Porosity Changes of Compacted Soil Percolated with Acidic Leachate

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Abstract. This paper evaluates porosity changes in compacted soil subjected to acidic leachate percolation through different dry unit weights. The porosity of compacted soil is presented in different nominal porosities or dry unit weights (41.9% and 15.5 kN/m³, 43.8% and 15.0 kN/m³, and 45.7% and 14.5 kN/m³) percolated with a sulfuric acid solution under a constant vertical stress of 280 kPa. Porosity was evaluated via X-ray microtomography (μ-CT) and mercury intrusion porosimetry (MIP). The results demonstrated that percolation by a 2% sulfuric acid solution in compacted clay soil caused changes in pore size distribution, increased the pore diameter in all specimens’ layers, and increased the porosity in specimens’ upper layers due to acidic attack on the soil’s microstructure. The porosity assessed by mercury intrusion showed a good correlation with the macroscopically measured porosity. The same behavior was not observed via μ-CT due to the limited resolution of the images and the inability to characterize the micropores.

Keywords: compacted soil, containment barriers, mercury intrusion porosimetry (MIP), soil percolation, X-ray microtomography (μ-CT).

1. Introduction

Compacted clay soils percolated by aggressive chemical agents, such as leachate from industrial waste, can be affected in the soil structure, resulting in an increase of hydraulic conductivity and a consequent reduction of reactivity, harming the ability of the soil to retain and attenuate contaminants (Broderick & Daniel, 1990; Favaretti et al., 1994; Hueckel et al., 1997; Knop et al., 2008). According to Francisca and Glatstein (2010), the hydraulic behavior of fine or recently compacted soils is mainly influenced by interactions between percolated liquid and mineral particles. Thus, acid attack in clay soils can result in their chemical alteration and release of ions; it can also influence several physical, biological, and chemical processes (Agbenyeku et al., 2016).

To understand the phenomena resulting from interaction between acid leachate and compacted soil particles, it is essential to evaluate the microstructure of the soil, since acid leachate has a substantial influence on the mechanical behavior of both natural and compacted soils (Burton et al., 2015). Therefore, one of the essential parameters for microstructure alteration studies under different geotechnical conditions is porosity. Two porosity scales should be considered: microporosity, which can be defined as the saturated pores space; and macroporosity, considered as a two-phase system, which may contain both liquid and steam (Sedighi & Thomas, 2014).

Many studies have evaluated porosity in clayey, sandy, or cemented soils via image analysis from scanning electron microscopy (Rozenbaum et al., 2007; Schoonderbeek et al., 1983), 2D/3D X-ray tomography (Lima et al., 2007; Luo et al., 2008; Pires et al., 2010; Trong et al., 2008) or a combination of techniques, such as mercury intrusion porosimetry (MIP) with image analysis (Amirtharaj et al., 2010; Gribble et al., 2011; Labus, 2001; Marcelino et al., 2007; Roels et al., 2001; Rouquerol et al., 2012; Tovey & Houslow, 1995). However, only a few studies have explored the performance of compacted materials in containing acid solutions due to difficulties in obtaining data at the micropore scale. In addition, the performance of compacted materials is continuously monitored at a macrostructural scale by settlement observation, which does not guarantee efficiency in blocking the percolation of contaminants. Therefore, determining the porosity and pore size distribution of compacted clayey soils is an essential complementary study.

The goal of this study is to evaluate variations in the porosity of compacted soil submitted to sulfuric acid (H₂SO₄) leachate percolation in different conditions (percolated with water and with 2% H₂SO₄). Sulfuric acid was chosen because it has high acidic characteristics similar to those of the leachate generated by most industrial and mining residues. Two different porosity quantification techniques were used: X-ray microtomography (μ-CT) and...
MIP. Examining the porosity and pore size distribution of the compacted clay soils was necessary to explain changes at the microstructural scale. Additionally, the examination may contribute to prediction studies and to the technological development of new materials that could ensure the effectiveness of compacted clay soils as an impermeable containment barrier.

2. Experimental Procedures

The studied soil samples were obtained from the University of Passo Fundo’s Geotechnical Experimental Site in southern Brazil. The samples were characterized by their chemical and mineralogical compositions, content of organic matter, pH, and particle size distribution.

The chemical composition of the soil samples was determined for both pulverized and compacted samples (then compared to reference materials from approximately 290 national and international analytical standards - NIST) using a PANalytical® Axios Advanced X-ray fluorescence spectrometer (XRF) with a 4-kV rhodium X-ray tube, a detection capacity above 0.1%, and a scan time of approximately 6 min. Loss on ignition (LOI) was carried out at 1000 °C for 2 h.

The mineralogical composition of the samples was assessed by X-ray powder diffraction (XRD) with a PANalytical® Empyrean X-ray diffractometer. The analytical conditions were as follows: 2θ angle, ranging from 3° to 70°, and 10-second time steps. The identification of the crystalline phases was performed by comparing the sample diffractogram with the PDF-2 reference database from the International Centre for Diffraction Data (n.d.) and the PAN-ICSD - PANalytical Inorganic Crystal Structure Database (PANalytical, 2007).

Organic matter content was determined via the organic matter oxidation method using a sulfochromic solution, as presented by Tedesco et al. (1995). The pH was measured in H₂O (Tedesco et al., 1995). The particle size distribution was determined by sedimentation according to standard procedures (ABNT, 1984, 2005).

To define the variables for the percolation tests, different nominal porosities and dry unit-specific weights were evaluated according to the normal and modified compaction energy values of the soil, which were 41.9% (15.5 kN/m³) and 45.7% (14.5 kN/m³), respectively, with 26% moisture in both cases. Only one value was used for moisture because it is the optimum value for both normal and modified compaction energy and modified energy (plus 2%) typically used in engineering projects. The tests were carried out in 2 blocks, with each block comprising 2 repetitions for the adopted nominal porosities. In addition, 4 repetitions were performed in each block for a central point (43.8% - 15 kN/m³) in order to evaluate the experimental error for mean comparison (identified by “CP” 1 to 8). In one of the experimental blocks, percolation was conducted with distilled water; in the other, 2% sulfuric acid (H₂SO₄) was used.

The percolation tests were conducted over an extended period of time: 30 to 70 days. The tests included specimens 7 cm in diameter and 6 cm in height, and percolation was performed with a hydraulic gradient of 8.33 m/m under the application of a constant vertical stress of 280 kPa to simulate a 15-m height of waste mining over the barrier, with a total specific weight of 18.6 kN/m³ based on literature data (Bedin, 2010; Schnaid et al., 2006).

After acidic percolation, the specimens were cut into three layers (top, middle, and bottom layers, considering downward flow). Samples from each layer were cut into prismatic shapes with approximate dimensions of 2.0 cm × 0.7 cm × 0.7 cm and were identified by layer (T = top, M = middle, B = bottom). After the samples were leached, they were dried. For each layer, the macroscopically measured porosity was determined by theoretical relation to dry unit-specific weights. Porosity was also determined by high-resolution µ-CT with a Bruker® SkyScan 1172 and by MIP with Micrometrics Autopore IV equipment according to the procedure described in ISO 15901-1 (ISO, 2016). With the µ-CT and MIP techniques, the average cumulative distribution curve of the pores and variations in the pore size distributions in the specimens’ layers were determined.

The characterization by microtomography comprised three phases: (1) data acquisition via rotation of the sample in 0.4° steps, resulting in a minimum pixel size of 5 µm; (2) 3D image reconstruction; and (3) binarization of the generated images (Fig. 1) and grayscale segmentation corresponding to voids and solids to determine the void volume (porosity). The segmentation was performed using a numerical algorithm (LI method) available in the Image J® software. Comparatively speaking, this method best represents the magnitude of values of porosity evaluated.

Regarding image processing, the collection and magnification conditions used in µ-CT define the image resolution and, therefore, its constituents. In this study, the detected pixel size was 5 µm (each pixel). For segmentation, to define a pore, at least 2 pixels were considered, so it was possible to characterize only pores larger than 10 µm (10 000 nm).

MIP was performed in the following operating conditions: contact angle of 130°, mercury pressure from 0.5 psi to 40 000 psi, equilibrium time of 10 s, and mercury surface tension of 485 dynes/cm. The pore diameter (dₚ) accessible to mercury depends on the applied pressure, mercury surface tension, and contact angle with the studied material, as described by the Washburn equation: \[ d_p = -\frac{4 \gamma \cos \theta}{\text{Pressure}} \] (Washburn, 1921). In the adopted operating conditions, considering an intrusion pressure up to 40 000 psi, it is possible to characterize the pores down to 45 nm.
3. Results

The sampled soil possessed a low organic matter content (< 0.8%), a high clay-size particle content (68%), and an acidic pH (pH = 5.5). According to X-ray diffraction analysis (Fig. 2) and chemical composition (Table 1), the soil was a kaolinite-based clay with a significant presence of hematite (Fe₂O₃ content of 11.7% - Table 1), quartz (SiO₂ content of 47.9%) and aluminum oxide (Al₂O₃ content of 26.6%). These characteristics represent promising conditions for use as a base material for containment barriers.

Table 2 shows the porosity results obtained from the macroscopically measured value determination, via MIP and µ-CT, for specimens tested by percolation with a 0% and 2% sulfuric acid solution. The specimens were presented according to their central and factorial points, both of which were related to the nominal porosity values - P (nominal). Moreover, the median pore diameter (D50) was...
presented. Comparative data are shown in Fig. 3. Figure 3 also illustrates the average porosity of 8 specimens from the top, middle, and bottom layers, percolated with water (Fig. 3a) and 2% sulfuric acid solution (Fig. 3b) and assessed by MIP, µCT, and macroscopically measured.

Figure 4 shows the average porosity assessed by MIP for the nominal initial porosity of each specimen’s layers percolated with water (Fig. 4a) and 2% sulfuric acid solution (Fig. 4b).

In Fig. 5, the top row shows the average cumulative distribution curve of the pores of the top, middle, and bottom layers, assessed by MIP and µCT, of specimens subjected to percolation with 0% and 2% sulfuric acid solution. The variations in the specimen layers’ pore size distributions, measured by MIP and µCT after leaching with water (Fig. 5b) and 2% sulfuric acid (Fig. 5c), are also shown.

Figure 6 shows the correlation between the porosity obtained from MIP (Fig. 6a) and µCT (Fig. 6b) and the macroscopically measured values for samples percolated with water and 2% sulfuric acid in different layers.

4. Discussion

The average porosity of the samples percolated with 2% sulfuric acid solution (Table 2, Fig. 3b) was higher in the upper layers than in the middle and lower layers, with the exception of samples with a value of 41.9 for nominal porosity, which had similar porosity values for all layers. In this case, more efficient compaction may have promoted more homogeneous percolation of the acid solution in the samples, besides reducing the transport of particles to the lower layers.
This behavior, i.e., higher average porosity values for samples percolated with 2% sulfuric acid solution in upper layers, might represent evidence for acidic attack on soil structure, since this result was not observed in samples percolated with aqueous solution, in which the porosity tended to be similar across layers (0% acid, Fig. 3a). The lower porosities observed in the lower layers after acid percolation may possibly be due to both the filling of voids in these layers by products from the chemical attack and the closure of micropores caused by the impact of the applied load of the upper layers under compression.

Regarding nominal porosity, a total average porosity reduction of 12% occurred for samples treated with water and 2% acid when compared with nominal porosity values (41.9, 43.8, and 45.7). This effect may have been caused by the vertical load application, not acid percolation.

The disparity in results between MIP and \(\mu\)CT occurred due to the different resolutions of each technique, i.e., \(\mu\)CT does not detect micropores. Therefore, the total porosity assessed by \(\mu\)CT was noticeably lower when compared to MIP and macroscopically measured porosity (Table 2, Fig. 3a,b) (10 to 20% lower). Additionally, the median pore diameter (D\(_{50}\)) (Table 2) demonstrated a large difference between the applied techniques: The pore diameter in MIP measurements was up to 50% larger than in \(\mu\)CT; this difference is even more evident in samples percolated with acid solution. Thus, MIP showed smaller D\(_{50}\) values, reflecting a range of smaller-diameter pores and enabling the identification of micropores (< 2 nm) and mesopores (between 2 and 50 nm) according to the classification proposed by IUPAC (Rouquerol et al., 1994); \(\mu\)-CT, on the other hand, only allowed the identification of macropores (> 50 nm).

The pores’ cumulative distribution curve (Fig. 5) clearly demonstrates differences in terms of range between the techniques (MIP and \(\mu\)-CT). The minimum pore size evaluated by \(\mu\)CT was 10 000 nm (10 \(\mu\)m), whereas MIP detected pores as small as approximately 4 nm (0.004 \(\mu\)m). Regarding pore size distribution, percolated samples of 2% sulfuric acid (Fig. 5a) demonstrated clear changes in microstructure from the point of view of increasing pore diameter. Moreover, it was observed that percolation with 2% sulfuric acid equalized the pores’ size distribution, especially in the upper layers (Fig. 5c).

The modification of pore size distribution among the layers can be explained by the acidic attack on the structure, which caused an increase in both pore diameter and total porosity, especially in the upper layers of the tested speci-
mens. This evidence would not have been obtainable had only a macrostructural analysis of compacted barriers been performed, in which changes in hydraulic conductivity and mechanical behavior would have been observed without knowing their cause being known. Knowledge about the impact of pores on soil microstructures can also provide a better understanding of, for example, which contaminant transport process is most relevant to the study of subsurface contamination vulnerability and how to better predict performance with greater certainty and reliability.

In regard to the analytical determination of porosity, the best correlation was found between the MIP results and the macroscopically measured porosity (Fig. 6a and Table 2). On the other hand, the porosity determined by μ-CT had a low correlation with the macroscopically measured porosity (Fig. 6b) because the detection limit of the technique does not allow the quantification of micropores. Although the micropores contributed little to the total porosity of the specimens when compared to the volume of macropores, they did significantly influence the calculation of the median diameter.

It should be noted that the maximum possible resolution from the μ-CT technique is equivalent to 1 μm, which is far weaker than the resolution obtainable by MIP (4.5 nm for 40 000 psi of intrusion pressure). To reach a similar resolution in μ-CT, the sample size would have to be reduced to about 1 mm, which would lead to the loss of the sample’s representativeness.

Analyses by μ-CT are often mentioned in the literature because the method is non-destructive and allows the pore structure to be viewed. Several researchers have successfully used μ-CT to quantify porosity, but only for materials with larger particle diameters than clay fractions; besides, these researchers were more interested in macroporous

![Figure 5 - Pore size distribution of average specimen’s layers by MIP and μCT when leached with: a) water and 2% sulfuric acid; b) water; c) 2% sulfuric acid.](image)
characterization (Lima et al., 2007; Luo et al., 2008; Neto et al., 2011; Pires et al., 2005). For the study of compacted soils, µ-CT is only partially effective due to the presence of microporosity.

The use of mercury intrusion under high pressure can erroneously quantify the porosity of a sample due to the effects of compression or structural changes (Giesche, 2006; With & Glass, 1997) - this factor should be carefully considered. In addition, ordinary calculations consider pores as cylinders, which may not represent their actual sizes and dimensions. Despite these disadvantages, this study noted that mercury intrusion showed the best correlation with the macroscopically measured porosity as well as the best sensitivity for micropore characterization. The intrusion, which curved up to 40 000 psi, did not indicate structural changes in the samples.

In this sense, limitations can be overcome, and the most satisfactory and conclusive results can be obtained by using a combination of different techniques. Some studies in the literature have used a combination of MIP with tomography and other techniques to assess the porosity of porous materials (Abel et al., 1999; Gribble et al., 2011; Roels et al., 2001); this approach was also considered in this study and allowed for the characterization of porosity and pore size distribution.

5. Conclusions

Samples percolated with a solution of 2% sulfuric acid in compacted clay soil samples suffered changes in the pore size distribution and an increase in pore diameter in the specimens; a greater increase in porosity in the specimens’ upper layers was observed due to acidic attack on the soil microstructure. The porosity assessed by mercury intrusion porosimetry (MIP) showed the best correlation with the macroscopically measured porosity. The same behavior was not observed for µ-CT results due to limited image resolution, which precluded the identification of micropores.

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