

Experimental assessment of adsorbed water for geomechanical applications

Évaluation expérimentale de l'eau adsorbée pour les applications géomécaniques

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ABSTRACT: One of the major factors controlling behavior of clays is their chemical structure. Active clays in particular are notable for their high-swelling and hydro-isolating properties, which make them valuable in various geotechnical applications, including deep repositories for nuclear waste and landfills. The properties mentioned above arise from the water that is physically attracted to clay particles. This water, often described as "adsorbed" or "physisorbed," can exhibit an ordered structure, greater density, and a distinct dielectric constant compared to water in its bulk liquid form. The attracted water is influenced – among other factors – by salinity of the pore water, degree of saturation, temperature of the waste repositories. The mechanical response of the material, like swelling upon hydration, can be predicted by advanced modelling approach accounting for the physical-chemical interactions between water and clay particles. Such complex multi-physical predictions require precise microstructural investigations, which are critical for understanding the active clays behavior. This work proposes a novel methodology for quantitatively assessing the adsorbed water in active clays using Thermogravimetric Analysis (TGA). Following the proposed methodology, new insights into the types and amounts of water retained at various saturation levels of MX-80 bentonite are provided. These insights can be integrated into mechanical prediction models to enhance their accuracy.

RÉSUMÉ: La structure chimique des argiles est un facteur clé dans la compréhension de leur comportement. Les argiles actives se distinguent par leur capacité à gonfler et à isoler l'eau, ce qui les rend utiles dans diverses applications géotechniques, notamment le stockage souterrain des déchets radioactifs et autre projets d'enfouissement. Ces propriétés sont dues à la forte interaction et attraction entre l'eau et les particules d'argile. Cette eau, qualifiée d'"adsorbée" ou de "physio-absorbée", possède des caractéristiques différentes de l'eau libre, notamment une structure ordonnée et une densité plus élevée. Les propriétés de l'eau attirée sont notamment influencées par la salinité, le degré de saturation et la température des dépôts de déchets. Une approche de modélisation avancée prenant en compte les interactions physico-chimiques entre l'eau et les particules d'argile permet de prédire le comportement mécanique du matériau. Le développement d'un modèle multi-physique complexe nécessite une étude poussée de la microstructure des argiles, essentielle à la compréhension du comportement des argiles actives. Cette étude propose une nouvelle méthodologie utilisant l'analyse thermogravimétrique (TGA) pour quantifier l'eau adsorbée dans les argiles actives. Elle permet notamment une meilleure quantification de l'eau retenue dans la bentonite MX-80 à différents degrés de saturation, ainsi qu'une caractérisation du type d'eau. Ces informations peuvent être intégrées dans les modèles de prédiction mécanique pour améliorer leur précision.

Keywords: Bentonite; expansive clay; adsorbed water; thermogravimetry.

1 INTRODUCTION

Bentonite is a widely used material in waste disposal, (Laine, Karttunen, 2010). Its favorable properties for waste disposal include swelling and reduced hydraulic permeability upon wetting, preventing the migration of contaminants from waste disposals. Bentonite acts as a "seal" for nuclear waste (Pusch et al. 1998; Laine, Karttunen, 2010).

Presence of salts in the environment affects physicochemical interactions between clay particles

and bulk water, leading to changes in hydro-mechanical behavior, such as decreased swelling and increased permeability (Slade, 1991; Likos, 2004; Tester et al, 2016). However, those interactions are not fully understood (Wang et al, 2020).

Understanding water adsorption in clay is vital for assessing changes in mechanical properties. Existing modeling approaches allow predicting hydration isotherms of bentonite by combining different mechanisms connected to types of water adsorbed

(e.g., Wang et al, 2022). Existing experimental assessments of adsorbed water are limited to platelets spacing assessment by X-Ray Powder Diffraction (XRPD) and it is assumed the space between platelets is filled with water. Moreover, XRPD requires fine powders and is unable to detect amorphous structure (such as water or randomly located surface cations) (Cockcroft and Fitch, 2008).

Montmorillonite, a key mineral in bentonite, attracts water in two forms: tightly bonded crystalline hydrates and weakly bonded osmotic hydrates. Mercury Intrusion Porosimetry (MIP) is unable to capture crystalline hydration (e.g. Norrish, 1962), occurring at humidities above 25% (Cases et al, 1992). Additionally, at low humidity levels, most of the surface area remains vacant from water layers.

Thermogravimetric Analysis (TGA) is a technique that allows to obtain the change of mass of a small specimen as a function of temperature (dynamic heating) or time (Tajeddine et al, 2015). Each temperature level corresponds to the energy needed for sublimation/evaporation of certain molecules in the sample (Vieillard, Tajeddine L, 2015). Thus, higher-level bonds removal would be visible at a higher temperature.

In case of clays, similar processes were distinguished to take place in kaolinite, montmorillonite, saponite and other clay minerals during heating from 30°C to 950°C: first step – evaporation of adsorbed water; second one – dehydroxylation – the release of structural OH in the form of water molecules, third – silica phase transformation. It is generally assumed that by the start of dehydroxylation no adsorbed water is left (Vieillard et al, 2016; Saadatkhan et al, 2020, Zeng et al, 2022), however, that assumption remains not proved. Additionally, there is no consensus between authors on the temperature levels when all adsorbed water is removed.

Discrepancies between water retention mechanisms in literature require development of new experimental tools capable of detecting water-clay particle interactions at the nanoscale across different chemo-hydro-mechanical states. These tools are essential for later implementation into accurate modeling approaches.

In the present contribution, a new methodology for quantifying the different types of water retained by active clays is proposed. The proposed methodology involves using thermogravimetric analysis (TGA) on active clay specimens at different hydration stages, as well as using TGA on water samples having the chemical composition of the active clay specimens of interest.

2 MATERIALS AND METHODS

2.1 Tested material

Bentonite MX-80 mixture was obtained by mixing the grains of fractions up to 4 mm with Fuller granulometry distribution. Smectite content of the material is 85%, Specific Surface Area (SSA) is 523m²/g, specific gravity 2.74 (Seiphoori et al, 2014). Liquid and plastic limits are 544% and 110% respectively. Hygroscopic water content of the resulting mixture under laboratory conditions (imposed total suction 140 MPa, T=25°C) is 5.9%, dry density – 1.3 Mg/m³.

2.2 Methodology

The proposed methodology involves, after an initial specimen preparation phase, performing TGA on clay and water samples (using the same heating programme for all samples). A comparison of the temperature-water content curves of the clay specimens and of the water specimens reveals the temperature ranges required to remove a certain type of retained water and allows the corresponding water content to be quantified.

2.2.1 Hydration procedure

Bentonite was placed into 3 “Microcells” (cells made of brass able to create constant volume conditions with small openings) for confined hydration in desiccators with the imposed total suction values of 1, 26, 59 MPa (D, C, B states on Figure 1a.) Total suction of bentonite was measured by WP4C dew point chilled-mirror potentiometer (Leong et al, 2003). Total suction value of 1 MPa was measured on fully saturated bentonite (saturation was performed in Microcell in a chamber with water pressure 2.5 MPa for 2 days until no change in water volume in the pump was observed).

2.2.2 Thermogravimetric analysis

Experimental part of TGA consists of 2 sub-parts: testing of bentonite samples and of distilled water (Figure 1b).

Bentonite samples, taken immediately after opening microcells, are put in ceramic crucibles in the heating chamber of a Perkin Elmer TGA 4000 apparatus (Figure 1c). The following heating (for all heating steps the rate is 10°C/min) is adopted: (i) isothermal step for 1 min at 30°C for equilibration; (ii) heating from 30 to 80°C; (iii) isothermal step for 15 min at 80°C; (iv) heating from 80 to 950°C; (v) isothermal step 1 min at 950°C. Bentonite samples included also those oven-dried (105°C) for more than 1 month to ensure the evaporation of all water in the

sample. These long-dried samples are taken as reference state later in the analysis.

Water samples are put into crucibles in a form of a drop using syringe. The initial mass varied from 2mg to 21mg (Figure 1d). The following heating program is adopted: (a) isothermal step for 1 min at 30°C; (b) heating from 30 to 80°C; (c) isothermal step at 80°C; (d) heating from 80 to 150°C.

2.2.3 Accuracy of measurements

The Perkin Elmer TGA 4000 apparatus makes measurements with accuracy of the balance 0.01% (for most of samples 0.005mg), temperature accuracy 0.8°C.

Additionally, the influence of total mass of sample and granulometry on accuracy was measured. Mass of samples influences the first part of the normalized curves (30...450°C) with coefficient of variation 0.53% (standard deviation 0.57%). Granulometry of the sample influences predominantly the part between 600 and 800°C with coefficient of variation 0.42%, standard deviation 0.4%.

2.3 Results analysis

The experimental results are analyzed implementing the following procedure: (i) normalization of all bentonite TGA curves with respect to the final mass; (ii) combination of water evaporation curve with the long-dried sample TGA curve (Figure 1e), representing the change of mass of bentonite without adsorption phenomena; (iii) difference between the actual sample with adsorbed water and the modelled curve. The combined curve is modelled in a way that it has the same water content as the samples in hydration path (Figure 1a), in this way, the only difference between actual and modelled curve is the mass of water bonded to clay platelets. That mass is expressed as the mass of water per unit mass of dry clay on Figure 1f (the normalisation changed to initial mass for interpretation of results).

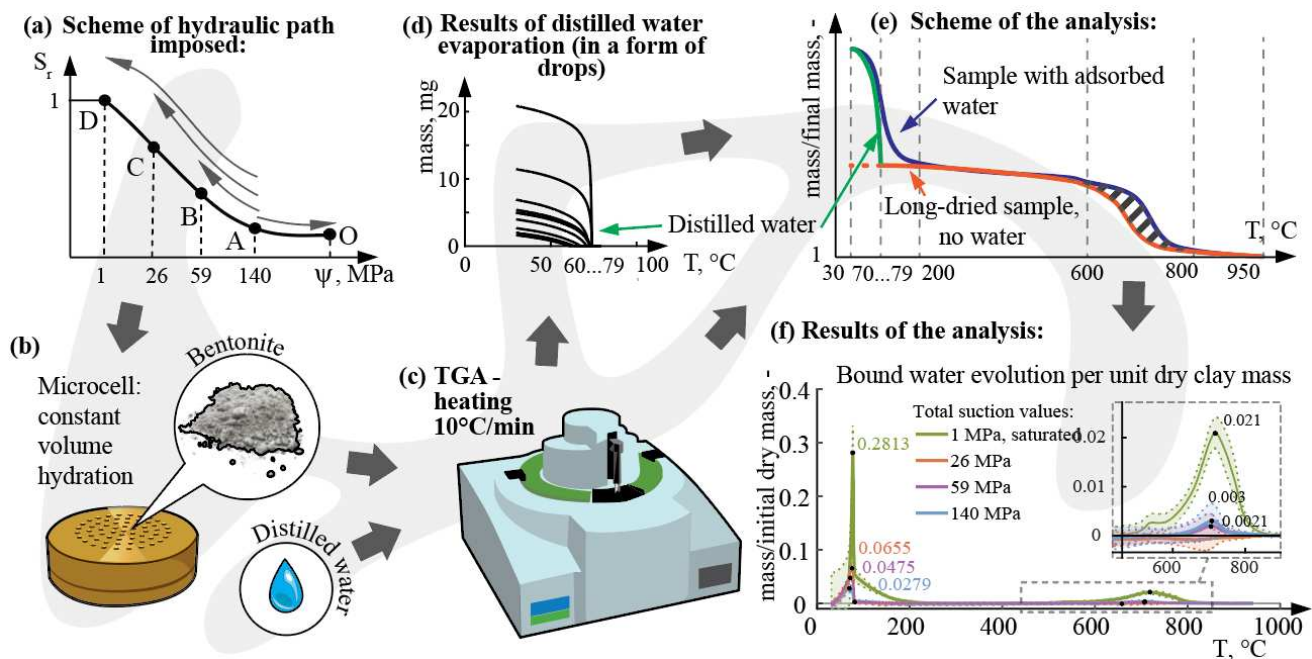


Figure 1. Methodology and results of the present work.

3 RESULTS AND DISCUSSIONS

Figure 1f represents the results of presented methodology. Two main regions could be identified: (i) 30...200°C with sharp peaks at around 80°C and (ii) 600°C...800°C with peaks starting from 0 to 0.021. The first region of the difference represents the water bonded to clay, thus, this region corresponds to adsorbed water (bulk water was removed by difference operation). According to the second region, the states of total suction 26, 59 and 140MPa show peaks of

around zero, and the saturated sample has a higher value of 0,021. That fluctuation most probably corresponds to the change of fabric during saturation, as the accuracy evaluation due to granulometry was the highest at similar temperature zone. As samples from the mixture were picked randomly, most probably the variation in grain size and in the amount of water retained by big and small grains resulted in scatter data. Therefore, this methodology should be targeted on the grain size of interest.

Overall, the values of adsorbed water obtained in present analysis is similar to some of the other methodologies (Warr and Berger, 2007 reported half of water stored in adsorbed form). On Figure 2 the interpretation of results is presented in a form of soil water isotherm, representing the water types' amounts change upon hydration (capillary and adsorbed).

4 CONCLUSIONS

In present work a novel thermogravimetric methodology for experimental quantification of adsorbed water was developed for the first time. The advantage of this methodology lies in its reliance on energy-based measurements.

It was found that the adsorbed water and capillary water are present simultaneously and vary upon hydration. The abovementioned water types were quantified and a water isotherm was presented based on the findings. The results were presented as a soil water isotherm.

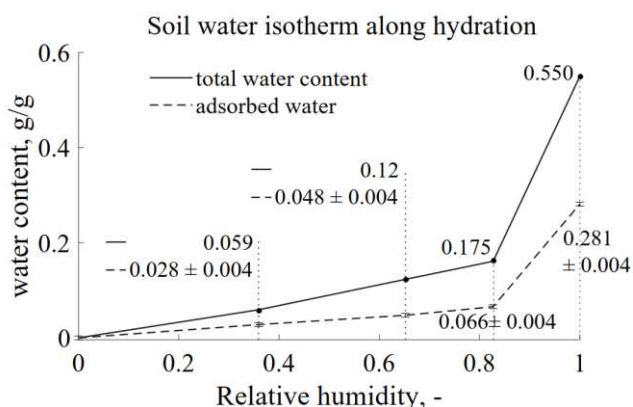


Figure 2. Outcome of the analysis.

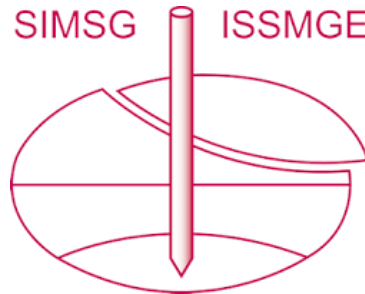
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