

Quantifying microstructural stability of South-Brazilian soils by the application of rheological techniques and zeta potential measurements

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Abstract

Rheological and zeta potential measurements were performed with South-Brazilian soils, a kaolinitic, Fe-oxide-rich Oxisol, and a smectitic Vertisol, respectively. Hence, a low active clay and a high active clay system were compared. Furthermore, the phenomenon of pseudosand was investigated. Stiffness degradation was measured by conducting amplitude sweep tests with a rotational rheometer in oscillatory mode. By using loss factor $\tan \delta(\gamma)$, elasticity and viscosity of substrates can be defined in detail and calculated. Zeta potential measurements show a clear trend of agglomeration for Oxisols, whilst Vertisol suspensions remain stable over a wide range of pH 10...2; the isoelectric point (IEP) is reached at pH 2 in case of the Oxisol. A synopsis of rheological and zeta potential results may explain both pseudosand effects due to Fe-oxides and microstructural stability deriving from physicochemical properties i.e. texture, clay mineralogy, and CEC.

Key Words

Rheology, zeta potential, microstructural stability, Fe-oxides, pseudosand, IEP

Introduction

Amplitude sweep tests with controlled shear deformation have been conducted on homogenised substrates deriving from kaolinitic, Fe-oxide-rich Brazilian Oxisol and a smectitic Vertisol in order to (semi-)quantify stiffness degradation. The influence of Fe-oxides, and clay minerals on micromechanical shear behaviour under oscillation has been tested under saturated and pre-drained conditions. From collected data, which include parameters as G' (storage modulus), G'' (loss modulus), loss factor $\tan \delta$ results, which indicates the dissipation of elasticity in a viscoelastic substance (=soil). Furthermore, rheological findings were complemented by zeta potential measurements, with the intention to investigate agglomeration behaviour.

Material and Methods

South-Brazilian soils, in detail an Oxisol (S. Ângelo, natural forest) and a Vertisol (Santana do Livramento, pasture) were investigated; rheological findings are presented by Markgraf and Horn (2007) in detail. Analyses i.e. texture, CEC, pH, and C_t , were conducted according to standard methods as described in van Reeuwijk (2002). Iron oxides were extracted by Na-dithionite according to Mehra and Jackson (1960). The Oxisol is dominated by a kaolinitic clay fraction, whereas the Vertisol shows a smectitic clay mineralogy and a typical, high content of Mg^{2+} and Ca^{2+} in a ratio of 1:2.5 (Table 1).

Table 1. Physicochemical properties of the investigated soil material.

	Sand	Silt	Clay	Na	Mg	Ca	pH	C_t
		(%)			(mmol _e /kg)		(-log _{H+})	(%)
Oxisol	6	25	69	1.5	17	41	4.4	6.6
Vertisol	3	32	65	2.7	157	396	5.5	3.4

Rheological measurements

Markgraf *et al.* (2006) give a detailed description of amplitude sweep tests, including a theoretical background of rheology and its application. A parallel-plate-rheometer, MCR 300 (Anton Paar Company, Stuttgart, Germany), was used. During all tests a constant temperature of 20°C was maintained, regulated by a Peltier unit. Amplitude sweep tests (AST) under oscillatory conditions were conducted, with controlled shear deformation (CSD) $\gamma = 0.0001 \dots 100\%$, an angular frequency $\omega = \pi/s$ ($f = 0.5$ Hz), and 30 measuring points, which led to an average test duration of 16 minutes. A plate distance of 4 mm was pre-set according to a plate radius of the rotating bob of 25 mm and the given texture ($>2 \mu m$). The tests were controlled by the

software US 200 (Anton Paar Company, Stuttgart, Germany).

In Figure 1 three stages of stiffness degradation are given. Loss factor $\tan \delta$ includes both elastic and viscous parts; it furthermore is the ratio of elasticity (=storage modulus G') and viscosity (=loss modulus G'') (Markgraf and Horn 2009). If $\tan \delta = G''/G' = 1$ substances are creeping or yielding; considering stress-strain relationships of soils on a particle-to-particle scale, at this stage a microstructural breakdown occurs. Hence, values $<\tan \delta = 1$ indicate an elastic or stiff character, whilst a viscous behaviour predominates at values $>\tan \delta = 1$.

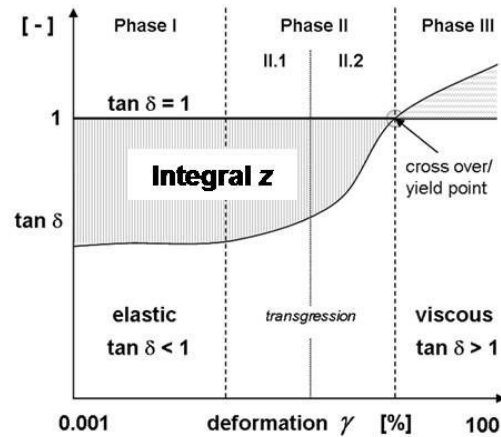


Figure 1. Idealized graph of conducted amplitude sweep test, loss factor $\tan \delta$ (γ). Values below $\tan \delta = 1$ (Phases I and II.1) indicate a elastic or pseudo-elastic behaviour; a yield point is given at the intersection of the graph with the $\tan \delta = 1$ -line (Phase II.2); viscous behaviour is given in Phase III $\tan \delta > 1$, resulting in a microstructural, irreversible breakdown.

Electrokinetic investigation

Electrophoresis measurements were performed with a Zetasizer Nano ZS by Malvern Instruments Ltd., UK equipped with a 633nm He/Ne laser. By using the M3-PALS technology the electrophoretic velocity of the particles in an applied electric field of 40 V was determined. The M3-PALS technique (Minor *et al.* 1997) was developed to perform measurements at any point within the measuring cell independent of the electroosmotic flow. This technique is a combination of the 'Mixed Mode Measurement' technique of Laser Doppler Velocimetry and the application of Phase Analysis Light Scattering. The zeta potential was calculated from the electrophoretic velocity ($v=v/E$) by the Helmholtz Smoluchowski (v. Smoluchowski, 1921) equation ($\kappa a \gg 1$):

$$\frac{v}{E} = \frac{\epsilon \epsilon_0}{\eta} \zeta$$

where κ is the Debye Hueckel length, a is the particle radius, v is the particle velocity, E is the electric field strength, ϵ is the relative and ϵ_0 is the absolute dielectric constant, η is the viscosity of the liquid, and ζ is the zeta potential.

Sample preparation

100 mg of the soil was inserted in 50 ml of the respective electrolyte solution and dispersed 5 min in an ultrasonic bath. After 30 minutes rest 10 ml have been transfused and refilled with 40 ml of the equal electrolyte solution which was used before.

Results

An ideal behaviour is demonstrated with the data on the untreated saturated and pre-drained Vertisol samples. A sliding shear behaviour predominates, which results from a smectitic clay mineralogy. If graphs of $\tan \delta$ (γ) are compared, a smoother curve progression occurs in case of the smectitic Vertisol, either under saturated or pre-drained conditions; whilst graphs of the kaolinitic, Fe-oxide- rich Oxisol, as well as the Fed-leached modification, indicate frictional heat (=increase of $\tan \delta$ at $\gamma=0.01 \dots 1\%$), and a turbulent shear behavior. These findings can be related to the semi-quantitative classification of stiffness degradation in Markgraf and Horn (2009). Furthermore, by calculating integral z of both the Oxisol and Vertisol (including all treatments), $Z_{\text{Vertisol}} > Z_{\text{Oxisol}}$; this instant can be also referred to a higher degree of elasticity in Vertisols,

which is also responsible for a high shrinkage and swelling behaviour (HAC), whereas kaolinitic soils (LAC) tend to show a more rigid, stiff structure, which leads to the occurrence of frictional heat. Due to Na-dithionite treatment of the oxisol, strengthening effects are decreased noticeably. Kaolinite piles may function as single grains with regard to shear behaviour, if one assumes stable structural conditions of partially sharp-edged grains. In this case, a direct surface-to-surface or edge-to-edge contact can be assumed during AST. Aggregate formation and strengthening are strongly enhanced by the remobilization of iron and the conversion of ferrihydrite to hematite (Ohtsubo *et al.* 1991).

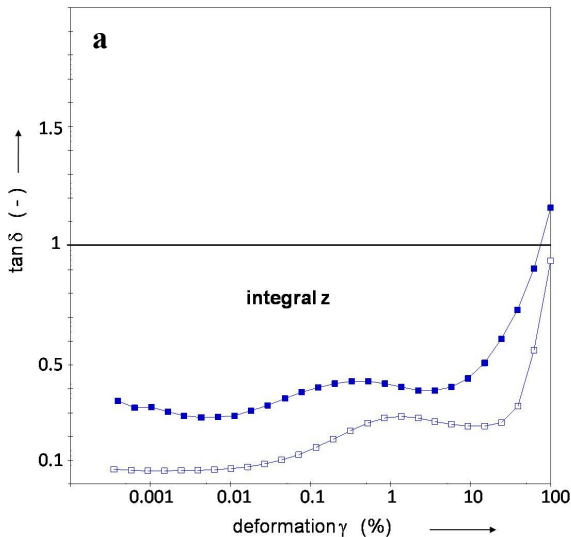


Figure 2a. Resulting graphs of conducted amplitude sweep tests with the kaolinitic, Fe-oxide-rich Oxisol (natural conditions, forest); Na-dithionite treated (filled squares) and untreated (blank squares) conditions.

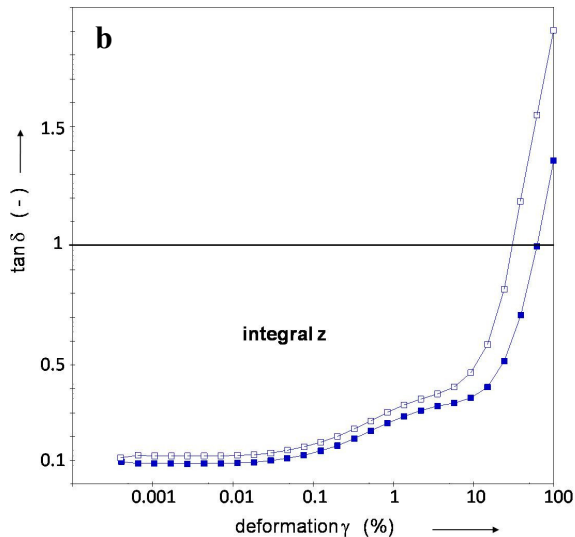


Figure 2b. Corresponding to Figure 1a resulting graphs of the investigated smectitic Vertisol are presented; saturated (blank squares) and pre-drained (filled squares) samples are compared.

Results of zeta potential measurements (Figures 3a and b) show a corresponding affinity to agglomeration in case of the oxisol (Figure 3a), which is strongly dependent on the pH. The isoelectric point is reached at a pH of ~ 2 , whereas suspensions are stable from pH 10...5.5 at a zeta potential ζ of appr. -32 mV; a maximum particle size of 3000...4500 nm is reached at the IEP. In comparison, the smectitic Vertisol (Figure 3b) remains stable over the whole pH range from 10...2 at a corresponding zeta potential ζ of -30 ... -20 mV. At pH 2.5 a slight trend of agglomeration becomes obvious, as the particle size increases from >1500 to 4500 nm.

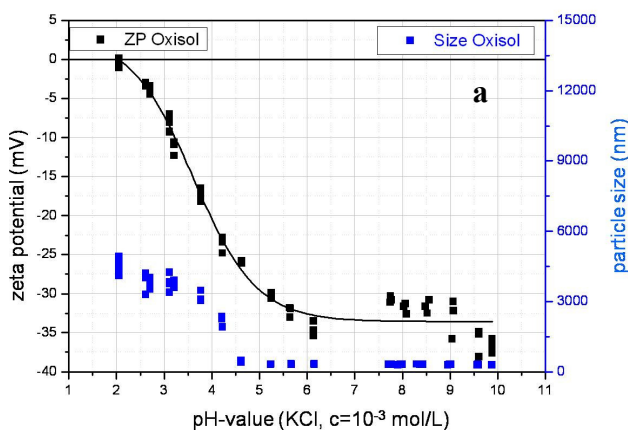


Figure 3a. Zeta potential and particle size measurements of the investigated Oxisol; suspensions remain stable in a range of pH 10...5.5; the IEP is reached at \sim pH 2, whereas agglomeration is indicated at pH 4.5...<2.

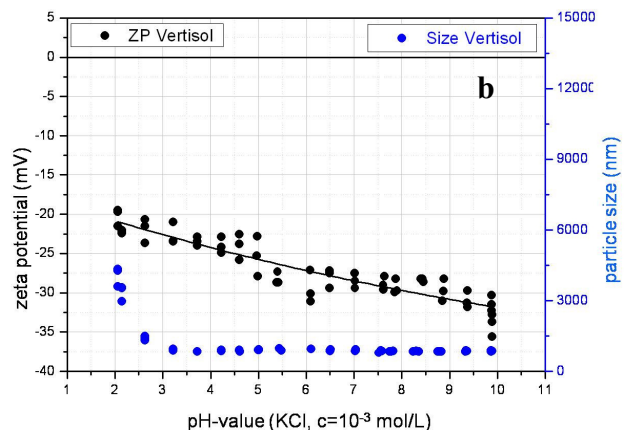


Figure 3b. Suspensions of the smectitic Vertisol remain stable over a range of pH 10...2; the IEP is not reached, and particle sizes indicate a trend of agglomeration at pH <2 only.

Conclusions

Rheological investigations as well as zeta potential measurements led to a reliable consistency. On one hand stiffness degradation could be (semi-) quantified by applying amplitude sweep tests, and be complemented by zeta potential results. Both methods showed a higher degree of agglomeration of the kaolinitic, Fe-oxide-rich Oxisol, indicating the phenomenon of ‘pseudosand’ in dependency of pH; furthermore, a stable, elastic structure was obvious for smectitic Vertisol samples. Hence, rheology may function as useful tool between the colloidal (particles <1µm) and micro scale (particles 1-250µm)), if structural effects need to be defined.

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