this system is the ability of serial investigations and also the convenience of the experiment and the possibility of computer processing of the experimental results. The accuracy of the determination is \(\pm 0.1 \, ^\circ C\). Especially should be stressed the fact that all
the sensors are calibrated with high-precision thermometer with 5 preset temperatures (-30 to +10). The software allows to preset calibration results and take into account nonlinearity of the error in temperature determination.

4 RESULTS

The study was conducted in vitro on the model soils with different particle size distribution: sand, salt, salty clay and clay. To study the effect of oil, salt and joint influence of oil and salt pollution on soil properties the ground pastes were preparing with different degrees of salinity and oil pollution.

Salinization was carried out using solutions of the respective concentrations, which were calculated with the following formulas:

\[
D_{\text{sal}} = \left( \frac{g_s}{g_d} \right) * 100, \\
D_{\text{sal}} - \text{soil salinity}; \\
g_s - \text{the mass of salts contained in the soil}; \\
g_d - \text{mass of dry soil sample (including the weight of the salts contained in the soil)}; \\
C_{\text{ps}} = \frac{D_{\text{sal}} + W_{\text{tot}}}{D_{\text{sal}}}; \\
D_{\text{sal}} - \text{soil salinity}; \\
C_{\text{ps}} - \text{the concentration of the pore solution}; \\
W_{\text{tot}} - \text{total soil moisture (National Standard 25.13330.2012)}. \\
\]

The total water content for sand was - 9%, for salt - 22% for salty clay - 25%, for clay - 40%. The values of soil moisture were chosen deliberately more than maximum molecular moisture capacity. Also degree of pore filling is 80-100% in soils with such values of moisture. Adding the oil was held after moistening the soil and mixing it thoroughly. In this paper, we consider the results obtained for non-saline unpolluted soil (Figure 5), and salinizated polluted soils (Figure 6), the salinity which is 1%, and oil pollution - 8%. In modern classifications these values correspond to higher degree of salt and oil pollution.

Comparison of the data demonstrated the complete agreement of the results of freezing/thawing point determination received on devices IRS-1, ITS-λC-10, IRT-2, KSP-4. The data presented in the figures is obtained on the device ITS-λC-10 in a series of experiments of thermal properties determination.

Let’s consider the thawing thermograms obtained for nonsaline uncontaminated soil. Different moisture of samples causes the differences in the duration of the phase transition in the investigated soils. Duration increases with increasing of soil moisture. Thus, sand has minimal moisture and duration of phase transition is about 850 seconds; for clay with a maximum moisture the time of phase transitions is about 2800 seconds. The thawing temperature of the soils decreases among the sand-silt-silty clay from 0 to -0.4 °C. This fully confirms the known patterns and is a result of the influence of the energy density of the active surface.

Let’s have a look at thawing thermograms obtained for nonsaline non-polluted soils: 1 – sand, 2 – silt, 3 – silty clay, 4 - clay

Let’s consider the thawing thermograms of saline polluted soil (Fig. 6). The pattern relating to the time of phase transitions is stored the same as for non-saline non-polluted soil, but the phase transition is reduced in comparison with the non-saline non-polluted soil. So the duration of phase transitions for the sand is about 700 seconds, for clay - about 1900 seconds. This is dealt with the fact that saline samples content more unfrozen water and less ice in comparing with non-saline non-polluted samples. Also temperature range of phase transitions extends. The thawing temperature significantly reduces compared with non-saline non-polluted soil, due to high salinity of the samples and as a result - a high concentration of the pore solution. For sand and silt another phase transition is fixed in a temperature range from -21 to -23 °C. It is caused by the formation of sodium chloride cryohydrates. Terms and conditions of its formation - the solution concentration of 23% and the temperature -21,2 °C. The fact that the point of inflection on the graph is connected with the cryohydrates formation is confirmed by the calculation of the pore solution concentration $C_{\text{ps}}$ at ~ -20 °C for the investigated soil. So for sand and silt pore solution concentration was more than 23%, and for silty clay and clay - less than 23%.
Figure 6. Thawing thermograms of \((D_{\text{sal}}=1\%)\) soil polluted with salt and oil \((z=8\%)\) soils: 1 – sand, 2 – silt, 3 – silty clay, 4 – clay

Fig. 7 presents the data obtained for the non-saline non-polluted soils with different particle size distribution. The content of unfrozen water increases regularly from sand to clay and for -15 °C in the sand is 0.1% and in clay - 2.8%

Fig. 8 shows the data for soils with different particle size distribution with maximum values of salinity and oil pollution. The character of changes in the unfrozen water content with temperature changes is different for soils with different granulometric composition. There is a general pattern of increasing the unfrozen water content in a series of sand – silt- silty clay - clay. However, at the same salinity 1% the change of the unfrozen water content with temperature decreasing in silty clay and clay is monotonous, but in the sand and silt there is a violation of the monotony. The abrupt change in the unfrozen water content occurs at the temperature range -21 ÷ -23 °C.

As noted above, in this temperature range the concentration of eutectic forms cryohydrates. That was observed in sand and silt because the unfrozen water content for these soils is less than for silty clay and clay. This leads to the fact that the concentration of the pore solution in the same salinity differs for soils with different granulometric composition. For silty clay and clay - a fine-grained soils - the unfrozen water content is more than for sand and silt, and for such values the concentration of pore solution is less than the eutectic concentration despite the fact that the salinity is the same for all types of soils.

The laboratory study was conducted for saline and contaminated soil in order to determine the effect of these factors separately. The data obtained for saline soil totally coincide with the data obtained for saline and polluted soil. The data obtained for polluted soil totally coincide with the data obtained for non-saline non-polluted soil.

Thus the influence of particle size distribution on the water phase composition is increasing of unfrozen water content with increasing of dispersion. The effect is largely occurs through specific active surface and in saline soils this leads to cryohydrate formation in fine-grained soils.

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