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Thermodynamic calculation of freezing temperature of gas-saturated pore water in talik zones

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Abstract

Nowadays, there are some unusual craters, associated with gas release from permafrost on the northern part of West Siberia (the Yamal Peninsula). One of possible mechanism is the freezing of gas-saturated talik zones and increasing gas pressure up to 1.5 - 2.0 MPa with a gas blowout and crater formation. In this case the thermodynamic technique of freezing temperature calculation of gas-saturated pore water under the gas pressure is developed. Methane, carbon dioxide and their mixtures are considered. It is shown that the solubility of gases in water should be taken into account when the pressure grows up during freezing of gas-saturated talik zones (especially when carbon dioxide is present in the gas phase). The influence of three factors on the freezing point of a gas-saturated pore water is analyzed: the external pressure created by the gas, the presence of a gas dissolved in water and the water mineralization.

Keywords: thermodynamic calculation, talik, gas saturated water, freezing temperature, pressure

Introduction

Recently, several large-diameter craters have occurred in the Yamal Peninsula, the nature of which remains unclear. Nowadays, a number of hypotheses have been proposed: the climate warming, the freezing of the sub-lakes talik zone, the decomposition of intra-permafrost relict gas hydrates, the migration of a deep gas through talik zone (Leibman *et al,* 2014; Olenchenko *et al,* 2015; Bogoyavlenskiy *et al,* 2016; Khimenkov *et al,* 2017; Buldovicz *et al,* 2017).

We assume an important role in the formation of craters is given to the processes of freezing of gas-saturated talike zone. So the current research proposes a thermodynamic analysis of the conditions of crystallization of pore water in gas-saturated soils. It includes an assessment of the influence of gas composition and pressure, and salinity of pore water on freezing temperature in gas-saturated sediments. These investigations are based on previously performed research (Isomin *et al,* 2009; Isomin *et al,* 2017).

Method and results

The thermodynamic analysis led to the dependence of freezing temperature of pore solution (moisture) on the gas pressure:

$$t_{fr} = 103.25 \cdot \ln(b) + 5.57 \cdot (1-b)^2,$$

$$b = a \cdot (1 - x_g) \cdot \exp\left(-\frac{\Delta V \cdot (P - P_0)}{R \cdot (t_{fr} + 273.15)}\right).$$

Where:

P - external pressure, which effects on thermodynamic system, it is gas pressure in our case, MPa; $P_0 = 0.101325$ – atmospheric pressure, MPa; t_{fr} - freezing temperature of pore water, °C; x_g - molar fraction of gases, dissolved in pore water; $x_g = \sum_i x_i$, where x_i - molar fraction of i gas in pore water;

R - universal gas constant, $R = 8.3146$ J/(mol K);

a - activity of pore water in saline solution (electrolyte solution) under atmospheric pressure P_0 (for fresh pore solution and high soil moisture content $a \approx 1$);

V_w, V_{ice} - molar volume of water and ice, cm³/mol;

$\Delta V = V_{ice} - V_w$ - difference between molar volume of water and ice, $\Delta V = 1.635$ cm³/mol.

If we put in the formula for the quantity b on the right-hand side $t_{fr} = 0$, we obtain an approximate analytical dependence of the freezing temperature of the aqueous pore mineralized solution.

On the base of developed thermodynamic method of calculation, the effect of pressure on the freezing temperature of pore water containing dissolved gases (CH_4 and CO_2) and their mixtures (Fig. 1) was calculated.

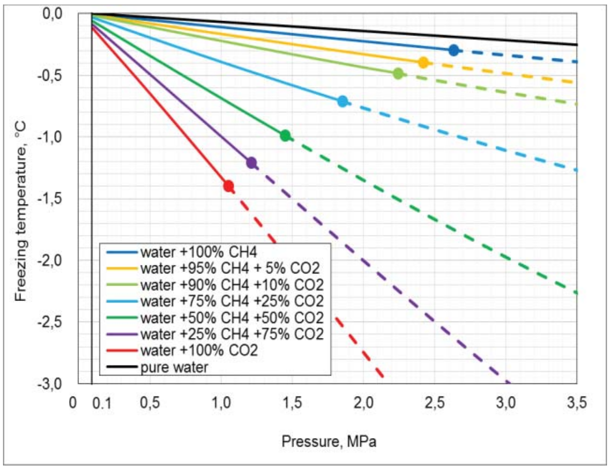

Fig. 1. Dependence of external gas pressure on freezing temperature of gas-saturated pore water. Dots are the appearance of gas hydrate phase, the dashed lines are the continuation of the "gas-gas-saturated water-ice" equilibria in the metastable region.

The performed calculations show that the freezing temperature of gas-saturated pore water in talik zones in conditions of pressure increasing can be markedly reduced even in the absence of mineralization. Thus, the freezing temperature of pore water with a high CO_2 content may drop by 1-1.5 ºC below 0 ºC. This allows accumulate a large amount of gas in the porous water of cold sediments at high negative temperature due to high solubility. Later, during sharp pore pressure decreasing, due to destruction of the frozen roof of talik zone, the gas will be actively allocated, creating a "champagne effect."

Conclusions

The technique of thermodynamic calculation of the freezing temperature of gas-saturated and mineralized pore solutions under the external gas pressure is presented. Different gas compositions (CH_4, CO_2 and mixtures of CH_4 with CO_2) are observed. The influence of three factors on freezing temperature of gas-saturated pore solutions are analyzed: the external gas pressure, the presence of a gas dissolved in pore water and water mineralization.

The obtained results show solubility of gases in water should be taken into account when considering the dynamics of pressure increasing during freezing of gas-saturated talik zones (especially when carbon dioxide is present in the gas phase).

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