Research paper

Micro porosity evolution in compacted swelling clays — A chemical approach

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Majid Sedighi *, Hywel R. Thomas

Geoenvironmental Research Centre, Cardiff School of Engineering, Cardiff University, Cardiff CF24 3AA, UK

ABSTRACT

This paper presents a new approach to investigate the variation of microscopic porosity/pore water interactions in compacted swelling clays. The aim of the research has been to develop a theoretical formulation for the prediction of micro-porosity variations with suction and temperature in compacted smectite. The model developed is based on a geochemical formulation of interlayer hydration/dehydration of smectite.

An established theoretical approach based on regular solid-solution theory is adopted to describe the water adsorption/desorption in the interlayer of smectite. The thermodynamic parameters of the model for the case of two bentonite clays, namely MX-80 and FEBEX are presented. Thermodynamic parameters of the hydration model including Margules parameter (W_s) and logarithm of the equilibrium constant ($\log K_{eq}$) at ambient temperature were found to be -2420 cal/mol and -1.42, for compacted MX-80 and -3330 cal/mol and -2.79, for compacted FEBEX, respectively.

Micro/macro-porosity evolutions with dry density and relative humidity are presented. The results are compared with alternative approximations reported in the literature which show a close correlation. Variations of the micro and macro-porosity in compacted bentonite with hydration processes are also studied through the application of the model under restrained swelling and isothermal conditions. The results provide an insight into the evolution of pore water in compacted bentonite during saturation and quantify the distribution of water in micro and macro pores.

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1. Introduction

An improved understanding of the engineering behaviour of compacted swelling clays remains an interesting and important challenge. Numerous application areas spring to mind, including the disposal of high level nuclear waste. A complex clay fabric system and the interaction between water and clay minerals add to the complexity of the basic set of issues (e.g. Yong, 2003).

Two scales of porosity are considered in this study, the "micro porosity" which includes the pore spaces between the smectite unit layers, i.e. interlayer space and the "macro porosity" which comprises the spaces between particles (inter-particle pore) and between aggregates of particles (inter-aggregate pore). It is noted that only the interlayer water and exchangeable ions exist in the "micro porosity". Fig. 1 presents a schematic of the "micro porosity" and "macro porosity" concepts considered in this paper.

"Micro porosity" can be considered as a saturated pore space. Hydration and dehydration processes can only alter the interlayer distance between clay layers by adding/removing water molecules. In contrast, macro porosity is a two-phase system which may contain both liquid and vapour. Water molecules are exchanged between these two scales of porosity.

The physical state of water has been reported to be different in microscopic pore spaces, i.e. the interlayer, to that of free water (e.g. Hueckel, 1992; Pusch and Yong, 2006). Water transport can therefore be expected to be significantly restricted within this porosity level (Hueckel, 1992). The water that exists in the macro porosity can be divided into free water and diffuse double layer water (Bradbury and Baeyens, 2003).

With regards to chemical transport in compacted swelling clays, different diffusion behaviours for anions and cations have been found. This phenomenon has similarly been found to be related to the accessible porosity and preferential pathways due to clay–ion interactions (e.g. Bourg et al., 2003). Additionally, various geochemical reactions between the chemical components present in the system occur only in macroscopic pore system (Bradbury and Baeyens, 2003).

The micro/macro fabric system can be altered during hydration and dehydration processes (e.g. Saiyouri et al., 2000; Salles et al., 2009). Saiyouri et al. (2000) have shown that during hydration of compacted bentonite, particles are divided along with the progressive adsorption of the water in the micro and macro pores. The number of layers in a particle has been reported to reduce significantly during hydration, forming smaller

* Corresponding author.
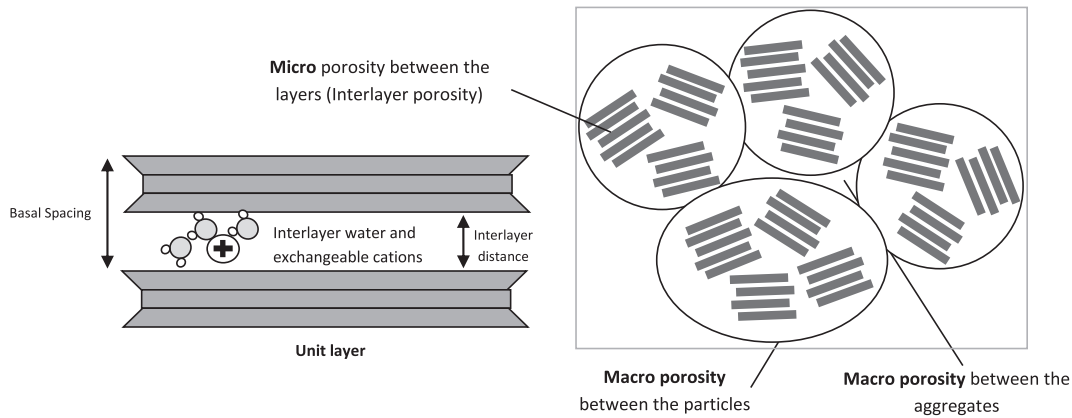 E-mail addresses: SedighiM@cf.ac.uk (M. Sedighi), ThomasHR@cf.ac.uk (H.R. Thomas).

Fig. 1. A schematic of "microporosity" and "macro porosity" in compacted smectite.

particles with up to approximately 10 layers in MX-80 bentonite (Saiyouri et al., 2004). Such alteration in the fabric of the clay can affect the transport properties of the soil system. Studies of the hydraulic behaviour of highly compacted bentonite have shown that considering the entire porosity for modelling the moisture flow may result in significant discrepancy between simulation results and observed behaviour (Thomas et al., 2003; Sedighi, 2011; Sánchez et al., 2012; Villar et al., 2012).

Some attempts have been made to include the processes related to expansion of clay microstructure during re-saturation in modelling the hydraulic or hydro-mechanical behaviour of compacted bentonite (e.g. Kröhn, 2003; Thomas et al., 2003; Xie et al., 2004; Sánchez et al., 2012). For example, the effects of interlayer swelling on water flow have been studied in a field scale test on isothermal and non-isothermal moisture flow in compacted bentonite by introducing a micro/macro phenomenon in hydraulic transport properties (Thomas et al., 2003; Thomas et al., 2009; Thomas and Sedighi, 2012). Consideration of microscopic swelling effects on hydraulic behaviour using a diffuse double layer approach has also been suggested (Xie et al., 2004). Double porosity constitutive models have also been suggested which encounter the effects of deformation at microscopic level by coupling the deformation with flow formulations (Sánchez et al., 2012).

Prediction of the interlayer porosity, defined as microporosity in this paper, in compacted bentonite and its variation with dry density under saturated conditions has been reported in a number of studies (Kozaki et al., 2001; Bourg et al., 2003; Pusch and Yong, 2006). Studies have also reported the interlayer pore water variation with relative humidity in partially saturated and compacted bentonite clays (Likos and Lu, 2006; Warr and Berger, 2007; Likos and Wayllace, 2010; Holmboe et al., 2012). The above predictions are based on extracting the basal spacing between the layers, observed for XRD analysis, and calculating the porosity associated considering a homogeneous distribution of parallel clay layers in the system.

This paper presents an approach to this problem which is based on chemical/geochemical relationships between and the clay's micro structure. The development of a more chemical based approach for micro porosity/water interaction and its evolution with processes involved in hydration and dehydration is the main focus of this paper. The approach is based on a thermodynamic formulation of interlayer hydration/dehydration, proposed by Ransom and Helgeson (1994) which describes the interlayer water adsorption/desorption as a geochemical solid solution reaction. This is extended herein to develop a mechanistic model for calculating the interlayer porosity and water content in compacted smectite.

The theoretical background and formulation for hydration/dehydration of smectite is first presented. The work is then extended via a theoretical calculation of micro porosity in compacted bentonite.

The approach proposed is calibrated for two bentonite clays, MX-80 and FEBEX, where the thermodynamic parameters required are retrieved. The variations of the micro porosity with environmental variables associated with hydration/dehydration of these clays, under highly compacted conditions, are investigated.

2. Thermodynamic approach for modelling the interlayer hydration/dehydration of smectite

The interlayer hydration and dehydration of smectite involve one to three discrete layers of water molecules, adsorbed/desorbed in the interlayer space between the clay layers (Pusch and Yong, 2006) with no alteration in the crystalline structure of the mineral (Ransom and Helgeson, 1994). It has been suggested that the interlayer hydration and dehydration of smectite can be described as a geochemical reaction between water molecules and a symbolic hydrous and its homologous anhydrous counterparts of smectite (Tardy, 1990; Ransom and Helgeson, 1994; Vidal and Dubacq, 2009). Such chemical reactions have been described as

Hydrous smectite (hs) ↔ Anhydrous smectite (as) + n_cH$_2$O

where, n_c represents the number of moles of water in the interlayer adsorption or desorption reaction, given as the moles of water per smectite half formula unit, i.e. $O_{10}(OH)_2$ (Ransom and Helgeson, 1994).

Under equilibrium conditions, applying the mass action law to the solid-solution reaction, following Ransom and Helgeson (Ransom and Helgeson, 1994) yields:

$$\log K_{eq} = \log\left(\frac{a_{as}}{a_{hs}}\right) + n_c \log a_{\mathrm{H_2O}} \tag{1}$$

where K_{eq} represents the equilibrium constant of the reaction. a_{as} and a_{hs} denote the activity of the anhydrous and hydrous components of the smectite solid-solution, respectively. $a_{\mathrm{H_2O}}$ refers to the activity of the interlayer water.

Ransom and Helgeson (1994) also showed that the interlayer water hydration/dehydration reaction can be expressed as a regular solid solution reaction. According to the proposed approach, the smectite solid phase is considered as a regular solid-solution, consisting of hydrous and anhydrous components. The hydrous and anhydrous components of the smectite solid-solution differ only by the number of moles of water adsorbed in the interlayer pore space. Considering the reaction as a regular solid solution, Ransom and Helgeson (1994) presented the mass action law as:

$$\log K_{eq} = \log\left(\frac{1-X_{hs}}{X_{hs}}\right) + \frac{W_s}{2.303RT}(2X_{hs}-1) + n_c \log a_{\mathrm{H_2O}} \tag{2}$$