

Technical feasibility analysis of using phosphogypsum, bentonite and lateritic soil mixtures in hydraulic barriers

Yago Isaias da Silva Borges¹ , Bismarck Chaussê de Oliveira² ,

Maria Eugênia Gimenez Boscov¹ , Márcia Maria dos Anjos Mascarenha^{2#} 

Article

Keywords

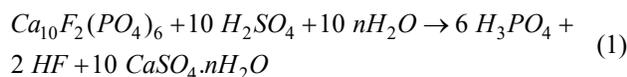
Di-hydrated phosphogypsum
Liner
Hydromechanical performance
Compatibility

Abstract

Every year, millions of tons of phosphogypsum, a by-product of the fertilizer industry, are produced worldwide. As just a small part of this amount is reused, this study analyzed a new alternative to reuse this material in geotechnical works, in mixtures with lateritic soil and bentonite for the construction of liners for sanitary landfills. Four compositions were tested: 100% soil, 10% phosphogypsum + 90% soil, 10% phosphogypsum + 3% bentonite + 87% soil and 10% phosphogypsum + 6% bentonite + 84% soil. X-ray diffraction and scanning electron microscopy were used to analyze the mineralogy, while the hydromechanical performance was evaluated through compaction, hydraulic conductivity, and unconfined compressive tests. Modified free swell tests and modified Atterberg limits were used to test compatibility with NaCl, NaOH and ethanol. A solubilization test was carried out to investigate the presence of inorganic contaminants in the phosphogypsum. The addition of phosphogypsum increased the optimum water content in the compaction curves, did not change the hydraulic conductivity and decreased the unconfined compressive strength of the mixtures. The addition of bentonite increased the optimum water content, reduced the hydraulic conductivity, and increased the unconfined compressive strength. The possibility of dissolution of gypsum (main component of phosphogypsum), the problems that may arise from the interaction with chemical products, and the risk of manganese release in the subsoil lead to the conclusion that phosphogypsum is not suitable to be used in liners. However, soil-bentonite-phosphogypsum mixtures were considered eligible materials to be used in impermeable layers of other geotechnical works.

1. Introduction

Phosphate rocks are an important source of raw materials for the fertilizer industry, which consumes about 71% of these mined rocks in the world (IAEA, 2013). In this process, represented by the idealized chemical reaction presented in Equation 1 (Hull & Burnett 1996), the phosphate rock ($\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$) reacts with sulfuric acid (H_2SO_4) to form two products: the phosphoric acid (H_3PO_4) and the hydrofluoric acid (HF), and one by-product, the phosphogypsum ($\text{CaSO}_4 \cdot n\text{H}_2\text{O}$).



In Equation 1, n may be 0, 0.5, or 2, depending on the industrial process employed. In the wet process, n is equal to 2, resulting in the di-hydrated form of phosphogypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), a material similar to gypsum, except for

the presence of impurities, such as fluorides, phosphates, organic matter, heavy metals (Mascarenha et al. 2018), and radionuclides of uranium and thorium (Nisti et al. 2015).

This process generates about 2.5 tons of phosphogypsum per ton of phosphate rock (Pérez-Moreno et al. 2018) resulting in a global production of 200 million tons of this by-product per year (Saadaoui et al. 2017). In Brazil, 5 million tons of phosphate rock exploited per year (Brazil, 2019) generate about 10 million tons of phosphogypsum. It is estimated that only 15% of the global production of phosphogypsum is reused – mainly in agriculture – while 85% is disposed in stockpiles and water bodies, representing a potential risk of environmental contamination (IAEA, 2013; Rashad, 2017).

To reduce this volume of stocked material, several studies have been carried out aiming at reuse, such as addition in cements, mortars, concretes, and bricks (Rashad, 2017). In geotechnical engineering, phosphogypsum has been used, especially, for road construction (Rezende et al., 2016;

[#]Corresponding author. E-mail address: marciamascarenha@ufg.br

¹Universidade de São Paulo, Escola de Engenharia, São Paulo, SP, Brasil.

²Universidade Federal de Goiás, Escola de Engenharia Civil e Ambiental, Goiânia, GO, Brasil.

Submitted on September 14, 2022; Final Acceptance on May 18, 2023; Discussion open until November 30, 2023.

<https://doi.org/10.28927/SR.2023.009622>



This is an Open Access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Silva et al., 2019; Amrani et al., 2020; Li et al., 2020) and backfilling (Dang et al., 2013; Li et al., 2017; Chen et al., 2017; Jiang et al., 2018). However, there is a lack of studies regarding its use in environmental geotechnical works, such as hydraulic barriers.

A key point to ensure security and efficiency of a geotechnical work is a good characterization of materials, including their hydromechanical and geochemical properties. When using wastes and by-products, it is furthermore necessary to guarantee that these materials will not be a source of environmental contamination. In this context, this paper presents a geoenvironmental characterization of soil mixtures containing phosphogypsum and bentonite in order to analyze their technical feasibility as geomaterials for hydraulic barriers.

2. Materials

The di-hydrated phosphogypsum (P) was collected at a plant located in the state of Goiás (Midwest Brazil) which generates 720,000 tons of this by-product per year, most of which stored in piles (Rezende et al., 2016). Its chemical composition (Table 1) shows a predominance of sulfur oxides (which form sulfates) and calcium oxide. There are also lower levels of iron, titanium and aluminum oxides and phosphate. This material was classified as non-hazardous and non-inert (Rezende et al., 2016) according to Brazilian regulations (ABNT, 2004).

The lateritic soil (S) from Aparecida de Goiânia, Goiás, was collected at a depth of 0.4 m. This soil is mainly composed of quartz, gibbsite, hematite, and kaolinite (Rezende et al., 2016). It is classified as low plasticity silt (ML) according to the Unified Soil Classification System (ASTM, 2017) and as sandy lateritic soil according to the Brazilian Compacted Tropical Miniature Classification System (MCT) (Villibor & Nogami, 2009). Mixtures of this soil with phosphogypsum have already been investigated in previous studies (Rezende et al., 2016; Mascarenha et al., 2018; Ribeiro et al., 2018; Silva et al., 2019).

Since the predominant fraction of the soil is sand (Table 2), sodic bentonite was added to the soil-phosphogypsum mixtures because of its well-known ability to reduce hydraulic

conductivity (Amadi & Eberemu, 2012; Amadi & Osinubi, 2017; De La Morena et al., 2018). The bentonite (B) used in this study was commercially available and produced in north-eastern Brazil.

The mixtures were prepared with 10% phosphogypsum in dry weight, the maximum content that can be added to this lateritic soil without impairing its hydromechanical performance, according to Mascarenha et al. (2018). Contents of 3% and 6% of bentonite in dry weight were added to the mixtures SPB3 and SPB6, respectively. These contents are expected to reduce the hydraulic conductivity coefficients of the mixtures to values close to or lower than 1×10^{-9} m/s (Morandini & Leite, 2012; Ribeiro et al., 2018).

The composition of the mixtures, their Atterberg limits and grain size distribution are presented in Table 2.

3. Methods

3.1. Thermal analysis of phosphogypsum

A preliminary thermal analysis was performed to determine the ideal temperature to measure the moisture content of phosphogypsum. Excessive heat can cause di-hydrated phosphogypsum to lose microstructural water, transforming it into hemi-hydrated phosphogypsum, a material with different properties (Rezende et al., 2016).

Phosphogypsum samples were oven dried until mass constancy at two different temperatures (70 °C and 90 °C), based on previous studies (Rezende et al., 2016). X-ray diffraction tests (XRD) showed that the sample dried at 70 °C was basically composed of gypsite (di-hydrated phosphogypsum) and quartz, while the sample dried at 90 °C contained more than 74% basanite (hemi-hydrated phosphogypsum) and only 8.54% gypsite (Table 3). Hence, 70 °C was the temperature chosen to determine moisture of samples containing phosphogypsum.

Ribeiro et al. (2018) observed that the required temperature to achieve mass constancy for sodium bentonites is 130 °C, while temperatures ranging from 105 °C to 110 °C are recommended to measure the moisture content of soils (ABNT, 2016). Since each material has an ideal temperature for determining the moisture content, the moisture content of the mixtures was obtained by mathematical correlations.

For that, soil and bentonite were moisturized with different water contents and oven dried at temperatures of 70 °C, 110 °C and 130 °C. Linear correlations were then determined, as presented in Figure 1(a) for soil and 1(b) for bentonite.

The moisture of samples dried at 70 °C was corrected according to these correlations and to the bentonite and phosphogypsum contents in each mixture. Although phosphogypsum and bentonite have greater affinity for water molecules than soil, water was assumed to be proportionally distributed among these three materials.

Table 1. Chemical composition of phosphogypsum.

| Oxide | Percentage |
|---|------------|
| Silicon dioxide (SiO ₂) | 1.8 |
| Titanium dioxide (TiO ₂) | 0.2 |
| Aluminum oxide (Al ₂ O ₃) | 0.3 |
| Iron oxide (Fe ₂ O ₃) | 0.5 |
| Calcium oxide (CaO) | 33.6 |
| Phosphorus oxide (P ₂ O ₅) | 0.8 |
| Sulfur oxide (SO ₃) | 42.7 |
| Loss on ignition | 20.1 |

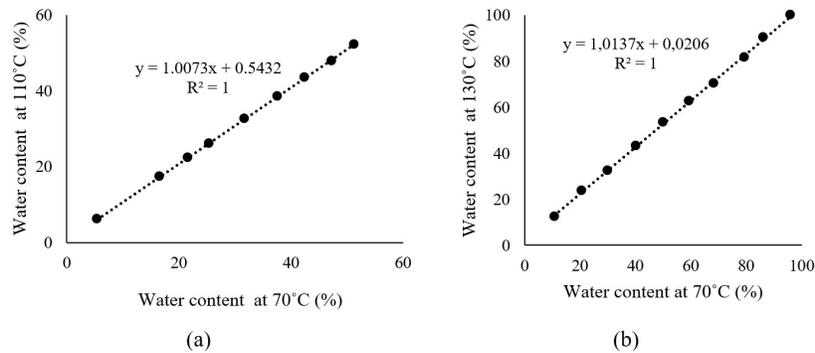


Figure 1. Mathematical correlation: (a) soil; (b) bentonite.

Table 2. Geotechnical characterization of the mixtures of soil, bentonite and phosphogypsum.

| Item | Mixture | | | | | |
|---------------------------------------|---------|-------------|------|------|------|------|
| | S | P | B | SP | SPB3 | SPB6 |
| Soil (%) | 100 | - | - | 90 | 87 | 84 |
| Phosphogypsum (%) | - | 100 | - | 10 | 10 | 10 |
| Bentonite (%) | - | - | 100 | - | 3 | 6 |
| Specific gravity (g/cm ³) | 2.64 | 2.36 | 2.71 | 2.59 | 2.59 | 2.58 |
| Liquid limit (%) | 37 | - | 47 | 36 | 40 | 44 |
| Plastic limit (%) | 27 | - | 48 | 27 | 23 | 24 |
| Plasticity Index (%) | 10 | Non plastic | 422 | 9 | 17 | 20 |
| Grain size distribution ¹ | | | | | | |
| Gravel (%) | 0.1 | 0.0 | 0.0 | 0.1 | 0.1 | 0.1 |
| Sand (%) | 56.6 | 26.6 | 8.0 | 51.6 | 52.5 | 42.0 |
| Silt (%) | 29.2 | 65.4 | 83.0 | 33.9 | 37.8 | 44.8 |
| Clay (%) | 14.0 | 8.0 | 9.0 | 14.4 | 9.6 | 13.1 |

¹Terminology according to ABNT (1995). The percentages of gravel, sand, silt, and clay in all mixtures were obtained from the granulometric distribution curves. Sodium hexametaphosphate was used as a dispersant agent for the sedimentation test.

3.2. Compaction tests

Compaction tests were carried out according to the Brazilian MCT methodology (DNER, 1994; Villibor & Nogami, 2009). Specimens were compacted in a miniature MCV apparatus inside a cylindrical mold of 130 mm height and 50 mm diameter, following procedure A, described by DNER (1994) for the normal energy compaction. In this procedure, the material to be compacted, which must pass through the sieve with a 2.0 mm opening, is distributed in two layers. In each layer, five blows of a 2,270 g hammer are applied, with a falling height of 305 mm. The specimen is considered suitable when its final height (after compaction) is 50±1 mm.

This methodology was chosen to decrease the time necessary to saturate samples for the hydraulic conductivity tests, since the specimens are smaller (≈ 50 x 50 mm) than those obtained by conventional compaction tests.

Compaction curves were not obtained for samples P (100% phosphogypsum) and B (100% bentonite), once the interest of this study was focused on the mixtures with soil.

Table 3. Phosphogypsum mineralogy obtained from XRD analysis.

| Mineral | Percentage (%) | |
|-------------|----------------|-------|
| | 70°C | 90°C |
| Basanite | <DL | 74.08 |
| Anidrite | <DL | 14.79 |
| Gypsite | 93.37 | 8.54 |
| Ettringite | <DL | <DL |
| Quartz | 2.27 | 2.42 |
| Gibbsite | <DL | <DL |
| Hematite | <DL | <DL |
| Portlandite | <DL | <DL |

Note: <DL: value below the detection limit.

3.3. Hydraulic conductivity tests

Hydraulic conductivity tests were performed in rigid wall permeameters, using the same cylinders of the compaction tests. To avoid preferential leakage along the wall (Shackelford et al., 2000; Chapuis, 2012), the specimens

were compacted directly inside the permeameters (with an inner diameter of 50 mm, 25 times greater than the maximum diameter of soil particles, i.e., 2 mm). Similar approaches were used by Razakamantsoa & Djeran-Maigre (2016) and De Camillis et al. (2016).

Specimens were compacted at the optimum water content (w_{op}) and maximum apparent dry weight (γ_{dmax}), presented in Table 4, and were saturated by backpressure. A hydraulic gradient of 10 m/m (≈ 0.5 m of water column) was applied. The hydraulic conductivities were calculated according to ASTM D5856–15 (ASTM, 2015), as the average value of four measurements that showed a pattern of stability.

3.4. Unconfined compressive tests

Specimens with 5 cm diameter and 10 cm height were compacted at w_{op} and γ_{dmax} (Table 4) following the procedures described in Section 3.2, doubling the mass of material and the number of layers. Compacted specimens were wrapped in plastic film and kept in a closed box for 28 days, the ideal curing time verified in previous studies with phosphogypsum-lateritic soil mixtures (Rezende et al., 2016; Silva et al., 2019). The failure process followed the prescriptions of ABNT (1992) and ASTM (2016).

3.5. Compatibility tests

The term compatibility refers to the ability of a material to maintain its properties after contact with chemicals (Shackelford, 1994; Farnezi & Leite, 2007). In this study, compatibility was analyzed through modified free swell tests and modified Atterberg Limits. In both cases, the following solutions were used: sodium chloride (NaCl, 0.125 mol/L), sodium hydroxide (NaOH, 0.001 mol/L) and ethanol (1 mol/L). Similar solutions were used by Morandini & Leite (2012) to simulate saline, alkaline and organic miscible liquids that might be in contact with the mixtures in geotechnical works.

The modified free swell tests were performed as suggested by Sivapullai et al. (1987): 10 g in dry mass of the material, passing through a sieve of an opening size of 0.42 mm, are poured into a 100 cm³ graduated jar, which is then filled with the liquid of interest. The initial volume of the solids and the volume after 24 hours are registered, and the swelling potential is calculated by (2):

$$SI = (V - V_i) / V_i \quad (2)$$

Where SI is the modified free swelling index, V is the volume after 24 hours swelling and V_i the initial volume of solids.

The modified Atterberg limits were determined following the standard method (ASTM, 2000) with water and the aforementioned solutions. The effect of the solutions on the plastic properties of the mixtures was analyzed using the plastic incompatibility index (PIC), as proposed by Farnezi & Leite (2007):

$$PIC = ((PI_s - PI_w) / PI_w) \times 100 \quad (3)$$

Where PI_s is the plasticity index with the solution and PI_w is the plasticity index with water.

3.6. Microstructural analysis

Scanning electron microscopy (SEM) was used to analyze possible changes in the microstructure of the specimens used in the hydraulic conductivity and unconfined compressive tests. The samples were air dried and covered with a thin layer of gold (via sputtering). Images were obtained using a high vacuum technique in a scanning electron microscope (model Jeol 6610), in the Multiuser laboratory of high-resolution microscopy (LabMic) of Federal University of Goias.

3.7. Solubilization tests

Due to the possible presence of impurities in the phosphogypsum, such as heavy metals, solubilization tests were performed to analyze the risks of environmental contamination.

For these tests, solubilized extracts were obtained from the samples S and SP, following the Brazilian standard NBR 10006 (ABNT, 2004): a suspension of 250 g in dry weight and 1000 mL of distilled water was prepared and kept at rest for seven days. The suspension was mixed by a rotational mixer for five minutes before and after the rest period, and then the solution was filtered using a 0.45 μ m pore size membrane.

The solubilized extract was analyzed to measure the concentration of inorganic chemical species, and the values were compared with reference values available in Brazilian environmental standards (CONAMA, 2008).

4. Results and discussion

4.1. Compaction tests

Compaction curves are presented in Figure 2. Values of γ_{dmax} , w_{op} and void ratio (e) are shown in Table 4.

Table 4. γ_{dmax} , w_{op} , and e of samples S, SP, SPB3 and SPB6.

| Sample | γ_{dmax} (kN/m ³) | w_{op} (%) | e |
|--------|--------------------------------------|--------------|------|
| S | 14.7 | 25.3 | 0.79 |
| SP | 14.6 | 26.1 | 0.77 |
| SPB3 | 14.6 | 26.3 | 0.77 |
| SPB6 | 14.7 | 26.1 | 0.76 |

The w_{op} of the mixtures was higher than that of the soil because the addition of phosphogypsum and bentonite increased the percentage of fines (Table 2) resulting in a greater specific surface, so that more water is needed in the hydration process (Eberemu et al., 2013; Eberemu, 2013; Osinubi et al., 2015).

Addition of phosphogypsum has been reported to cause flocculation in soils, due to the replacement of adsorbed ions by calcium, creating a more porous structure and, therefore, reducing γ_{dmax} (Rezende et al., 2016; Mascarenha et al., 2018). In this study, flocculation does not seem to be an important phenomenon, since γ_{dmax} and void ratios of soil and mixtures containing phosphogypsum are alike. The low percentage of phosphogypsum in the mixtures (10%) was probably not enough to cause an expressive flocculation process.

4.2. Hydraulic conductivity tests

The hydraulic conductivity of the samples, at a temperature of 20 °C (k_{20}), are presented in Table 5. A ratio (KRC) between the k_{20} of soil and the k_{20} of the mixtures was calculated, as proposed by Morandini & Leite (2015).

Sample SP presented a KRC of 0.97, which indicates that the addition of phosphogypsum practically did not affect the hydraulic conductivity of the soil. On the other hand, for a bentonite content of 3% (SPB3) k_{20} decreased by approximately one order of magnitude (KRC=14.5). Morandini & Leite (2015) also observed similar results for hydraulic conductivity tests carried out with Brazilian lateritic-bentonite soil mixtures in flexible wall permeameters: for an effective confining stress of 80 kPa, an addition of 3% bentonite produced values of KCR ranging from 11.4 to 18.9, while a 6% addition produced KCR values ranging from 65.3 to 76.4.

Bentonite is mainly composed of montmorillonite. During the hydration process, montmorillonite has a great potential to adsorb water molecules and hydrated ions, due to its large specific surface and negative net charge (Shackelford et al. 2000). These water molecules and cations are essentially immobile and occupy most of the pores, forming irregular flow channels. Thus, although the void ratio is similar for all samples, the pores of samples containing bentonite are partially filled by a gel formed around soil particles (Amadi, 2013).

A comparison between the porous aspects of the soil and a mixture of soil with bentonite is provided in Figures 3(a) and 3(b). A more detailed explanation of the swelling and hydration processes of bentonites can be found in Liu (2013), Yu et al. (2018), and Jadda & Bag (2020).

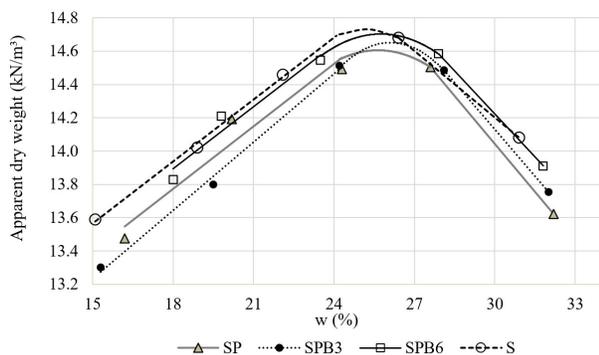


Figure 2. Compaction curves of samples S, SP, SPB3, and SPB6.

Table 5. Hydraulic conductivity at 20°C.

| Sample | k_{20} (m/s) | KRC |
|--------|-----------------------|------|
| S | 3.4×10^{-8} | 1.0 |
| SP | 3.5×10^{-8} | 0.97 |
| SPB3 | 2.3×10^{-9} | 14.5 |
| SPB6 | 4.7×10^{-10} | 72.3 |

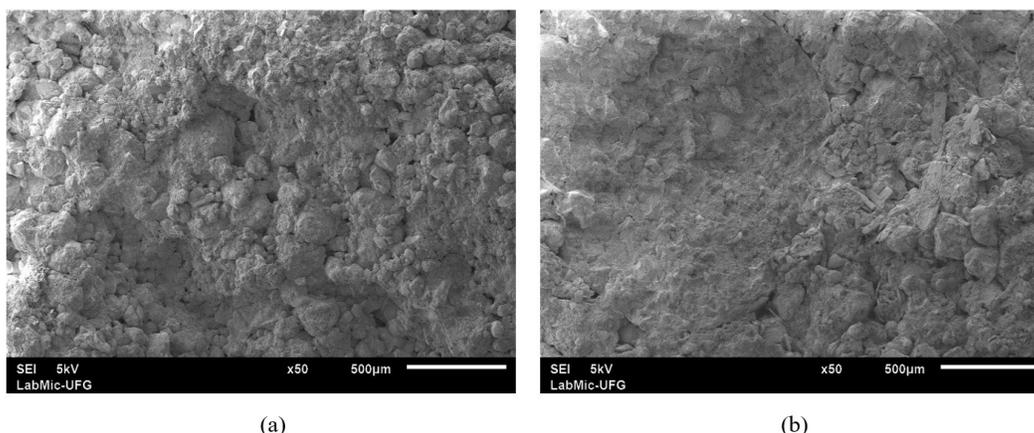


Figure 3. Comparison between the porous aspects of the soil (a) and a mixture of the soil with bentonite (b).

4.3. Unconfined compressive tests

The results of the unconfined compressive tests are presented in Table 6.

The addition of phosphogypsum decreased the unconfined compressive strength (UCS) of the compacted soil, a result expected for the addition of a non-cohesive material. Moreover, di-hydrated phosphogypsum is mainly composed of gypsite, a mineral that has a tabular structure, with particles in the form of large and thin plates (Mascarenha et al., 2018) (Figure 4). This geometry favors the breakage of phosphogypsum particles, further decreasing the UCS. Rezende et al. (2016) also reported a decrease in UCS with the addition of phosphogypsum to soil mixtures such as those analyzed in this study.

Sample SPB6 showed higher UCS than sample SPB3, which in turn was higher than SP, indicating that the addition of bentonite improved the UCS of the mixtures. During the process of adsorption of water molecules and hydrated ions, bentonite promotes an attraction between soil particles, increasing the contact area (Ahmed, 2015), plasticity and cohesion (Malizia & Shakoor, 2018), which may explain the increase in UCS values.

Neither phosphogypsum nor bentonite altered the strain at failure, which was around 3% for the soil and for the mixtures. Mascarenha et al. (2018) analyzed the compressibility (in one-dimensional consolidation tests) of a mixture composed of 90% lateritic soil and 10% phosphogypsum, with the same

Table 6. Results of unconfined compressive tests.

| Sample | UCS (kPa) | Strain at failure (%) |
|--------|-----------|-----------------------|
| S | 304 | 2.8 |
| SP | 207 | 2.8 |
| SPB3 | 272 | 2.9 |
| SPB6 | 362 | 2.9 |

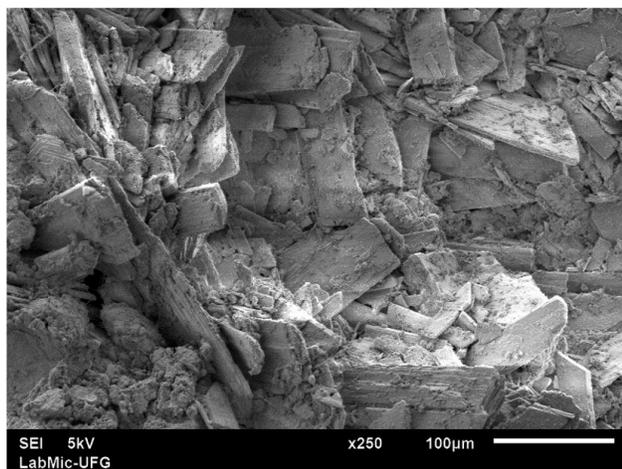


Figure 4. Phosphogypsum plates in sample SP.

materials used in this study, and reported a strain of about 2% for an effective vertical stress of 200 kPa.

4.4. Compatibility tests

The results of the modified free swell tests are presented in Figure 5. For comparison, the values of SI obtained in the tests carried out with NaCl, NaOH and ethanol (SI_s) were divided by the values of SI with distilled water (SI_w). Values higher than one mean that swelling was higher in contact with solutions than with water.

Figure 5 shows that the swelling potential of the mixtures was mainly affected by the solution containing NaOH. This alkaline medium (pH 11) favors the development of negative surface charges on the minerals present in the mixtures. Because of electrostatic repulsion, particles tend to move as far away from each other as possible, increasing swelling.

Liquids with dielectric constants lower than water can also affect the swelling of minerals, shrinking their electrical double layer (Shackelford et al., 2000). In this case, the mineral will present less swelling than in water, as observed in tests carried out with ethanol. No significant variations were observed in the tests performed with NaCl.

The influence of these solutions on the plastic properties of the mixtures can be seen in Figure 6, where the results of

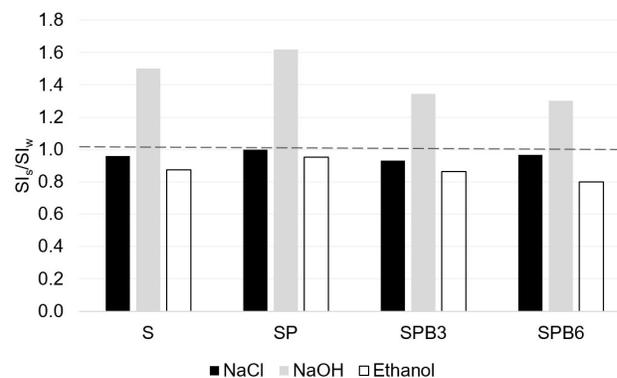


Figure 5. Modified free swell indexes.

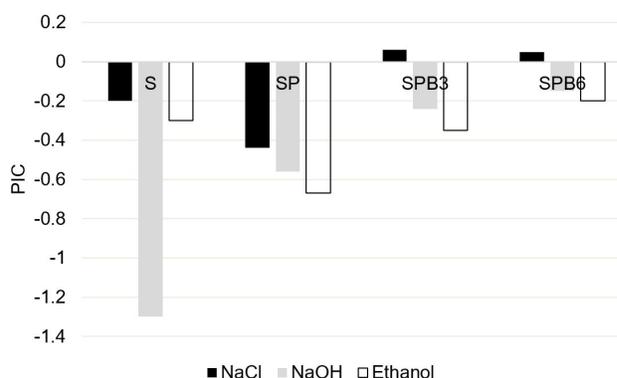


Figure 6. Plastic Incompatibility Indexes (PIC).

the modified Atterberg limits in terms of plastic incompatibility indexes (*PIC*) are presented. Negative values indicate that the solutions used in the tests decreased the plasticity of the mixtures, except for samples SPB3 and SPB6 in contact with NaCl, which showed a small increase in plasticity.

Although it is not possible to establish a direct comparison between the results presented in Figure 5 and 6, they clearly show that the chemical composition of the liquids can affect the geotechnical properties of the analyzed materials. In practical terms, it means the possibility of unexpected geotechnical problems, including swelling, heaving, shrinkage and collapse, for example.

4.5. Solubilization tests

The results of the chemical analysis of the inorganic groundwater contamination parameters are shown in Table 7.

The concentrations of iron and manganese in sample SP exceed the limits of the Brazilian technical standard for inert solid waste (ABNT, 2004), 0.3 mg/L and 0.1 mg/L, respectively. However, these metals are not considered for hazardousness, and SP can be classified as a non-inert and

non-hazardous material. These concentrations also exceeded acceptable limits prescribed by Brazilian regulations for water use (CONAMA, 2008) and United States Environmental Protection Agency prescriptions for drinking water (USEPA, 2009).

The excess of iron can be attributed to the soil, where this metal is abundant in form of oxides and hydroxides, like goethite and hematite, for example (Villibor & Nogami, 2009; Osinubi et al., 2015). Since sample S did not present excess of manganese, this metal can be related to phosphogypsum. These patterns were also observed by Mascarenha et al. (2018) in chemical analysis of water percolated through compacted specimens of soil-phosphogypsum mixtures, from the same sources and in the same proportions as those used in this study.

The emission of radionuclides by phosphogypsum is another environmental concern, but many phosphogypsum samples collected in different plants in Brazil were classified as non-hazardous from a radiological point of view (Nisti et al. 2015; Rezende et al., 2016; Campos et al., 2017; Silva et al., 2019). In addition, Brazilian legislation requires the measurement of the emission of radionuclides

Table 7. Chemical analysis for inorganic parameters.

| Parameter | Limit for human consumption (mg/L) ¹ | Results (mg/L) | | |
|------------------------|---|----------------|---------|---------|
| | | Background | S | SP |
| Antimony | 0.005 | <0.005 | 0.005 | <0.005 |
| Arsenic | 0.010 | <0.005 | 0.010 | 0.010 |
| Barium | 0.700 | <0.003 | 0.096 | 0.116 |
| Beryllium | 0.004 | <0.0004 | <0.0004 | <0.0004 |
| Boron | 0.500 | 0.0640 | 0.0700 | 0.0850 |
| Cadmium | 0.005 | <0.001 | <0.001 | <0.001 |
| Lead | 0.010 | <0.005 | 0.0100 | 0.0100 |
| Cyanide | 0.070 | <0.001 | <0.001 | <0.001 |
| Cobalt | - | <0.003 | <0.003 | <0.003 |
| Copper | 2.000 | 0.0920 | 0.0940 | 0.1120 |
| Chromium (III) | 0.050 | <0.100 | <0.100 | <0.100 |
| Chromium (IV) | 0.050 | <0.100 | <0.100 | <0.100 |
| Lithium | - | 0.0100 | 0.0100 | 0.0110 |
| Manganese | 0.100 | 0.0110 | 0.0230 | 1.1140 |
| Mercury | 0.001 | <0.0002 | <0.0002 | <0.0002 |
| Molybdenum | 0.070 | <0.0070 | <0.0070 | <0.0070 |
| Nickel | 0.020 | <0.0070 | <0.0070 | <0.0070 |
| Silver | 0.100 | <0.0050 | <0.0050 | 0.0070 |
| Selenium | 0.010 | <0.0100 | <0.0100 | <0.0100 |
| Uranium | 0.015 | <0.0100 | <0.0100 | <0.0100 |
| Vanadium | 0.050 | <0.0300 | <0.0300 | <0.0300 |
| Zinc | 5.000 | <0.0200 | 0.0400 | 0.0900 |
| Aluminum | 0.200 | <0.0200 | <0.0200 | <0.0200 |
| Chlorides | 250.0 | 10.800 | 30.100 | 32.500 |
| Iron | 0.300 | <0.0100 | 4.920 | 1.380 |
| Fluorides | 1.500 | <0.100 | <0.100 | <0.100 |
| Total dissolved solids | 1000.0 | 3.000 | 31.000 | 954.000 |

¹ After CONAMA (2008).

of Ra²²⁶ and Ra²²⁸ and prohibits samples containing more than 1,000 Bq/kg of these radionuclides from leaving the plant for commercial purposes (CNEN, 2007). Therefore, the risk of radiological contamination is very low.

5. Conclusion

This study was motivated by the attempt to find a new alternative to reuse phosphogypsum, i.e., as a soil additive in geotechnical works. The chemical and mineralogical analysis demonstrated that this material is mainly composed of gypsite, a di-hydrated calcium sulphate whose crystals have the shape of tabular plates.

The addition of phosphogypsum to the soil increased the optimum water content at standard compaction energy, but almost did not affect the maximum apparent dry weight and the void ratio of the compacted specimens. This was reflected in the hydraulic conductivity tests by the similar hydraulic conductivities obtained for the soil and for the sample containing soil and phosphogypsum. Conversely, a reduction in the unconfined compressive strength was observed and attributed to this by-product being non cohesive and to its microstructure characteristics.

The samples containing phosphogypsum and bentonite presented a better hydromechanical performance than that composed only by soil. The unconfined compressive strength of about 300 kPa is a value acceptable for several small and medium-sized geotechnical works, while hydraulic conductivities in the range of 10^{-9} – 10^{-10} m/s meet the requirements of materials used in hydraulic barriers of sanitary landfills.

Regarding environmental aspects, there are some problems in the reutilization of this by-product: possibility of dissolution of gypsite, additional problems that may arise from the interaction with chemical products, and the risk of manganese release in the subsoil.

Although these aspects lead to the conclusion that phosphogypsum is not a suitable material to be used in hydraulic barriers, the soil-bentonite-phosphogypsum mixtures could be considered eligible materials for impermeable layers in geotechnical works, provided that the surface loads are greater than the swelling pressure of these mixtures and the environmental impact of manganese release in the subsoil is evaluated.

Acknowledgements

The authors are thankful for the funds provided by Brazilian Research Agencies (CNPq, process 408756/2016-0 and CAPES, Finance code 001) and CMOC International Brazil to support this study, as well as the partner laboratories in the Federal University of Goiás and in the University of Brasília.

Declaration of interest

The authors have no conflicts of interest to declare. All co-authors have observed and affirmed the contents of the paper and there is no financial interest to report.

Authors' contributions

Yago Isaias da Silva Borges: writing – original draft, methodology, investigation, formal analysis. Bismarck Chaussê de Oliveira: methodology, investigation, formal analysis, writing – review & editing. Maria Eugênia Gimenez Boscov: formal analysis, writing – review & editing, Márcia Maria dos Anjos Mascarenha: methodology, formal analysis, writing – review & editing, supervision, funding acquisition, project administration.

Data availability

The datasets of this current study are available from the corresponding author on request.

List of symbols

| | |
|----------------------|---|
| e | void ratio |
| k_{20} | hydraulic conductivity coefficient at 20 °C |
| n | number of water molecule |
| B | bentonite |
| $Ca_{10}F_2(PO_4)_6$ | phosphate rock |
| $CaSO_4 \cdot nH_2O$ | phosphogypsum |
| CL | low plasticity clay |
| HF | hydrofluoric acid |
| H_2O | water |
| H_2SO_4 | sulfuric acid |
| H_3PO_4 | phosphoric acid |
| KRC | ratio between the k of natural soil and the k of the mixtures |
| LabMic | Multiuser laboratory of high-resolution microscopy |
| MCT | Brazilian Miniature Compacted Tropical |
| NaCl | sodium chloride |
| NaOH | sodium hydroxide |
| PIC | plastic incompatibility indexes |
| PI_s | plasticity index with the solution |
| PI_w | plasticity index with water. |
| S | lateritic soil |
| SI | modified free swelling index |
| SP | soil - phosphogypsum |
| SEM | Scanning electron microscopy |
| SI | modified free swelling index |
| UCS | Unconfined compressive strength |
| V | volume after swelling |
| V_s | volume of solids |
| XRD | X-ray diffraction tests |
| w_{op} | optimum water content |
| γ_{dmax} | maximum apparent dry weight |

References

- ABNT NBR 1004 (2004). *Solid wastes Classification*. ABNT - Associação Brasileira de Normas Técnicas, Rio de Janeiro, RJ. (in Portuguese).
- ABNT NBR 6457 (2016) *Soil samples – Preparation for characterization and compaction tests*. ABNT - Associação Brasileira de Normas Técnicas, Rio de Janeiro, RJ. (in Portuguese).
- ABNT NBR 6502 (1995). *Rocks and soils. Terminology*. ABNT - Associação Brasileira de Normas Técnicas, Rio de Janeiro, RJ. (in Portuguese).
- ABNT NBR12770 (1992). *Cohesive soil – Determination of unconfined compression strength*. ABNT - Associação Brasileira de Normas Técnicas, Rio de Janeiro, RJ. (in Portuguese).
- Ahmed, A. (2015). Compressive strength and microstructure of soft clay soil stabilized with recycled basanite. *Applied Clay Science*, 104, 27-35. <http://dx.doi.org/10.1016/j.clay.2014.11.031>.
- Amadi, A.A. (2013). Swelling characteristics of compacted lateritic soil-bentonite mixtures subjected to municipal waste leachate contamination. *Environmental Earth Sciences*, 70, 2437-2442.
- Amadi, A.A., & Eberemu, A.O. (2012). Delineation of compaction criteria for acceptable hydraulic conductivity of lateritic soil-bentonite mixtures designed as landfill liners. *Environmental Earth Sciences*, 67, 999-1006.
- Amadi, A.A., & Osinubi, K.J. (2017). Transport parameters of lead (Pb) ions migrating through saturated lateritic soil-bentonite column. *International Journal of Geotechnical Engineering*, 12(3), 302-308.
- Amrani, M., Taha, Y., Kchikach, A., Benzaazoua, M., & Hakkou, R. (2020). Phosphogypsum recycling: new horizons for a more sustainable road material application. *Journal of Building Engineering*, 30, 101267.
- ASTM D4318 – 00. (2000) Standard test method for liquid limit, plastic limit and plasticity index of soils. ASTM International, West Conshohocken, USA.
- ASTM D2166 – 16. (2016) *Standard test method for unconfined compressive strength for cohesive soils*. ASTM International, West Conshohocken, USA.
- ASTM D5856 – 15. (2015) *Standard test method for measurement of hydraulic conductivity of porous material using a rigid-wall, compaction-mold permeameter*. ASTM International, West Conshohocken, USA.
- ASTM D2487. (2017). *Standard Practice for Classification of Soils for Engineering Purposes (Unified Soil Classification System)*. ASTM International, West Conshohocken, USA.
- Brazil. (2019). *Mineral sector bulletin*. Ministry of Mines and Energy. (2nd issue, 28 p.).
- Campos, M.P., Costa, L.J.P., & Nisti, M.B. (2017). Phosphogypsum recycling in the building material industry: assessment of the radon exhalation. *Journal of Environmental Radioactivity*, 144, 120-126. <http://dx.doi.org/10.1016/j.jenvrad.2017.04.002>.
- Chapuis, R.P. (2012). Predicting the hydraulic saturated conductivity of soils: a review. *Bulletin of Engineering Geology and the Environment*, 71, 401-434.
- Chen, Q., Zhang, Q., Fourie, A., & Xin, C. (2017). Utilization of phosphogypsum and phosphate tailings for cemented paste backfill. *Journal of Environmental Management*, 201, 19-27.
- Comissão Nacional de Energia Nuclear – CNEN. (2007). Portaria DRS N. 9 de 28 de maio de 2013. *Diário Oficial [da] República Federativa do Brasil*. (In Portuguese).
- Conselho Nacional do Meio Ambiente – CONAMA. (2008). Resolução 397 de 3 de Abril de 2008. *Diário Oficial [da] República Federativa do Brasil*. (In Portuguese).
- Dang, W.G., Liu, Z., He, X., & Liu, Q. (2013). Ixture ratio of phosphogypsum in backfilling. *Mining Technology*, 122(1), 1-7.
- De Camillis, M., Di Emidio, G., Bezuijen, A., & Verástegui-Flores, R.D. (2016). Hydraulic conductivity and swelling ability of a polymer modified bentonite subjected to wet-dry cycles in seawater. *Geotextiles and Geomembranes*, 44, 739-747.
- De La Morena, G., Asensio, L., & Navarro, V. (2018). Intra-aggregate water content and void ratio model for MX-80 bentonites. *Engineering Geology*, 246, 131-138. <http://dx.doi.org/10.1016/j.enggeo.2018.09.028>.
- Departamento Nacional de Estradas de Rodagem – DNER. (1994). *ME-228: Soils, compaction in miniature apparatus*. Departamento Nacional de Estradas de Rodagem. (In Portuguese).
- Eberemu, A.O. (2013). Evaluation of bagasse ash treated lateritic soil as potential barrier material in waste containment application. *Acta Geotechnica*, 8, 407-421.
- Eberemu, A.O., Amadi, A.A., & Osinubi, K.J. (2013). The use of compacted tropical treated with rice husk as a suitable hydraulic barrier material in waste containment applications. *Waste and Biomass Valorization*, 4, 309-323.
- Farnezi, M.K., & Leite, A.L. (2007). Lateritic soil and bentonite mixtures assessment for liner usage purpose. *Soil and Rocks*, 30(2), 103-112.
- Hull, C.D., & Burnett, W.C. (1996). Radiochemistry of Florida phosphogypsum. *Journal of Environmental Radioactivity*, 32(3), 213-238.
- International Atomic Energy Agency – IAEA. (2013). Radiation protect and management of norm residues in the phosphate industry. In International Atomic Energy Agency (Ed.), *Safety Reports Series*. IAEA. (Vol. 78).
- Jadda, K., & Bag, R. (2020). Variation of swelling pressure, consolidation characteristics and hydraulic conductivity of two Indian bentonites due to electrolyte concentration. *Engineering Geology*, 272(105637), 1-14.
- Jiang, G., Wu, A., Wang, Y., & Lan, W. (2018). Low cost and high efficiency utilization of hemihydrate phosphogypsum:

- used as binder to prepare filling material. *Construction & Building Materials*, 167, 263-270.
- Li, B., Sha, W., & Zhen, Y. (2020). An effective recycling direction of water-based drilling cuttings and phosphogypsum co-processing in road cushion layer. *Environmental Sciences and Pollution Resources*, 27, 17420-17424.
- Li, X., Du, J., Gao, L., He, S., Gan, L., Sun, C., & Shi, Y. (2017). Immobilization of phosphogypsum for cemented paste backfill and its environmental effects. *Journal of Cleaner Production*, 156, 137-146.
- Liu, L. (2013). Prediction of swelling process in different types of bentonites in dilute solutions. *Colloids and Surfaces. A, Physicochemical and Engineering Aspects*, 434, 303-318.
- Malizia, J.P., & Shakoor, A. (2018). Effect of water content and density on strength and deformation behavior of clay soils. *Engineering Geology*, 244, 125-131. <http://dx.doi.org/10.1016/j.enggeo.2018.07.028>.
- Mascarenha, M.M.A., Cordão Neto, M.P., Matos, T.H.C., Chagas, J.V.R., & Rezende, L.R. (2018). Effects of the addition of phosphogypsum on the characterization and mechanical behavior of lateritic clay. *Soil and Rocks*, 4, 157-170.
- Morandini, T.L.C., & Leite, A.L. (2012). Characterization, hydraulic conductivity and compatibility of mixtures of tropical soil and bentonite mixtures for barrier usage purpose. *Soils and Rocks*, 35(3), 267-278.
- Morandini, T.L.C., & Leite, A.L. (2015). Characterization and hydraulic conductivity of tropical soils and bentonite mixtures for CCL purposes. *Engineering Geology*, 196, 251-267. <http://dx.doi.org/10.1016/j.enggeo.2015.07.011>.
- Nisti, M.B., Saueia, C.R., Malheiro, R.H., Groppo, G.H., & Mazzilli, B.P. (2015). Lixiviation of natural radionuclides and heavy metals in tropical soils amended with phosphogypsum. *Journal of Environmental Radioactivity*, 144, 120-126. <http://dx.doi.org/10.1016/j.jenvrad.2015.03.013>.
- Osinubi, K.J., Moses, G., & Liman, A.S. (2015). The influence of compactive effort on compacted lateritic soil treated with cement kiln dust as hydraulic barrier material. *Journal of Geotechnical Geological Engineering*, 33, 523-535.
- Pérez-Moreno, S.M., Gázquez, M.J., Pérez-Lopez, R., Vioque, I., & Bolívar, J.P. (2018). Assessment of natural radionuclides mobility in a phosphogypsum disposal area. *Chemosphere*, 211, 775-783.
- Rashad, A.M. (2017). Phosphogypsum as a construction material. *Journal of Cleaner Production*, 166, 732-743. <http://dx.doi.org/10.1016/j.jclepro.2017.08.049>.
- Razakamanantsoa, A.R., & Djeran-Maigre, I. (2016). Long term chemo-hydro-mechanical behavior of compacted soil bentonite polymer complex submitted to synthetic leachate. *Waste Management*, 53, 92-104.
- Rezende, L.R., Curado, T.S., Silva, M.V., Mascarenha, M.M., Metogo, D.A.N., Cordão Neto, M.P., & Bernucci, L.L.B. (2016). Laboratory study of phosphogypsum, stabilizers, and tropical soil mixtures. *Journal of Materials in Civil Engineering*, 29(1), 1-16.
- Ribeiro, M.E.S., Mascarenha, M.M.A., & Santos, T.L. (2018). Estudo de viabilidade técnica do fosfogesso hemidratado para aplicação em sistemas de cobertura de aterros sanitários. *Revista Eletrônica de Engenharia Civil*, 14(2), 263-277. <http://dx.doi.org/10.5216/reec.v14i2.51458>. [In Portuguese]
- Saadaoui, E., Ghazel, N., Romdhane, C.B., & Massoudi, N. (2017). Phosphogypsum: potential uses and problems - a review. *International Journal of Environmental Studies*, 74(4): 558-567.
- Shackelford, C.D. (1994). Waste-soil interactions that alter hydraulic conductivity hydraulic conductivity and waste contaminant transport in soil. ASTM International.
- Shackelford, C.D., Benson, C.H., Katsumi, T., Edil, T.B., & Lin, L. (2000). Evaluating the hydraulic conductivity of GCLs permeated with non-standard liquids. *Geotextiles and Geomembranes*, 18, 133-161.
- Silva, M.V., Rezende, L.R., Mascarenha, M.M.A., & Oliveira, R.B. (2019). Phosphogypsum, tropical soil and cement for asphalt pavements under wet and dry environmental conditions. *Resources, Conservation and Recycling*, 144, 123-136. <http://dx.doi.org/10.1016/j.resconrec.2019.01.029>.
- Sivapullaih, P.V., Sitharam, T.G., & Rao, K.S.S. (1987). Modified free swell index for clays. *Geotechnical Testing Journal*, 10(2), 80-85.
- United States Environmental Protection Agency – USEPA. (2009). *National primary drinking water regulation*. USEPA.
- Villibor, D.F., & Nogami, J.S. (2009) *Pavimentos econômicos: tecnologia e uso dos solos finos lateríticos*. Arte e Ciencia. (In Portuguese).
- Yu, H., Sun, D., & Gao, Y. (2018). Effect of NaCl on swelling characteristics of bentonites with different diffuse double layers. *Applied Magnetic Resonance*, 49, 725-737.