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Estimating thermo-osmotic coefficients in clay-rocks: I. Theoretical insights

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ABSTRACT

The conditions to obtain a macroscopic model for the thermo-osmotic coupling coefficient which is needed for practical calculations of fluid flow in clay-rocks subjected to temperature gradients are investigated in this paper. A theoretical expression for the thermo-osmotic coupling coefficient proportional to the hydraulic conductivity was obtained. The theoretical expression of the thermo-osmotic conductivity involves the excess Gibbs energy of the fluid between adjacent charged surfaces. The interaction energy was calculated using disjoining pressure data. Our calculations suggest a crucial role of the so-called hydration or structural energy of interaction to explain the thermo-osmotic process. The mean pore size, i.e. the mean interparticle spacing, the concentration of the equilibrium solution and the temperature are determinant variables in this process. Some exploratory comparisons between the model and the available data for pure clays are proposed.

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1. Introduction

The electrical properties of clay minerals yield severe alterations of the transport equation in consolidated clays. In such media, the occurrence of the so-called coupled fluxes is well known [1–5]. The conjugated driving forces appearing in the classical transport laws (e.g. the pressure gradient for fluid flow) are not sufficient to describe the fluxes. Other forces termed non-conjugated such as the concentration, electrical potential or temperature gradients have to be considered [1,2]. Therefore, the coupled fluxes correspond to fluid, solute, heat fluxes or current density which share the same driving forces. The resolution of these fluxes coupled with balance equations allows the identification of the distribution of the variables and thus their gradients. Consequently, these fluxes should be calculated simultaneously whence the notion of coupling. Here, we will focus on the fluid and heat fluxes. For fluid flow, the non-conjugated terms, i.e. those which are not proportional to the pressure are referred to as osmotic flows. In coupled flow theories, the fluid velocity is linearly proportional to the driving forces. The coefficient of proportionality are the so-called coupling coefficients. For clay materials, a large amount of studies aimed at characterizing the chemical or electro-osmotic coefficients (see e.g. [5–18]). Whether theoretical or experimental, these studies have been often carried out under isothermal conditions. Consequently, theoretical expression for the chemical osmotic coefficient [2,5,7] or for the electro-osmotic coefficient [2,5,12] are available. To our knowledge, the same cannot be said for the thermo-osmotic coefficient. Thermo-osmotic flow which is defined as a fluid flow under thermal gradients was measured by Derjaguin and Sidorenkov (reference in [19]) for porous glasses. On the basis of such experiments, Derjaguin and co-workers built the only available theory on thermo-osmosis. Interestingly, the experimental conditions of the experiment by Derjaguin and Sidorenkov but not the existence of such process were largely questioned by Hutchison et al. [20] who argued that the volume flux measured by these authors was mostly due to the thermal expansion of the fluid. Careful experiments have been subsequently conducted to identify a rigorous thermo-osmotic behavior in different materials. Some of these studies were carried out on compacted clays such as the work by Dirksen [21], Srivastava and Avasthi [22,23] or more recently by Rosanne et al. [18]. But it must be pointed out that this process has not been as widely studied as the chemical osmosis in clays for instance. Therefore, and despite the presence of high temperature gradients across natural shale layers in sedimentary basins due to the low thermal conductivity of clays, this process has attracted weak attention. Although a theoretical basis for the prediction of the thermo-osmostic coefficients has been provided by Derjaguin et al. [19], a clear and convenient expression for this parameter is missing. In the present paper, we investigate the conditions to obtain such an expression.

2. Theory on thermo-osmosis

2.1. Water-interface interaction

As will be seen in the following section, Derjaguin et al. [19] invoked the major alteration of the structure of the water adjacent to

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a solid surface to explain the mechano-caloric and related thermo-osmotic process. For this reason, we start with a brief description of such interaction.

Isomorphic substitutions in the clay minerals lattice such as the substitution of Si^{4+} by Al^{3+} in tetrahedral-Si sheets or that of Al^{3+} by Fe^{2+} and/or Mg^{2+} octahedral-Al sheets yields a net permanent negative charge of the basal surfaces at natural pH values. For minerals such as kaolinite or illite, hydroxyl groups at the edges contributes by hydroxylation reactions to the overall charge of the mineral. In smectite type clays, these edge surfaces are negligible (see e.g. [24]). The negative charge is balanced by an accumulation of ions close to the surface, and an electrical double layer develops [3,25]. The distribution of the counterions can be accurately described by the Stern–Grahamme model. In this model, it is assumed that a substantial part of the negative surface charge is balanced by ions adsorbed on the surface (hydrated or not) forming the well-known Stern layer [26]. This adsorption to the clay minerals surface involves the formation of two types of complexes, i.e. inner and outer sphere complexes (Fig. 1). Inner sphere complexes correspond to ions directly bound to the surface and thus partially or fully dehydrated while outer sphere complexes are hydrated ions electrostatically bound to the surface. The remaining unbalanced surface charge is balanced by the ions in the diffuse layer. Therefore, in the Stern–Grahamme view of surface interactions, two layers are considered, the Stern layer involving one or two planes (inner and outer Helmholtz planes in Fig. 1) containing the ions closely packed to the surface, and the so-called Gouy–Chapman or diffuse layer made of more dispersed ions weakly attracted by the surface [25]. The consequence of these electrochemical interactions is the presence of an electric field normal to the clay mineral surfaces. If the adjacent diffuse layers overlap, the whole interplatelet space is subjected to an electric field. This contributes to a major alteration of the structure of the fluid at the solid surface. This alteration is schematically depicted in Fig. 1, where oriented water dipoles at the surface and in the hydration spheres of ions are shown. This change in water structure (hydrogen-bond network) takes two forms: (i) an ordering of water molecules associated with the solvation of the counterions and (ii) a preferential orientation of the water dipoles close to the surface. The layer of specifically structured water associated with interface interaction could extend to several nanometers from the surface [19,27].

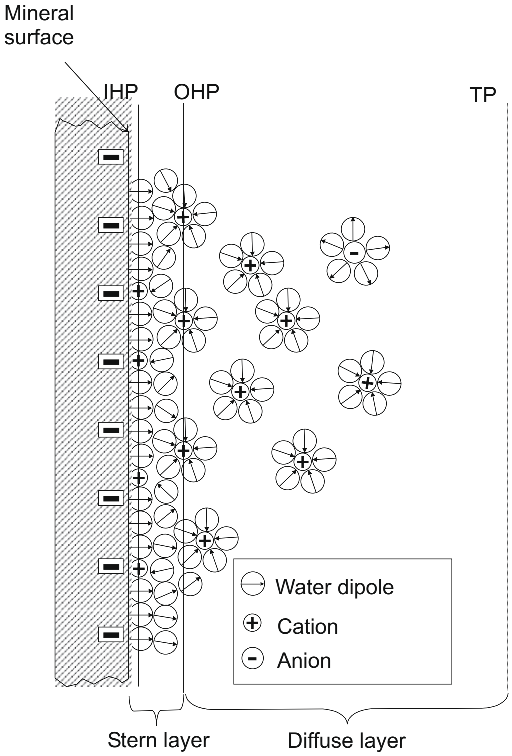

Fig. 1. Schematic view of solution–mineral interactions. OHP and IHP stand for Outer Helmholtz Plane and Inner Helmholtz Plane respectively. TP stands for Truncation Plane.

2.2. From Derjaguin's theory to macroscopic coupling coefficients

The only fully comprehensive theoretical model that was developed for the thermo-osmotic flow was due to Derjaguin et al. [19]. The authors use non-equilibrium thermodynamics concepts and considered the reciprocal process, i.e. the mechano-caloric process to identify a theoretical expression for the thermo-osmotic coupling coefficient at the pore scale. The interaction between a solid surface and the electrolyte at the contact with this surface yields a substantial alteration of the water structure in terms of hydrogen-bond network. This causes an alteration of the specific enthalpy of the solution in the pore space of a clay for instance. Let H (J m^{-3}) denote the specific enthalpy of the bulk solution (the solution in a reservoir in thermodynamic equilibrium with the clay), the specific enthalpy of the water film in the pores is then $H + \Delta H$, where ΔH is the mean "excess" specific enthalpy due to surface interactions. An isothermal fluid flow across the porous media would thus produce an "excess" heat flow and a related temperature gradient. This is the well-known mechano-caloric effect. Non-equilibrium thermodynamics requires that the reciprocal processes, i.e. a fluid flow due to a temperature gradient must exist. Let's consider a volume of clay-rock characterized by a membrane behavior separating two reservoirs so that pressure or temperature differences Δp (Pa) or ΔT (K) can be applied between the reservoirs. For a single pore representative of the porous media and idealized as a parallel plate slit (see Fig. 2) subjected only to pressure or temperature differences, the non-equilibrium thermodynamics approach yields [1,19]

$$j_V = l_{11}\Delta p + l_{12}\frac{\Delta T}{T}, \tag{1}$$

$$j_Q - j_V h = l_{21}\Delta p + l_{22}\frac{\Delta T}{T}, \tag{2}$$

where j_Q is the total heat flux (J s^{-1}), j_V (m^3 s^{-1}) is the volumetric flow rate and h (J m^{-3}) is the microscopic specific enthalpy of the bulk ($\rho_f C_f T$, ρ_f is the fluid density in kg m^{-3}, C_f the specific heat of the fluid in J kg^{-1} K^{-1}). The coefficient l_{11} and l_{22} refer to the well known direct flows. The coefficients l_{12} and l_{21} are the thermo-osmotic and mechano-caloric coefficients respectively. For a single plate-parallel pore, Derjaguin et al. [19] identify indirectly the thermo-osmotic coefficient using the Onsager reciprocity principle $l_{12} = l_{21}$ and establishing the theoretical expression of the mechano-caloric coefficient. For a single pore, the authors write the net heat flux transferred from one side to the opposite side during an isothermal fluid flow. Taking into account the effect of the pore walls on the specific heat of the film of fluid between the solid surfaces, the authors obtained

$$(j_Q - j_V h)_{\Delta T=0} = L\int_{-b}^{b} \Delta h(z)\, v(z)\, dz, \tag{3}$$

where $v(z)$ is the local fluid velocity (m s^{-1}) and z (m) is a local coordinate associated with each pore. For a practical use at the scale of interest, i.e. the macroscopic scale, an upscaling method must be used to obtain some expressions for the coupling coefficients such as

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