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ScienceDirect
Microporous and Mesoporous Materials 109 (2008) 370–375
MICROPOROUS AND MESOPOROUS MATERIALS
www.elsevier.com/locate/micromeso

Preservation of the allophanic soils structure by supercritical drying

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Received 26 September 2006; received in revised form 9 May 2007; accepted 11 May 2007
Available online 26 May 2007

Abstract

Allophanic soils are interesting in terms of environmental properties especially because of their potentialities as sinks for "greenhouse gases": Allophane clays are natural mesoporous materials exhibiting organic carbon and nitrogen contents 3–4 times higher than those measured in other clay soils. We present results on the preservation of the porous features of allophanic soils, at the nanometer scale, by supercritical drying technique (SD).

We show that textural properties such as specific surface area are systematically higher for the supercritical dried samples compared to the classical dried samples, indicating the preserving effect of supercritical drying. Pore size distribution and small angle X-rays scattering data confirm specific surface area results. The structure at the nanometer scale is affected by classical dying, which reveals the interest of the SD method to correctly characterize natural and complex mesoporous material such as allophane. Thanks to this approach we show correlation between the true specific surface area and the carbon content, in allophanic soils.

Keywords: C-sequestration; Supercritical drying; Allophane; SAXS; Specific surface area

1. Introduction

The net emissions of greenhouse gases may be reduced either by decreasing the rate at which they are emitted into the atmosphere or by removing of greenhouse gases, through sinks (carbon sequestration [1,2]). In this way, agricultural soils which are large planet's reservoirs of carbon provide a prospective way of reducing the increasing atmospheric concentration of CO_2.

Volcanic soils containing allophanes (a mesoporous amorphous mineral) are interesting for their environmental properties. These soils called allophanic soils or andosols [3] exhibit higher organic carbon concentration (up to a factor of 4) [4] than other clay soils (kaolinic or smectitic) and can be considered as C sinks. They comprise weathering products such as allophanes originating from the leaching of volcanic ash and glasses and in a previous study [5] we have confirmed the clear influence of the allophane concentration on C concentration. A paper recently published [6] shows also a strong correlation between the C content and the poorly crystalline phase (allophane, proto imogolite).

There is then a need to establish correlation between the sequestration mechanism in allophanic soils and physical parameters in these soils. It is reasonable to admit that the ability of a soil for C sequestration could be related to the soil structure and pore features but the experimental techniques able to provide such information generally require dried solids samples. Unfortunately, during a

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1387-1811/$ - see front matter
doi:10.1016/j.micromeso.2007.05.019

classical drying, allophanic soils exhibit an important irreversible shrinkage which modifies the soil structure and porous features.

This irreversible shrinkage comes from capillary stresses in the pores and from the large compliance of the porous solids.

In the literature we can read that the same kind of problem (large shrinkage) has been solved in the case of synthetic sol–gel materials by supercritical drying (SD) [7]. The gel is a two-phase medium containing the solid network and the liquid (alcohol, water). The structure of the solid network can be described as an assembly of fractal clusters (~50 nm) [8], built by the aggregation of small particles (~1–2 nm). During classical drying, capillary forces collapse the gel structure resulting in a significant shrinkage. The magnitude of those stresses is dependent on the interfacial energy γ of the liquid. By supercritical drying techniques (SD) it is possible to suppress γ and capillary stresses if the pressure and temperature pass over the critical point of the liquid and preserve the porosity of the solid network [7].

So, it exist a similar behaviour during drying between synthetic gels and allophane aggregates and we propose to use the supercritical drying to preserve the pores features of allophanic soils. This new way to dry the soil before analysis would allow getting a more accurate and more realistic description of soil organization at the nanometer scale.

Thanks to this approach we present results on the structural and textural properties of the allophanic clays. We will also discuss the C content of these soils and find correlation between the allophane content, the "real" porous features (preserved by SD) and the carbon content in allophanic soils.

2. Experimental

We selected several (19) allophanic soils, allophane content is measured by the method of Mizota and van Reewijk [10] (Al and Si content are extracted by oxalate and pyrophosphate). In this study the term "allophane content" could correspond to different poorly crystalline alumino silicate compounds: allophane (hollows spheres of around 3–4 nm); proto imogolite allophane (allophane with a Al/Si close to 2) and proto imogolite (same short range structure than imogolite (Al/Si ~ 2) but with a weak fibrosity). Imogolite forms hollow tube (2 nm diameter). However, in a previous study [11] the IR spectra of the studied andosols do not present doublets of the band at 577 and 967 cm^{-1} characteristic of the imogolite structure and the TEM micrographs presented in this study (Fig. 2) will show that fibrous structure are not observed. We can assume that the major part of the allophane content measured is neither proto imogolite nor imogolite.

Soils have been sampled in A (humus surface) horizon or B (buried) horizon which correspond to two different kinds of soils samples. Samples were conserved in closed containers to avoid evaporation. Carbon contents were measured with a CHN (thermofinnigan) chromatograph analyzer with a relative error lower 4%.

To check the importance of the supercritical drying process, two series of dried soils samples have been prepared. The first set is obtained by a classical drying in an oven at 45 °C during 2 days and the second set of samples is dried by CO_2 supercritical drying (45°C and 80 bars). The supercritical drying process requires over passing the critical point of the liquid. In this study, the apparatus used is a Critical Point Dried Balzers, CO_2 supercritical drying needs a previous solvent exchange and the whole procedure is similar to that previously published [11,12].

In the following samples will be labeled as cdX or sdX, cd and sd referring to classical and supercritical drying, respectively, and X to the allophanic weight%.

To compare the influence of the supercritical drying on the soils properties different kinds of features have been studied or measured. The specific surface area (S) was measured by N_2 adsorption–desorption techniques (BET analysis) with a micromeritics ASAP 2010. The estimated relative error is 5%. The pore size distribution is calculated using the BJH method. The out gassing conditions are 24 h at 50 °C, with a vacuum 2–4 μm Hg. Transmission electron microscopy was performed on samples SD18 and CD 18 with a TEM JEOL Type 1200 EX (100 kV).

Structure at the nanometer scale will be studied by small angle X-ray scattering (SAXS). SAXS experiments were carried out on solid powders in 1 mm diameter glass capillaries. We worked in a transmission configuration. A copper rotating anode X-ray source (functioning at 4 kW) with a multilayer focusing "Osmic" monochromator giving high flux (10^8 photons/s) and punctual collimation was employed. An "Image plate" 2D detector was used. X-ray diagrams relating scattered intensity to the wave vector q were obtained. Scattered intensity was corrected by transmission and intensity background coming from scattering by an empty capillary.

3. Results

Fig. 1a and b show the evolution of the carbon content as a function of the allophane weight% in the samples. These figures confirm that the carbon concentration increase with the allophane weight% and the A horizons (more rich in humus) contain more carbon. These results are in agreement with the results announced in the literature [4–6].

Fig. 2a and b shows 2 TEM micrographs of sample sd18 at different focus. The allophane structure is very open made of aggregated small particles (3 nm) (Fig. 2a), building clusters with size close to 8–10 nm (Fig. 2a). This clusters can stick and form larger aggregates (~100 nm, Fig. 2b). The micrographs are similar to TEM micrographs of synthetic gels forming fractal structures. This description is in agreement with literature results [3,4] and with a qualitative fractal description of allophane aggregates [13–15].