A semi-empirical model for phase composition of water in clay–water systems

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Abstract

A semi-empirical model describing the variation of the unfrozen water content w_u in frozen soil–water systems as a function of temperature has been proposed based on the results of 141 DSC experiments on 6 monomineral soils. Taking into account the postulate of the simplicity of the model, the three-temperature-zone representation of the freezing process is assumed as an alternative to the five-zone image resulting from the DSC experiment. The characteristic temperatures are the freezing (or melting) point T_f and the temperature T_m, below which the unadsorbed water is all frozen. The main equation of the model describes the variation of the unfrozen water content in the mushy zone between T_f and the temperature T_m. In addition, the empirical equations for the freezing point and the unfreezable water are given. The model was validated with foreign empirical data. The results show a very good agreement between the simulated and the measured unfrozen water contents.
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1. Introduction

In contrast to typical solid materials which undergo a phase change at a fixed temperature, soils exhibit a specific temperature zone of phase change below the freezing point T_f, the latter being only the boundary temperature of phase change. At any temperature below freezing point, unfrozen water and ice in a soil–water system remain in a thermodynamic equilibrium state. It has been widely understood for many years, that the presence and phase changes of unfrozen water strongly influence the heat and mass transport processes in frozen soils and other porous media. Nevertheless, the nature of

the unfrozen water phenomenon still remains unclear. Many authors dealt with this topic during the last decade experimentally, using the nuclear magnetic resonance NMR (Turov and Leboda, 1999; Watanabe and Mizoguchi, 2002), the neutron spin-echo NSE (Swenson et al., 2002), calorimetry (Bronfenbrener and Korin, 2002; Kozlowski, 2003a,b), the time domain reflectometry TDR (Yoshikawa and Overduin, 2005), and the dielectric capacity method (Fen-Chong and Fabbri, 2005; Fabbri et al., 2006). The materials were various non-porous and porous silica (Turov and Leboda, 1999), glass powder and soils (Watanabe and Mizoguchi, 2002), cement pastes (Fen-Chong and Fabbri, 2005; Fabbri et al., 2006) and various soils or clays (Bronfenbrener and Korin, 2002; Swenson et al., 2002; Kozlowski, 2003a,b; Yoshikawa and Overduin,

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Table 1
Soil properties

Type of soil [a]	C.E.C (meq/100 g)	Major cation		Salt conc. Cl⁻ (g/100 g)	Fraction <2 μm [%]	Consistency limits		Spec. surface [m²/g]		Number of samples
		(meq/100 g)	(% C.E.C)			w_P (%)	w_L (%)	External	Total	
B–Ca^{2+}	108.05	104.15	96	0.02	34	69.7	106.8	122	732	26
B–Mg^{2+}	109.20	105.22	96	0.06	34	75.8	105.9	122	732	28
B–Na^+	111.12	90.49	81	0.62	92	86.5	253.7	110	644	26
B–K^+	49.98	38.12	76	0.43	30	66.0	93.2	56	336	27
K–Ca^{2+}	5.95	4.61	77	0.02	51	33.8	61.2	8	48	26
K–Na^+	5.93	3.57	60	0.02	54	36.8	62.9	10	60	26

[a] The symbols B and K in the soil type column mean bentonite and kaolin respectively.

2005). The results, very interesting theoretically, usually cannot be used for thermal modelling or other engineering applications. The differences between such materials as glass powder, cement pastes or zeolites and clay soils are too big to be omitted. The shape of flat clay particles, the expanding lattice of montmorillonite, the double layer phenomena and plasticity — these are only a part of the properties specific only or particularly to clay–water systems. Therefore, results obtained for other materials seem difficult to generalize to clay soils. Unfortunately, in the investigations carried out on soils, the variety of soils tested was too little to yield substantial statistical output (two soils were used by Bronfenbrener and Korin, 2002; Watanabe and Mizoguchi, 2002, Yoshikawa and Overduin, 2005, and one soil by Swenson et al., 2002). However, the search function of the unfrozen water content should yield an accurate description of the freeze–thaw process, depending on varied system properties. As reported by Lunardini (1991), the calculated temperature and phase-change depths are found to differ significantly according to the form of the function w_u. Therefore, it is essential to use a model on the one hand satisfactory theoretically, and on the other hand being in agreement with the empirical data. The model described below has been based on the large experimental data obtained by use of the DSC technique (Kozlowski, 2003a,b). However, its initial form satisfies boundary conditions specific to a soil–water system. Therefore, the ability of the model to describe the real phase equilibriums is expected to be improved compared to the other "purely empirical" models.

2. Outline of the DSC experiments

The DSC experiments have been conducted, using homoionic forms of montmorillonite and kaolinite. The forms had been obtained from natural bentonite from Chmielnik in Poland and kaolin from Sedlec in Czech

by repeated saturation of the fraction less than 0.063 mm and subsequent purifying from solutes by diffusion. The properties of the soils are given in Table 1.

For each soil sample, the unfrozen water content curves were determined on warming in the range between −28 and +10 °C by use of a comprehensive numerical analysis, presented elsewhere in detail (Kozlowski, 2003a). The total number of tests was 159. From these, in 141, phase effects were detected. The method makes it possible to monitor the continuous phase changes during freezing or thawing of an individual soil sample. The melting point was calculated together with the curves, as their immanent parameter. Thus, the obtained curves have got a reasonable "attaching point", in contrast to curves determined by means of approximation of several points obtained in a series of experiments.

3. Results

Below, the most significant of the results of the experiments are presented in relation to the shape of the unfrozen water content curves (Kozlowski, 2003b) and to the freezing point depression (Kozlowski, 2004).

3.1. The curves of the unfrozen water content

Most of the curves, independent of the soil type and total water content, indicated a similarity of shape. Analysis of the curves obtained suggested that the process of the ice melting in the soil–water system is not a continuous phase change. Absorption of the heat occurs at distinct temperature intervals and it is not strictly an increasing function of temperature. All obtained curves have shown the interval of the vanishing of the phase effects before the final intensive impulses near freezing point. This is represented by the occurrence of the characteristic plateau on the unfrozen water curves.