Effects of the Addition of Dihydrate Phosphogypsum on the Characterization and Mechanical Behavior of Lateritic Clay

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Abstract. This paper presents the effect of adding dihydrate phosphogypsum, which is a byproduct of the production of phosphate fertilizers, on the mechanical behaviour of a lateritic clay typical of Brazil’s Midwest region. Because of the distinction of the mechanical behaviours of both materials, laboratory experiments were conducted with soil, phosphogypsum and mixtures with 10%, 20% and 50% phosphogypsum content. One-dimensional consolidation, direct shear and scanning electron microscopy (SEM) tests were conducted on optimally compacted specimens to show the effect of the loading time on the mechanical parameters of the materials. Water percolated through the materials was chemically analysed to verify the groundwater level contamination potential due to cation lixiviation in phosphogypsum. The results show that the addition of phosphogypsum to the soil increases the compressibility without significant effect on the strength parameters, and the broken phosphogypsum particles make the mixture deformability depend on the loading time. With this study, one can conclude that the dihydrate phosphogypsum content in geotechnical works must be maintained below 20%, since higher ratios negatively affect the soil mechanical behaviour and ground water contamination potential. This study also presents an option to reuse and dispose of the most commonly produced phosphogypsum type in Brazil.

Keywords: deformation, environment, grain breakage, loading time, reuse, strength parameters.

1. Introduction

The main output of the industries in Catalão, which is a city in the state of Goiás (GO), Brazil, is phosphate fertilizer with local phosphate rocks as the raw material. One of the production outputs is a solid industrial byproduct known as phosphogypsum. Its chemical composition is identical to natural gypsum (CaSO₄.nH₂O) except for impurities such as fluorides, phosphates, organic matter, aluminium and iron minerals, toxic heavy metals and radioactive elements.

According to Hull & Burnett (1996) and Lapido-Loureiro & Nascimento (2009), the chemical process to obtain phosphogypsum as a byproduct is as follows:

\[
\text{Ca}_{10}F_2(PO_4)_6 + 10H_2SO_4 + 10nH_2O \rightarrow 10CaSO_4 nH_2O + 6H_3PO_4 + 2HF \tag{1}
\]

where \(\text{Ca}_{10}F_2(PO_4)_6\) is fluorapatite, \(H_2SO_4\) is sulfuric acid, \(H_2O\) is water, \(CaSO_4 nH_2O\) is phosphogypsum, \(H_3PO_4\) is phosphoric acid, and \(HF\) is hydrofluoric acid.

In Eq. 1, the coefficient \(n\) is related to the temperature during the process to obtain phosphoric acid, which can have the values of 0 (null) for anhydrous phosphogypsum (anhydrite), 1/2 for hemihydrate phosphogypsum (HH) and 2 for dihydrate phosphogypsum (DH). HH phosphogypsum is also known as bassanite, and DH is known as gypsum. The dihydrate process is used by the industries in Catalão and is the most common process in Brazil. It has low production costs because of the low temperature required in the reaction between phosphatic rock and sulfuric acid. However, the phosphogypsum produced in this process has more impurities such as residual sulfuric acid, phosphoric acid and toxic heavy metals, which may contaminate the environment (Canut, 2006).

For every ton of phosphoric acid produced across the industries in Goiás, approximately five tons of dihydrate phosphogypsum are also produced, which amounts to 60 thousand tons of this byproduct monthly and requires large areas for storage (Chagas, 2014). According to the NBR 10004 (ABNT, 2004), this phosphogypsum is classified as Class II A: not dangerous and not inert (Mesquita, 2007).

According to Jacomino et al. (2009), when analysing dihydrate phosphogypsum collected from a phosphoric acid industry in the city of Uberaba (MG), Brazil, the concentrations of \(^{226}\text{Ra}\) (251 Bq kg\(^{-1}\)) and \(^{228}\text{Ra}\) (226 Bq kg\(^{-1}\)) in the phosphogypsum samples were greater than the limits advised by the 402-R-98-008 document published in 1988 by the Environmental Protection Agency. The concentrations of \(^{210}\text{Pb}\) and \(^{210}\text{Po}\) were similar to those obtained for...
$^{226}\text{Ra}$ and $^{228}\text{Ra}$, whereas the concentration of $^{234}\text{U}$ was less than that obtained for a local clay soil (iatoisol). The authors also noted that the concentrations of toxic heavy metals and metalloids were less than the limits established by Resolution 375 (2006) from the Brazilian National Environmental Council (CONAMA).

Thus, Campos et al. (2017) analysed the $^{226}\text{Ra}$ emission rate of eighteen samples of plates and fifteen samples of brick manufactured with phosphogypsum produced in the cities of Cajati (SP), Cubatão (SP) and Uberaba (MG). The authors concluded that the use of these building materials for house construction posed no health risk because of the exhalation of radon.

Mesquita (2007) showed results from radiometry evaluations conducted both in the industrial plant and in specimens produced in the laboratory with the Goiás dihydrate phosphogypsum. The average exposition rate obtained at the plant was 0.09 $\mu$R/h or 2.32 $\times$ 10$^{-10}$ C/kg/h, whereas in the specimens compacted in the laboratory, the rate was 0.00 $\mu$R/h. Thus, there is no radioactive problem when this material is used in on-site pavement construction.

Many studies were conducted on the reuse of phosphogypsum in the cement industry (Altun & Sert 2004; Shen et al., 2012), brick production (Yang et al., 2009), concrete production (Smadi et al., 1999), soil stabilization (Degirmenci et al., 2007; James & Pandian, 2014), pavement layers (Parreira et al., 2003; Oliveira, 2005; Mesquita, 2007; Rufo 2009; Metogo, 2011; Kumar et al., 2014; Rezende et al., 2016) and asphalt mixture (Cuadrí et al., 2014). Altun & Sert (2004) used weathered phosphogypsum. Yang et al. (2009), Smadi et al. (1999) and Rezende et al. (2016) used HH phosphogypsum. Degirmenci et al. (2007), Cuadrí et al. (2014), James & Pandian (2014) and Kumar et al. (2014) did not specify the phosphogypsum type, and other studies used DH phosphogypsum. Generally, these studies proved the technical and environmental viability of reusing this byproduct in its different types.

The studies performed by Degirmenci et al. (2007), James & Pandian (2014), Mesquita (2007), Rufo (2009), Metogo (2011) and Rezende et al. (2016) discuss the behaviour changes that occur when phosphogypsum is mixed with soils because of the flocculation, carbonation, and cementing compound formation, such as ettringite and calcite, as mentioned by Ahmed (2015). These reactions depend on the phosphogypsum type, the soil type, the presence of a stabilizer and its type, and the contents of each material in the mixture.

In these studies, because of their intended use, the following mechanical tests were conducted: unconfined compression, California bearing ratio and dynamic triaxial. Mechanical tests (one-dimensional consolidation, direct shear, among others) that are frequently performed in geotechnical works (e.g., landfills, embankments and dams) were not performed and published before. Thus, this approach is the advancement of this study in relation to other earlier studies.

In this context, the present study aims to evaluate the effect of adding dihydrate phosphogypsum on the mechanical behaviour of a lateritic clay, which broadens the possibilities of its use. In addition, water percolated through the materials, obtained from permeability tests, was chemically analysed to verify the water table contamination potential due to cation lixiviation in phosphogypsum.

2. Materials and Methods

This section describes the studied materials and the methods used to execute the laboratory tests.

2.1. Materials

The soil used in the laboratory tests was obtained from Aparecida de Goiânia, GO, Brazil; it was collected at 0.8-1.2 m depth in the lateritic residual layer. It is classified as a low-plasticity silt according to the Unified Soil Classification System and as lateritic clay according to the typical soil classification proposed by Nogami & Villibor (2009). According to Rezende et al. (2016), the mineralogical constitution of the soil is quartz, gibbsite, haematite and kaolinite. This soil was selected because of its use in an experimental roadway construction with the local soil and phosphogypsum.

The dihydrate phosphogypsum is classified as a low-plasticity silt according to the Unified Soil Classification System. According to Rezende et al. (2016), its main mineral is gypsum.

The mixtures analysed in this study were made with three phosphogypsum contents: Mixture A (10%), Mixture B (20%) and Mixture C (50%). Mixture A’s content was set to evaluate the effect of the low phosphogypsum content on the soil behaviour. Mixture B was determined because it was used in the experimental roadway’s construction assessed by Metogo (2011). Mixture C’s content was set to be the most suitable to evaluate the effect of the high phosphogypsum content addition on the soil’s mechanical properties. The amounts of soil and phosphogypsum in each mixture were calculated according to the dry mass, and these materials were mixed in a concrete mixer for 10 min to obtain homogeneous mixtures. The geotechnical characterization of these materials is presented in Table 1 and the grain size distribution curves are shown in Fig. 1.

Matos (2011) showed that in the grain size distribution carried out with dispersant, sand content of mixtures are higher than soil and phosphogypsum content. The phosphogypsum added to the soil changes its pH and causes a reaction among the soil, phosphogypsum and dispersant agent, which prevents the breakdown of particle aggregations. Similar phenomena were observed in the particle size analyses of the soil and phosphogypsum mixtures in Mesquita (2007), Rufo (2009) and Metogo (2011).
The chemical composition of the studied mixtures is shown in Table 2 and was obtained from the initial studies of Matos (2011). The incorporation of phosphogypsum into the soil increases the cation exchange capacity (CEC) and reduces the pH. The low pH value for phosphogypsum corroborates the acidic characteristics, which were obtained by Ghafoori & Chang (1993), Rabelo et al. (2001) and Parreira et al. (2003).

Figure 2a shows SEM images of the phosphogypsum. The SEM images of the optimally compacted mixtures, which were obtained by Matos (2011) using Zeiss’ SteREO Discovery V20 with digital image capture, are presented in Figs. 2b, 2c and 2d. The studied phosphogypsum particles clearly exhibit plates with tabular format and large dimen-

### Table 1 - Geotechnical characterization of materials (modified from Matos, 2011).

| Materials       | $w_L$ (%) | $w_P$ (%) | $PI$ (%) | $\gamma$ (kN/m$^3$) | Classification |
|-----------------|-----------|-----------|----------|----------------------|----------------|
| Soil            | 38        | 25        | 13       | 27.4                 | ML A-6         |
| Mixture A       | 36        | 24        | 12       | 27.0                 | ML A-6         |
| Mixture B       | 35        | 23        | 12       | 26.9                 | ML A-4         |
| Mixture C       | 30        | -         | NP       | 26.5                 | ML A-4         |
| Phosphogypsum   | -         | -         | NP       | 25.5                 | ML A-4         |

### Table 2 - Chemical analysis of the materials (modified from Matos, 2011).

| Sortive complex | Phosphogypsum content (%) |
|-----------------|---------------------------|
|                 | 0 | 10 | 20 | 50 | 100 |
| $pH$ in H$_2$O  | 5.4 | 5.4 | 5.3 | 4.9 | 35 |
| P (meq/100 mL)  | 0.10 | 53.4 | 180.0 | 554.0 | 888.0 |
| Ca (meq/100 mL) | 2.50 | 64.9 | 55.1 | 66.2 | 69.9 |
| Mg (meq/100 mL) | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 |
| K (meq/100 mL)  | 0.10 | 0.06 | 0.06 | 0.08 | 0.06 |
| Na (meq/100 mL) | 0.02 | 0.39 | 0.40 | 0.49 | 0.31 |
| Al (meq/100 mL) | 0.10 | 0.40 | 0.70 | 0.90 | 1.30 |
| CEC (meq/100 mL)| 9.0 | 69.0 | 59.0 | 69.0 | 73.0 |
| C (g/kg)        | 2.5 | 5.3 | 0.9 | 2.9 | 1.5 |
| MO (g/kg)       | 4.3 | 9.1 | 1.5 | 5.0 | 2.6 |
| B               | 0.4 | 0.6 | 0.8 | 0.6 | 0.4 |
| Cu              | 0.9 | 0.9 | 0.7 | 0.8 | 0.5 |
| Fe              | 22.0 | 27.9 | 30.8 | 31.8 | 89.8 |
| Mn              | 31.3 | 23.0 | 19.7 | 13.7 | 4.5 |
| Zn              | 2.0 | 3.4 | 5.8 | 3.2 | 9.8 |
| S               | 139 | 186.0 | 160.0 | 154.0 | 145.0 |
| As              | $<0.01$ | $<0.01$ | $<0.01$ | $<0.01$ | $<0.01$ |

Note: $w_L = $ liquid limit; $w_P = $ plastic limit; $PI = $ plasticity index; $\gamma = $ specific gravity of grains; USCS = Unified Soil Classification System; AASHTO = American Association of Highway and Transportation Officials; G = gravel; S = sand; M = silt; C = clay.

Figure 1 - Grain size distribution curves (modified from Matos, 2011).
sions (Fig. 2a), which is typical of dihydrate phosphogypsum, as ascertained by Yang et al. (2009), Roy et al. (1996), Rutherford et al. (1993), Shen et al. (2012) and Alves (2015). There are small amounts of phosphogypsum crystals in Mixture A (Fig. 2b). When the content increases to 20% (Mixture B), more concentrated phosphogypsum crystals are observed, and phosphogypsum grains do not interact with the soil (Fig. 2c). The microscopy of Mixture C, which was obtained by Matos (2011), exhibits identical characteristics to Mixture B with a higher phosphogypsum crystal content (Fig. 2d).

The specimens for the mechanical tests of this study were molded from the compacted samples at optimal moisture content \( (w_{\text{opt}}) \) and maximal dry density \( (\gamma_{\text{max}}) \) using Proctor compaction test, as presented by Matos et al. (2012). These values are presented in Table 3. The phosphogypsum addition reduces the maximal dry density and increases the optimal water content. According to Sivapullaiah et al. (1998) *apud* Lovato (2004), the reason is the occurrence of flocculation, which is caused by the replacement of monovalent ions from soil by calcium, which creates a more porous structure and more water absorption.

2.2. Methods

One-dimensional consolidation tests were performed in a saturated condition according to NBR 12007 (ABNT, 1990) to understand the effect of phosphogypsum addition on the deformability parameters of the soil. The tests were made with pressures of 13.5 kPa, 32 kPa, 50 kPa, 100 kPa, 200 kPa, 400 kPa, 800 kPa and 1000 kPa in 48 h.

To verify the deformability of phosphogypsum over time, consolidation tests were performed in saturated conditions in the soil, Mixture A and phosphogypsum with three different loading conditions: 48 h stages to 800 kPa stress and direct loading to 800 kPa stress, which was maintained constant for 7 and 15 days.

After the saturated consolidation tests, which were conducted for loading times from 48 h to 15 days, the phosphogypsum samples were analysed using scanning electron microscopy (SEM) tests in the Multiuser Laboratory of High Definition Microscopy (LabMic) of the Federal University of Goiás (UFG). The test aimed to verify the changes that the loading time induced on the structural matrix of the material. It was not possible to perform the SEM test with compacted phosphogypsum and phosphogypsum...
after 7 days of consolidation because the samples suffered defragmentation during the metallization process.

Grain size tests were also performed according to NBR 7181 (ABNT, 2016) on phosphogypsum samples prior to compaction, after compaction and after submission to 800 kPa compression stress for 15 days. This test aimed to verify the occurrence of phosphogypsum particle fracture.

To understand the effect of the phosphogypsum addition on the soil, direct shear tests were performed according to D3080 - 04 (ASTM, 2004). The shear tests were of the consolidated and drained type (CD). To determine the Mohr-Coulomb failure envelope, the tests were conducted with four levels of normal stress: 50 kPa, 100 kPa, 200 kPa and 400 kPa. The consolidation time for each stress level was 37 h. To analyse how the specimen consolidation time can affect the strength parameters, direct shear tests with consolidation time of 12.5 h were also conducted on Mixture C.

To verify the ground water contamination potential caused by cation lixiviation in phosphogypsum in geotechnical constructions, water percolated through the soil samples, phosphogypsum and mixtures under hydraulic gradients of 2 and 10 was chemically analysed. For metals and boron, the chemical analyses were performed using MP AS 4200 with procedures described by SMEWW 3120 (APHA, 1992). The amount of water percolated through the soil and Mixture A under a hydraulic gradient of 2 was insufficient to perform the chemical analysis. The water samples were kept below 0 °C to eliminate any biological activity that could occur. The pure water in the test was collected and chemically analysed.

3. Results and Discussion

This section presents and analyses the results of the conducted laboratory tests, which studied the deformability and shear strength of the lateritic clay, phosphogypsum and mixtures, considering the effect of the phosphogypsum content and loading time.

### 3.1. Materials deformation

The deformation curves of the materials are presented in Fig. 3. It is verified that samples with 20% (Mixture B), 50% (Mixture C) and 100% phosphogypsum content have similar behaviour and can be explained by the SEM images in Fig. 2. The phosphogypsum grains do not interact with soil in the mixture with 20% phosphogypsum content (Fig. 2b), so the material has a greater effect on the deformability of the mixture.

Considering the 200 kPa stress, which is commonly used in earthworks, and the 1000 kPa stress, which is the maximum stress applied in the tests, phosphogypsum has less volumetric deformation than the recycled asphalt shingles (RAS), whose volumetric deformations were 17.5-30% for the stress of 200 kPa and 1000 kPa, according to Soleimanbeigi et al. (2013). By stabilizing the RAS with a fly ash (FA) content of 50%, the deformability of this mixture (RAS; FA) reduced to 2% and 5% for 200 kPa and 1000 kPa, respectively. These results are similar to values obtained for Mixture A and lateritic clay and presented in this study. RAS and FA are classified as well graduated sand and poorly graduated sand according to the Unified Soil Classification System (USCS).

Under 200 kPa stress, volumetric deformations as low as 5% were obtained for many recycled materials studied by Soleimanbeigi & Tuncer (2015), such as recycled concrete aggregate, bottom ash, foundry slag, foundry sand and recycled pavement material, which are classified by SUCS as well graduated gravel, poorly graduated sand, well graded sand, sandy loam and gravel, respectively. This range of deformation was also assessed by Kim et al. (2005) for fly ash (0, 25, 50 and 100%) and bottom ash mixtures, which are classified as low-compressibility silt or silty sand. The recycled asphalt pavement (RAP), which is classified as poorly graduated sand and was studied by Soleimanbeigi & Tuncer (2015), had similar volumetric deformation values to the soil in this study.

Figure 4 presents the variation of the deformability parameters according to the phosphogypsum content,

### Table 3 - Summary of the compaction test results (modified from Matos et al., 2012).

| Materials     | $w_{opt}$ (%) | $\gamma_{dmax}$ (kN/m$^3$) |
|---------------|---------------|----------------------------|
| Soil          | 22.7          | 15.40                      |
| Mixture A     | 22.7          | 15.30                      |
| Mixture B     | 22.9          | 15.10                      |
| Mixture C     | 24.0          | 13.70                      |
| Phosphogypsum | 28.0          | 12.10                      |

Note: $w_{opt}$ = optimum water content; $\gamma_{dmax}$ = dry maximum density.
where $\sigma_{pc}$ is the pre-consolidation stress, $C_c$ is the compression index, and $C_r$ is the recompression index. Increasing the phosphogypsum content also increases $C_c$ and $C_r$. With the suggested $C_c$ values and soil compressibility classification by Coduto (1999) *apud* Soleimanbeigi *et al.* (2013), the soil in this study is slightly compressible, phosphogypsum is notably compressible, and the mixtures are moderately compressible. The values found for phosphogypsum and mixtures are greater than the values observed for RAS (0.07) by Soleimanbeigi *et al.* (2013).

There is no logical relation between the reduction in pre-consolidation stress and the increase in phosphogypsum content. The obtained values are greater than the value of RAS, which is approximately 60 kPa according to Soleimanbeigi *et al.* (2013).

To evaluate the effect of the loading time on soil deformation, the soil compression curves for Mixture A and phosphogypsum samples submitted to different loading times are presented in Fig. 5. The deformation increases because the loading time changed from 48 h to 15 days and was 1.54%, 0.68% and 3.64% for soil, Mixture A, and phosphogypsum, respectively. The loading time has a greater effect on soil than on Mixture A.

Figure 6 presents the deformations of soil, Mixture A and phosphogypsum through time when the samples were loaded with 800 kPa stress regardless of previous deformations. In the 48 h tests, the stress was applied in stages; in this case, when 800 kPa stress was applied, the material had deformed because of previous stress, whereas in the 7- and 15-day tests, the 800 kPa stress was directly applied. Therefore, there are differences in the initial deformations in both situations, which were more notable for phosphogypsum.

It is verified that there is no stabilization trend for the phosphogypsum and Mixture A samples; after 500 min, there is a variation in inclination of the curve and an increase in deformation rate because of secondary consolidation, which is more notable with phosphogypsum. The secondary consolidation does not depend on the increase in effective stress and is characterized by the deformations of the material structure.

### Table 4 - Phosphogypsum grain size distribution before and after compactation and after the compression test.

| Type  | Grain size (mm) | PG before compaction (%) | PG after compaction (%) | PG after compression (%) |
|-------|----------------|--------------------------|-------------------------|-------------------------|
| Sand  | 0.6 ± 0.2      | 54.34                    | 41.28                   | 31.31                   |
| Silt  | 0.002 ± 0.06   | 41.17                    | 56.87                   | 64.33                   |
| Clay  | < 0.002 mm     | 4.49                     | 1.85                    | 4.35                    |

Note: PG = phosphogypsum.
The non-stabilization of the deformations over time was also ascertained by: 1) Soleimanbeigi & Tuncer (2015) by analysing the recycled asphalt pavement (RAP) and its mixtures with glacial outwash sand (GOS) and fly ash (FA) when the samples were submitted to 100 kPa effective stress for 20 days; 2) Soleimanbeigi et al. (2013) by analysing the recycled asphalt shingles (RAS) and its mixtures with fly ash (FA) when the samples were submitted to the effective stress of 100 kPa for 150 days.

To verify whether the non-stabilization of the deformations is related to phosphogypsum grain breakage, which is favoured by the grain tabular format (Fig. 2c), grain size distribution analyses were made with phosphogypsum prior to compaction, after compaction and after submission to 800 kPa load during 15 days. The observed clay, silt and sand percentages in phosphogypsum under these conditions are shown in Table 4.

Compactation and consolidation break the sand-sized grains and reduce them to silt-sized grains. There was a 13% and 10% increase of fines due to compaction and compression, respectively. Soleimanbeigi & Tuncer (2015) observed this behaviour for foundry slag: the fines ratio increased from 3% to 6% after compaction and 11% after consolidation (under 200 kPa load during 24 h).

The SEM images verify the occurrence of phosphogypsum grain breakage. Figures 7 and 8 show SEM images of phosphogypsum after consolidation in 48 h and 15 days, respectively. These figures show the grain breakage evolution relative to the loading time.

Because of the non-stabilization of phosphogypsum deformations over time, which results from grain breakage, the consolidation time is a primordial factor when one analyses the settlements that may occur in mixtures of soil and phosphogypsum.

### 3.2. Shear strength

The strength parameters of the studied materials (effective friction angle and effective cohesion) were obtained using shear tests at 50 kPa, 100 kPa, 200 kPa and 400 kPa normal stress and are presented in Table 5. The values were obtained with Mohr-Coulomb failure criterion considering the maximum strength and residual strength.

Small changes of the maximum and residual strengths of each mixture were observed as opposed to the observation of Haeri et al. (2005), who obtained different failure modes when using maximum or residual strength, where

| Material         | Maximum shear strength | Residual shear strength |
|------------------|------------------------|-------------------------|
|                  | $\phi^\prime$ (°) | $c^\prime$ (kPa) | $\phi^\prime$ (°) | $c^\prime$ (kPa) |
| Soil             | 38 | 37.5 | 40 | 11.0 |
| Mixture A        | 38 | 14.0 | 39 | 4.2  |
| Mixture B        | 38 | 9.1  | 39 | 4.9  |
| Mixture C        | 41 | 2.1  | 41 | 0.1  |
| Phosphogypsum    | 40 | 1.0  | 40 | 1.7  |

Note: $\phi^\prime$ = effective friction angle; $c^\prime$ = effective cohesion intercept.
the differences increase with more stabilizer (gypsum plaster).

Vakili et al. (2016) performed direct shear tests drained in kaolinitic clay ($c'_c = 12.5$ kPa and $\phi'_c = 19.9^\circ$) and mixtures of sodium silicate, ground granulated blast furnace slag (composed of gypsum and bassanite) and cement. In these mixtures, the cement content was maintained constant (2%), the sodium silicate contents were 1%, 1.5% and 2.5%, and the slag contents were 3%, 4% and 5%; the curing times were 7, 14 and 28 days. In this study, increasing

Table 6 - Shear strength parameters of cemented gravely sand and recycled asphalt shingles.

| Author          | Materials                         | % Stabilizer |
|-----------------|-----------------------------------|--------------|
| Haeri et al. (2005) | Cemented gravely sand              |              |
|                 |                                   | 0            |
|                 |                                   | 1.5          |
|                 |                                   | 3.0          |
|                 |                                   | 4.5          |
|                 |                                   | 6.0          |
|                 | $c'_c$ (kPa) $\phi'_c$ (°)        | $c'_c$ (kPa) $\phi'_c$ (°) |
|                 | 25 36                              | 136 39       |
|                 |                                   | 167 40       |
|                 |                                   | 229 41       |
|                 |                                   | 296 42       |
| Soleiman-beigi et al. (2013) | Recycled asphalt shingles         |              |
|                 |                                   | 0            |
|                 |                                   | 10           |
|                 |                                   | 20           |
|                 | $c'_c$ (kPa) $\phi'_c$ (°)        | $c'_c$ (kPa) $\phi'_c$ (°) |
|                 | 0 36 42                            | 31           |
|                 |                                   | 102 30       |

Note: $\phi'_c$ = effective friction angle; $c'_c$ = effective cohesion intercept.
slag also increased the cohesion and soil friction angle, possibly because of the presence of cement, low shear strength of soil, presence of bassanite in the slag and effect of the curing time. The best parameters ($c' = 60$ kPa and $\phi' = 44^\circ$) were found in the mixture with 1% sodium silicate, 2% cement and 5% slag after 28 days of curing.

Table 6 shows the strength parameters of a well-graded silty sand stabilized with gypsum plaster contents of 1.5%, 3.0%, 4.5% and 6.0%, as presented by Haeri et al. (2005) and obtained using triaxial undrained tests in saturated conditions. Table 6 also shows the strength parameters for recycled asphalt shingles stabilized with 10% and 20% fly ash, which were obtained using triaxial drained tests in saturated condition performed by Soleimanbeigi et al. (2013). The shear strength parameters of the recycled materials researched by Soleimanbeigi & Tuncer (2015) are summarized in Table 7.

The effective friction angles for all recycled materials (including phosphogypsum) are 31-45°, which are typical of compacted sandy soils according to Soleimanbeigi & Tuncer (2015) and are considered sufficient to provide stability for typical highway embankments. Similarly, Kim et al. (2005) observed a friction angle range of 28-48° (depending on the origin and content of each material) using triaxial drained tests for mixtures of fly ash and bottom ash.

As expected, like phosphogypsum, the recycled materials researched by Soleimanbeigi & Tuncer (2015), recycled asphalt shingles and cemented gravely sand, have low cohesion values, since the materials are granular. In this case, adding fly ash to recycled asphalt shingles increases the cohesion value possibly because of a better particle interaction.

Table 8 - Shear strength parameters of Mixture C for different sample consolidation times.

| Material | Consolidation time (h) | Maximum shear strength | Residual shear strength |
|----------|------------------------|------------------------|------------------------|
|          |                        | $\phi'$ (°)  | $c'$ (kPa) | $\phi'$ (°)  | $c'$ (kPa) |
| Mixture C | 37.0                   | 41          | 2.1      | 41          | 0.1       |
|          | 12.5                   | 33          | 24.0     | 34          | 7.0       |

Note: $\phi'$ = effective friction angle; $c'$ = effective cohesion intercept.
rence of void closures because of grain breakage (verified in Table 4 and Figs. 7 and 8) and the consequent interlacing of phosphogypsum crystals.

Figure 10 shows the soil and phosphogypsum shear curves in the saturated condition under 50 kPa and 400 kPa normal stress. It is verified that the soil has peak strength, which is typical of pre-consolidated soils and coherent with the pre-consolidation stress in Fig. 4. Phosphogypsum behaved as a normally consolidated material, which is inconsistent with its pre-consolidation stress values (Fig. 4) because of the phosphogypsum plate breakage in this case.

When the loading stress increases, the residual stress curves of soil and phosphogypsum approach each other because the phosphogypsum plates break under high confining stress. This failure promotes an interlacing among the phosphogypsum grains and demands a great energy for overcoming the friction created among these particles. However, this question must be better addressed using microscopy tests.

3.3. Potential for groundwater contamination

The chemical analysis results of the water samples percolated through the specimen with hydraulic gradients of 10 and 2 are shown in Tables 9 and 10, respectively. Resolution 396 (CONAMA, 2008) was used to interpret the results because it provides the classification and environmental guidelines for the composition of groundwaters. The boldfaced values in Tables 9 and 10 indicate the concentrations of chemical elements in the percolated water that exceeded the maximum value allowed by the referred resolution.

The cadmium, copper and lead concentrations are above the reference values, but the water in the Geotechnical Laboratory of the University of Brasília had these concentrations above the allowed limit. The manganese concentration is above the limit established by the referred regulation, including soil. Only iron does not exhibit surpassing values in soil, but they exceed the allowed limit in Mixtures B, C and phosphogypsum.

Mixture A did not present metals with higher concentrations than the permitted values by Resolution 396 (CONAMA, 2008) beyond the original content in water and soil. Instead, the presence of phosphogypsum diminished the cadmium and copper concentrations in water and maintained an almost constant lead concentration. However, tests with water percolated under hydraulic gradient 2 were not performed for this mixture. Therefore, we suggest performing these tests with the samples submitted to clear water percolation under hydraulic gradient 2 for a more definitive conclusion of the environmental viability of this material.

4. Conclusions

In this paper, the mechanical behaviour of soil and phosphogypsum mixtures was analysed using one-dimen-

| Chemical element | Water-Caesb | Soil Mix. A | Mix. B | Mix. C | Phosph. | Maximum value allowed (VMP) - CONAMA # 396 |
|------------------|-------------|-------------|--------|--------|---------|-------------------------------------------|
| Arsenic          | < 0.01      | < 0.01      | < 0.01 | < 0.01 | < 0.01 | 0.01                                      |
| Cadmium          | 3.8         | 4.6         | 3.1    | 3.1    | 4.6     | 0.05                                      |
| Lead             | 2.3         | 2.3         | 0.4    | 0.4    | 2.3     | 0.05                                      |
| Copper           | 0.6         | 0.6         | 0.6    | 0.6    | 0.6     | 0.05                                      |
| Nickel           | < 0.01      | < 0.01      | < 0.01 | < 0.01 | < 0.01 | 0.02                                      |
| Iron             | 0.1         | 0.1         | 0.1    | 0.1    | 0.1     | 0.05                                      |
| Manganese        | 3.8         | 4.3         | 4.3    | 4.3    | 4.3     | 0.05                                      |
| Zinc             | 0.7         | 0.3         | 0.3    | 0.3    | 0.3     | 0.05                                      |
| Barium           | < 0.01      | < 0.01      | < 0.01 | < 0.01 | < 0.01 | 0.01                                      |
| Silver           | < 0.01      | < 0.01      | < 0.01 | < 0.01 | < 0.01 | 0.01                                      |
| Boron            | 0.1         | 0.1         | 0.1    | 0.1    | 0.1     | 0.05                                      |

Note: Unit: mg/L; Caesb = Environmental Sanitation Company of the Federal District; CONAMA = Brazilian National Council for the Environment.
sional consolidation and direct shear tests, highlighting the effect of the loading time, which changes the material structure by grain breakage. In addition, water percolated through the materials was chemically analysed to verify the water table contamination potential. From the results, we conclude that:

The dihydrate phosphogypsum content in the mixtures affects the mechanical behaviour of the soil because the tabular crystal shape of this byproduct interferes in the interactions between the grains and facilitates its breakage. The SEM images show that starting at 20% phosphogypsum content, the phosphogypsum particles are not involved by soil grains. Therefore, the mechanical behaviour of mixtures with phosphogypsum content above 20% is affected by phosphogypsum. In other words, there is a critical content of dihydrate phosphogypsum for use in geotechnical constructions.

The breakage of phosphogypsum particles was verified by a granulometric analysis of in natura material after compaction and after consolidation using scanning electron microscopy. The consolidation was under 800 kPa load, which was applied during different loading times (48 h and 15 days).

The breakage of phosphogypsum particles affects the deformability of the mixtures. Thus, the compressibility parameters are generally superior to the values in the literature for residue stabilized soils, and the pre-consolidation values cannot be obtained using standard methods because the particles are not incompressible. In addition, the deformations depend on the loading time. These behaviours are more noticeable above 20% phosphogypsum content.

The volumetric deformation due to only secondary consolidation must be considered when one analyses the use of phosphogypsum or soil and phosphogypsum mixtures in geotechnical conditions. The 800 kPa stress is high and not commonly observed in geotechnical works.

The friction angle values of the mixtures are typical of compacted sandy soils and exhibit subtle alterations with the variation in phosphogypsum content and their method of determination (if the maximum or residual strength is used). The cohesion values decrease with the increase in phosphogypsum content because of the increase in silt content.

The effect of phosphogypsum plate breakage is verified in the change of the stress-deformation curves, which present a typical behaviour of normally consolidated soil in phosphogypsum, and in the approach of the residual curves of soil and phosphogypsum for elevated loading stress.

In the water samples percolated through the specimens, the cadmium, copper, lead and manganese elements showed higher values than the permitted value according to Resolution 396 (CONAMA, 2008). Moreover, water (for the first four elements) and soil (for manganese) already presented these inadequate concentrations, whereas iron presented values above the established value by the re-

### Table 10 - Chemical analysis results of percolated water in the permeability tests: hydraulic gradient = 2 (modified from Matos, 2011).

| Chemical element | Water Caesb | Mix. C | Mix. B | Phosph. |
|------------------|------------|--------|--------|---------|
| Arsenic          | < 0.01     | < 0.01 | < 0.01 | < 0.01  |
| Cadmium          | 2.1        | 2.3    | 2.4    | 3.8     |
| Lead             | < 0.01     | < 0.01 | < 0.01 | < 0.01  |
| Copper           | 0.6        | 0.3    | 0.5    | 0.01    |
| Nickel           | < 0.01     | < 0.01 | < 0.01 | < 0.01  |
| Iron             | 1.2        | 1.2    | 1.2    | 1.2     |
| Manganese        | < 0.01     | < 0.01 | < 0.01 | < 0.01  |
| Zinc             | < 0.01     | < 0.01 | < 0.01 | < 0.01  |
| Barium           | < 0.01     | < 0.01 | < 0.01 | < 0.01  |
| Silver           | < 0.01     | < 0.01 | < 0.01 | < 0.01  |
| Boron            | 0.01       | 0.21   | 0.4    | 0.7     |

Note: Unit: mg/L; Caesb = Environmental Sanitation Company of the Federal District; Cons. human = Cons. human; Cons. animals = Cons. animals; Recreational = Recreational.
ferred Resolution for the mixtures with at least 20% dihydrate phosphogypsum content. Thus, a phosphogypsum content of 20% or more is not recommended in geological works where the mixtures are submitted to water flow because of the risk of contaminating the groundwater.

The mixture with the best mechanical behaviour is Mixture A with 10% of phosphogypsum content, due to the entanglement between soil grains and phosphogypsum plates and the low content of added phosphogypsum, which does not negatively interfere with the behaviour of this material. Nevertheless, in this mixture, there is no significant improvement of the mechanical behaviour compared to soil.

Although the use of 10% of phosphogypsum doesn’t improve the soil mechanical behaviour, it is important to highlight that these study results can indicate one important way to encourage the reuse of this by-product and minimize environmental problems.

Furthermore, the research group has been continuing this study scope to find other ways to make feasible the use of a higher phosphogypsum content, such as the thermal treatment technique to transform the dihydrate phosphogypsum.

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List of Symbols
AI: aluminum
As: arsenic
B: barium
C: carbon;
Ca: calcium
CaSO4.nH2O: phosphogypsum
Ca3(F2(PO4)6: fluorapatite
Cc: compression index
Cr: recompression index
CEC: cation exchange capacity
Cu: copper
Fe: iron
HF: fluoric acid
H2O: water
H3PO4: phosphoric acid
IP: plasticity index
K: potassium
Meq: milliequivalent
mL: milliliter
Mg: magnesium
Mn: manganese
MO: organic matter
Na: sodium
P: phosphor
pH: hydrogen potential
Pb: lead
PG: Phosphogypsum

Ra: Radio
S: sulfur
U: uranium
wL: liquid limit
wopt: optimum water content
wp: plastic limit
Zn: zinc
ϕ': effective friction angle
c*: effective cohesion intercept
σpc: pre-consolidation stress
γdmax: dry maximum density
γs: specific gravity of grains