Correlation between large water content and fractal structure in volcanic soils

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Abstract

Volcanic (allophanic) contain amorphous clays (allophanes), issued from the transformation of volcanic materials. These amorphous clays present completely different structures and physical properties compared to usual clays. Allophanes aggregates have peculiar physical features very close to those of synthetic gels: large pore volume and pore size distribution, a high specific surface area and very large water content.

We propose that this large water content can be due to the peculiar structure of the allophane aggregates. Because of a large irreversible shrinkage during drying we use the supercritical drying technique to preserve the porous structure and the solid structure of a set of allophanic soils. We study the fractal structure of the allophane aggregates, at the nano scale and show that the most important part of the water content is due to the fractal structure of the porous allophanic aggregates. From the fractal features we calculate the permeability and diffusivity inside the allophanic aggregates and propose that these physical properties could also explain why these soils are able to trap large C content (C sequestration) and pesticides used in crops production.

INTRODUCTION

The surface layer of volcanic soils often comprise weathering products such as imogolite and allophane originating from the sedimented volcanic ash and volcanic glasses. [1,2]. Under a high humidity climate, a leaching process of Ca, Mg, Na and K rapidly transforms volcanic glass and ash in allophane and other secondary products rich in Si and Fe.

Allophane are amorphous alumino silicate with Al/Si ranging between 1 and 2, the unit cell appears as spheres with diameter between 3 and 5 nm [3]. These alumino silicates have a bulk density close to 0.5 g/cm^3 [4] and develop a specific surface area as high as 700 m^2/g [3]. One important feature of allophanic soils is the large water content which can be as high as 300% and conversely to usual clays, these soils do not swell after a strong drying. The drying process could be irreversible. This irreversible shrinkage comes from capillary stresses in the pores and from the large compliance of the porous solids. The same kind of problems has been solved in the case of synthetic sol-gel materials by an appropriate drying called: the supercritical drying [5,6,7].

In this work, we propose to study the possible correlation between the water content in allophanic soils and structure features like fractal morphology of the solid structure. The experimental techniques able to give structural information generally require dried solids samples. However, during a classical drying, allophanic soils exhibit a large irreversible shrinkage which will affect the soil physical properties. A peculiar drying techniques (supercritical drying) has been successfully applied for drying without shrinkage silica gels [5,6,7] and other porous materials [8,9] and we will propose that the supercritical drying (SD) could be useful to preserve the organization of the solid phase of allophanic soils.

Finally, we present results on the structural and physical properties (permeability, diffusivity) derived from the fractal features of these volcanic soils.

2) EXPERIMENTAL

2a) Samples preparation: supercritical drying

The soils have been sampled in B (buried) horizon. As explained in introduction during a classical drying, allophanic soils exhibit a much larger shrinkage than the usual clay soils and it is clear that the porous features and soil structure will be strongly affected. Concerning the drying behaviour a soil can be considered as a two-phase medium containing the solid network and the water. During classical drying (evaporation of the liquid) capillary forces collapse the structure with a significant shrinkage. The goal of SD is to eliminate these capillary forces [5,6,7].

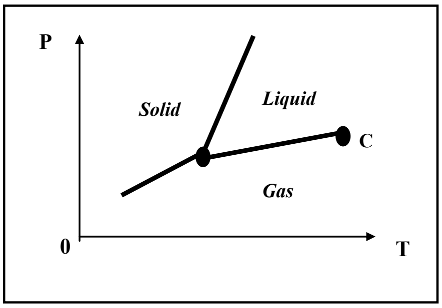

Figure 1: Typical pressure-temperature phase diagram.

The magnitude of those stresses is dependent on the interfacial energy γ of the liquid, but it is possible to cancel γ if the pressure and the temperature pass over the critical point of the liquid (point C in Figure 1). In this pressure and temperature domain, gas and liquid are no more distinguishable, no interface exists and consequently γ equals 0. The supercritical solvent is then isothermally evacuated by condensation outside the autoclave and the system is cooled down to room temperature. After supercritical drying, the soil porosity can be as high as 80 %. As expected SD preserves the porous structure and the porous features (porosity, specific surface area, e mean pore size, etc measured after a classical drying are systematically lower than the one measured after supercritical drying [10,11].

The set of soils samples have been dried by supercritical drying. The apparatus used is a Critical Point Dried Balzers and the whole procedure is similar to that previously published [7-11]. In the following the samples will be labeled as SDx, SD are for supercritical drying and x for the allophanic weight percent.

2b soils characterization

The allophanic content is measured by the method of Mizota and van Reewijk [12], using Al and Si content extracted by oxalate and pyrophosphate.

The shrinkage curve during drying is measured with the previously published procedure [13]: The water saturated soils samples where placed on a balance to measure loss of water during drying. In the same time the linear shrinkage of the height and diameter of each samples is measured by 3 spot lasers. The data are recorded and converted to specific volume and water content.

The irreversible volume loss is measured on cylindrical samples. We measure the initial volume Vo and the residual volume Vs after a complete drying at 105°C followed by a re humidification (24h at room temperature). The volume loss (Vo-Vs)/Vo is expressed in % .

The nano scale structure will be studied by Small Angle X-Ray Scattering (SAXS). SAXS experiments were carried out on solid powders in 1mm diameter glass capillaries. We worked in a transmission configuration. A cupper rotating anode X-Ray source (functioning at 4kW) with a multilayer focusing “Osmic” monochromator giving high flux (10^8photons/sec) and punctual collimation was employed. An “Image plate” 2D detector was used. X-Ray diagram were obtained giving scattered intensity as a function of the wave vector q. Scattered intensity was corrected by transmission and intensity background coming from diffusion by an empty capillary.

3) Results and discussion

3 a) Water content in allophanic soils

As mentioned above allophanic soils contain a large water content and during a classical drying, allophanic soils exhibit a much larger shrinkage than the usual clay soil [14]. The figure 1 compares the shrinkage curves during drying for allophanic soils with different allophane contents. These curves shows a specific volume and water content loss 4-5 times larger for the most allophanic soils compared to the classical clays soils (0%). The specific volume and the water content are directly related to the allophane content .

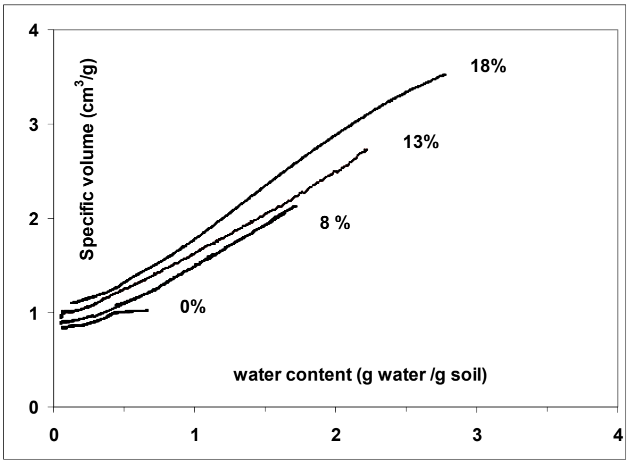

Figure 1: Drying curves of volcanic soils with different allophane contents.

In the case of non allophanic soils the shrinkage is generally reversible and usual clay soils generally swell and recover their volume when there are rewetted. In the case of allophanic soils the shrinkage behavior can be irreversible [13-15]. To quantify this behavior, we have measured the irreversible volume loss after drying and rewetting. Figure 3 shows that the irreversible volume shrinkage is related to the allophane content in soil and can be higher than 50%. The open circle on the figure 3 corresponds to calculated data from fractal features and will be explained in the discussion part. We will see later that this irreversible volume shrinkage is directly the consequence of the shrinkage of the fractal allophane aggregates.

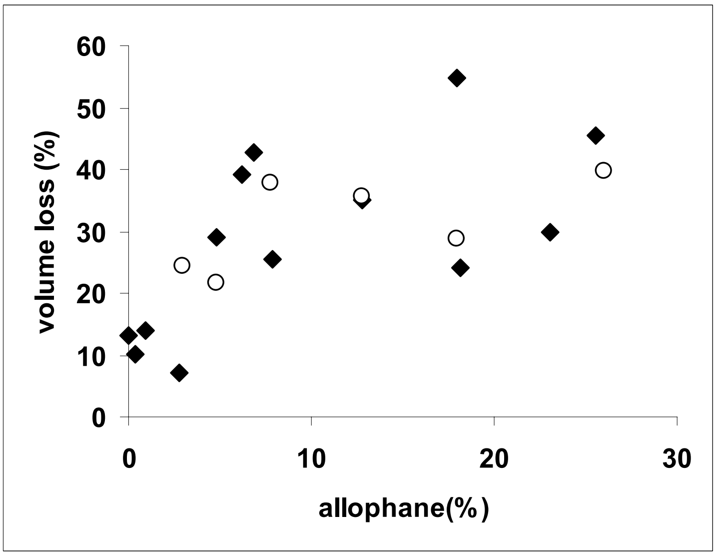

Figure 3: Irreversible volume loss during versus the allophane content (♦ experimental data, ϒ calculated data with the fractal features)

3 c) Structure of allophane aggregates

To understand why the allophanic soils contain more water than the other clays and why the shrinkage during drying could be irreversible, it is necessary to characterize the peculiar structure of the allophane aggregates. Figure 5 shows the transmission electron micrograph of the sample SD18. In this sample, the allophane structure is a very open structure made of aggregated small particles (≤ 5 nm) building clusters with size close to 10 nm. This clusters can stick and form larger aggregates. This description is in agreement with the results of the literature [16-18] and with a qualitative fractal description. Wada [16] describes allophane particles as nearly spherical with diameters in the range 3.5-5 nm, by way of comparison the plate-like particles of kaolinite clay are 300-3000 nm.

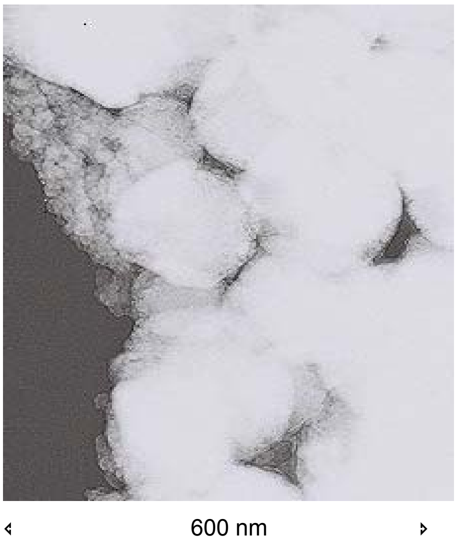

Figure 4: TEM micrograph of the sample SD18.

However transmission electron micrographs are not able to give quantitative information on the fractal features. To precise the fine structure of the soils samples we have performed SAXS experiments on the different allophanic soil (figure 5).

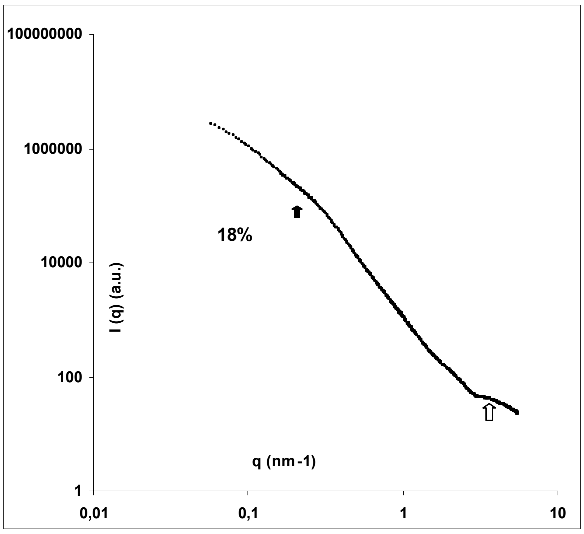

Figure 5: SAXS experiments on the soil containing 18% of allophane

The figure 5 shows the evolution of the scattered intensity (I) versus the wave vector (q) for the samples SD18. Analysed in terms of fractal geometry [19], SAXS experiments give three different information of the structure: the mean size of the fractal clusters (ξ), the mean size of the primary particles (a) which stick together to build the cluster, and the fractal dimension Df which express the clusters compactness. The power law part appearing as linear in a log log scale has a slope related to –Df (Df is in the range 2.5-2.7). The position of the two cross over (black and white arrows) are related respectively to the inverse of the cluster size (2π/ξ) and the inverse of the particle size (2π/a). The black arrow in the q range 0.4 nm^{-1} corresponds to a cluster size in the range 50-100nm. For q higher than 2 nm^{-1} the curve shows a hump which can be attributed to the particle size (3-4 nm) (white arrow). This description is in agreement with the results of the literature [16-18] and the above results of transmission electronic microscopy. From SAXS data we have calculated the fractal features of the different allophanic soils (Table 1).

Allophane content %	Df	ξ (nm)	a (nm)
3	2.7	12	3
5	2.6	23	4
8	2.7	32	3
13	2.5	35	3
18	2.6	45	4
26	2.7	62	4

Simulation of the allophane aggregate physical properties

4 a) water content of the fractal allophane aggregates

Fractal geometry can help us to derive some porous and structural properties of the allophane aggregates. In the case of a fractal aggregate the evolution of the local bulk density is $\rho(l) \propto l^{Df-3}$. Between the limits of the fractal aggregates, we get: $\rho(l) = \rho(a)[\frac{l}{a}]^{Df-3}$.The figure 6 shows the evolution of the local density between ξ and *a* (inside the aggregate). In a fractal aggregate the local density increases when the length scale decreases.

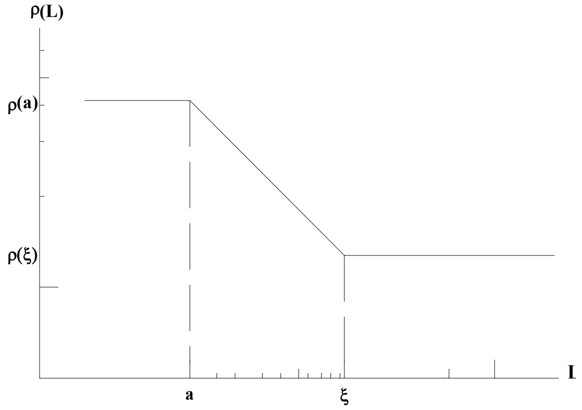

Figure 6: Evolution of the local density as a function of the length scale in a fractal structure: ξ et *a* are the limits of the fractal aggregates

From the data of the table 2 it is thus possible to calculate the bulk density ρ(ξ) of the fractal aggregates for the different studied samples. From the bulk density we have calculated the pore volume defined as 1/ρ(ξ) – 1/ ρ(*a*), with ρ(*a*) ≈ 2.5 g/cm3 [13] for the allophane aggregates before and after a complete drying. These data allow estimating the pore volume loss associated to the allophane aggregate shrinkage. On the figure 3 are plotted (open circles) the data calculated with the fractal features of the table 2. They are in quite good agreement with the data measured on the soils samples. These results show that the large part of the irreversible volume loss measured on the allophanic soils should be attributed to the shrinkage of the allophane aggregates. This new result confirms previous data [10,11] on the loss of specific surface area during drying which was also directly related to the allophane content. It also shows that it is the peculiar fractal structure which is responsible of the large pore volume, the high specific surface area and the large water content of the allophanic soils.

The specific structure of the allophane aggregates is also responsible of the irreversible shrinkage. The allophane clusters are made from the aggregation of allophane particles weakly connected and forming the compliant very open structure. In these aggregates the pore size distribution span between a few nanometres and one hundred nanometres. Because of this small pore size the capillary stresses (conversely proportional to the pore size) occurring during the drying are strong which leads to the collapse of the pore volume and the bonds between allophane particles are broken.

4 a) Permeability and diffusivity inside the fractal allophane aggregates

From the fractal structure we can also derive physical features responsible for the transport properties. The transport in porous materials depends on two kinds of mechanism: The permeability which associates the flux of liquid to the gradient in pressure in the liquid and the diffusion in the case of there is a concentration gradient in the liquid. In the following we will derive simple expressions of the permeability (*K*) and the diffusivity coefficient (*Di*) versus the fractal features. It is not possible to measure the permeability and diffusivity at the scale of the allophane aggregates. However the knowledge of the fractal structure allows deriving *K* and *Di* at the aggregates scale [20].

There is in the literature a relationship which relates the permeability *K* with the relative density ρ_r and the mean pore size *d* of a porous object. This relation is called Carman-Kozeni equation: $K \propto (1-\rho_r)\, d^2$. We have seen above that in the fractal range we can calculate $\rho(l)$: $\rho(l)=\rho(a)[l/a]^{Df-3}$; the relative bulk density *is* $\rho_r(l) = \rho(l)/\rho(a)$, consequently $\rho_r(l) = [l/a]^{Df-3}$. The pore size decreases when the length scale decrease and we find that the local permeability (inside the fractal aggregate) varies as: $K(l) \propto (1-(l/a)^{Df-3})\, l^2$, (with $K(a)=0$). We calculate that the permeability strongly decreases (almost 4 orders of magnitude) when the length scale decreases between 100 and 4 nm (Fig 7)

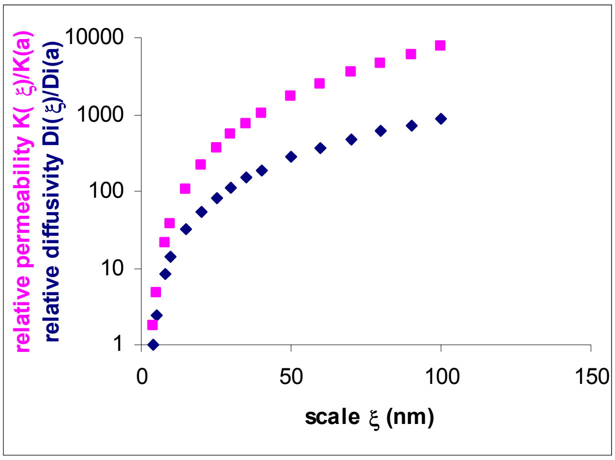

Figure 7: Evolution of the relative permeability and relative diffusivity as a function of the length scale in a fractal structure

In the case of a diffusion process in porous system it is proposed [21] that $Di \propto P/t$, where *Di* is the diffusivity in the porous structure, *P* is the pore volume and *t* the tortuosity [22]. In a fractal aggregate we can express the pore volume as:

$P(l) = 1-\rho_r(l) = 1-[l/a]^{Df-3}$. The tortuosity is also a power law function of the length scale:

$t \propto l^{\lambda}$ [23] which leads to :$Di(l) \propto (1-(l/a)^{Df-3})\, l^{\lambda}$. The λ value measured on similar fractal structures (silica gels) is closed to 1.6 [24]. So, we calculate that *Di* strongly decreases (close to 3 orders of magnitude) when the length scale decreases between 100 and 4 nm (Fig 7).

These results on permeability and diffusivity mean that fluids and chemicals species will have difficulty to migrate inside the porous and tortuous porosity of the fractal aggregates.

5) Conclusion

In this study, we have characterize the fractal structure and measure the fractal features of different allophanic soils. We have shown that there is a clear correlation between the allohane content , the fractal features and the large water content of the allophanic soils.

However, besides these hydrodynamics features allophanic soils exhibit also higher carbon and nitrogen content (among the most important components of green house gases) than the one measured in other clay soils. They are thus interesting in terms of environmental properties especially because of their potentialities as sinks for “greenhouse gases”. Last but not least, these soils retain also pesticides contents larger than in usual soils.

We propose that the low permeability and diffusivity that we have calculated for fractal allophane aggregates could also explain the carbon sequestration and the high pesticides content. Because of these low permeability and diffusivity, the fluid exchanges and chemical reactions are slow and the part of organic matter usually decomposed during soil respiration is lowered (as the soils allophane content increase), leading to the accumulation of carbon not chemically transformed [10,11]. Low permeability and diffusivity of allophane aggregates is also proposed to explain why these soils retain more pesticides, the peculiar structure of the allophane aggregates plays the role of a labyrinth which traps the chemical species.

These apparently different properties (large water content, C sequestration and pesticides affinity) could be due to the same factor: the fractal and tortuous structure of the allophane aggregates.

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