Mineralogical mechanisms of strength improvement in cement modification

Fernando H. M. Portelinha
Department of Geotechnical Engineering- School of Engineering of Sao Carlos - University of Sao Paulo, Sao Carlos, Sao Paulo, Brazil
Dario Cardoso de Lima & Carlos Alexandre Braz de Carvalho
Department of Civil Engineering – Federal University of Viçosa, Viçosa, Minas Gerais, Brazil
Mauricio Paulo Ferreira Fontes
Department of Soils – Federal University of Viçosa, Viçosa, Minas Gerais, Brazil

ABSTRACT
Strength properties of cement stabilization are related to soil mineral formations. In granular soils, the cement provides cementation of soils particles. In clayey soils, the cement particles form nucleus of cemented soils particles and the eventual mineral dissolutions resulted from pH soils increases. Hence, the strength improvement of stabilized soils may result from crystallization of gels formed in long term. The mechanisms of cement stabilization were well established in the 60`s, which normally is referred to stabilizers contents above to 3%. However, recent experiences has reported the use of low contents of cement in the modification of local soils for pavement applications. At this point, the objective of this paper is the investigatation of the relationship between mineralogical alterations and mechanical strength increases of a tropical soil modified with 1, 2 and 3% of cement, after 7 and 28 days of curing time. The process of mineralogical alterations was evaluated by amorphous minerals determinations via chemical sequential attack by barium chloride, ammonium oxalate and sodium hydroxide extractors, and simultaneously crystallization of minerals evaluation via XRD analyses. Unconfined compression strength (UCS) tests were carried out in order to analyze the mechanical strength of compacted mixtures. The results gained from the tests showed high quantities of amorphous minerals of calcium and silica after 7 days of curing time and decreases of these values after 28 days. In the XRD results, there was evidences of new crystalline minerals after 7 days only with 3% of cement, while the calcium silicate appeared in mixtures after 28 days with 2 and 3% of cement. In addition, highest strength increases were noted in samples after 28 days. Therefore, results support the relationship between crystalline mineral formations and strength improvement even with low contents of cement.

RESUMEN
Las propiedades resistentes de suelos estabilizados con cemento están asociadas con las formaciones minerales. En suelos granulares, el cemento promueve la cementación de las partículas del suelo. En arcillas activas, las partículas de cemento forman núcleos de partículas de suelo cimentado y pueden promover una disolución eventual de minerales debido al aumento del pH. Por lo tanto, el aumento de resistencia del suelo estabilizado puede ser producto de la cristalización de geles formados a largo plazo. Los mecanismos de estabilización de suelos con cal y cemento fueron bien establecidos en los años 60's, los contenidos típicos oscilan normalmente alrededor de 3%. Sin embargo, ha sido reportado en experiencias recientes el uso de contenidos bajos de cemento en la modificación de suelos locales en aplicaciones para pavimentos. En este contexto, el objetivo de este artículo es investigar la relación entre las alteraciones mineralógicas y la resistencia mecánica de suelos residuales modificados con 1, 2 y 3% de cemento después de 7 y 28 días de tiempo de curado. El proceso de alteraciones mineralógicas fue evaluado realizando determinaciones de minerales amorfos a través de ataques secuenciales de extractores de cloruro de bario, oxalato de amonio e hidróxido de sodio, conjuntamente a evaluaciones de la cristalización de minerales a través de análisis XRD. Ensayos de resistencia a la compresión simple fueron realizados para analizar la resistencia mecánica de mixturas compactadas. Los resultados obtenidos de los ensayos mostraron gran cantidad de minerales amorfos de calcio y sílice después de 7 días de curado y disminuyeron después de 28 días. Dentro de los resultados de XRD no hubo evidencias de la existencia de nuevos minerales cristalinos después de 7 días de curado, mientras que luego de 28 días apareció silicato de calcio en las mezclas de 2 y 3% de cemento. Además, fueron notados los mayores aumentos de resistencia para los especímenes después de 28 días. Estas evidencias muestran la cristalización de minerales a largo plazo. En consecuencia, los resultados confirman la relación entre la formación de minerales cristalinos y la mejora de la resistencia inclusive para contenidos bajos de cemento.

1 INTRODUCTION

Cement soil stabilization has provided a convenient solution in roadways structural layers in areas where high bearing capacity materials are difficult to obtain or are of expensive cost. Actually, Portland cement has been considered excellent stabilizers for the improvement of soils, including granular and clayey soils. In fact, the

better responses from cement stabilization are evident in granular soils; however, cement has been extensively applied in finer soils in Brazil. In granular soils, the cement provides cementation of soils particles, while in clayey soils, the cement particles form nucleus of cemented soils particles and eventual mineral dissolutions due to pH soils increases (Bell 1996, Prusinski and Brattacharja 1999). According to Moh (1965), during the hydration of the cement anhydrous components, there is release of lime (calcium hydroxide), which usually reacts with the chemical components of the non-inert soil particles, changing the pH and the chemical components previously formed by cement hydration. Calcium hydroxide has a quick and well defined effect on clayey soils, involving cationic exchange, carbonation, formation of calcium hydroxide crystals and/or flocculation, as referred in the soil-lime reaction mechanism.

Therefore, the geotechnical behavior of soils resulted from cement treatments depends on mineralogical, physical and chemical properties of soil, which are related with soil formation conditions and the matrix-rock. At this point, clayey soils composed by montmorillonites and smectites minerals can respond differently to cement stabilization than kaolinitic soils. Hence, soils formed in tropical climates, as have largely found in Brazilian territory, react differently those soils from temperate climates, when stabilized with Portland cement.

As well known, cement can provide plasticity reduction and grain size distribution modifications caused by flocculation reactions due to release of lime during the hydration reaction (Moh 1965; Osula et al. 1996), as well as promoting expressive mechanical strength increases due to the cementation of formed gels and/or Portland cement hydration reactions (Sariosseri and Muhunthan 2009).

In this study, the term soil stabilization refers to a substantial improvement of the soil mechanical behavior using high quantities of stabilizer (up to 4%). The term soil modification is applied to a significant improvement of the soil workability and compaction characteristics, and minor improvement of the soil mechanical strength using low contents of stabilizers (from 1 to 4%) (Solanki et al. 2009). From this point, it must be emphasized that the use of high contents of Portland cement generally produces materials with excellent mechanical behavior, while the addiction of low contents in soil modification can represent an economical and efficient solution for flexible pavement design.

Even though the final results of modification of soils is well known, there are no knowledge about the mineralogical and physics properties alteration in short and long term. According to Rogers and Glendinning (2000), the minimum amount of lime required for full stabilization is around 3%. This evaluation was based on the pH alterations provided by lime. Regarding that the cement modification process releases low quantities of lime, it is possible that cement addition can promote increases in pH of soils and the dissolution of clay minerals in short term, as well as the crystallization of the gels formed during hydration cement in long term.

The purpose of this paper is to evaluate the mineralogical mechanisms of strength improvement in the soil modification by the addition of 1, 2 and 3% of Portland cement in a Brazilian lateritic soil. The experimental program was directed to observed mineralogical alteration in two aspects: in short term when the reactions results in amorphous gel (no crystallized); and, in long term, when gels pass to the crystallize forming a new mineral. Additionally, unconfined compression strengths (UCS) values were evaluated simultaneously with the mineralogical changes associating the improvement to the mineralogical modifications.

2 EXPERIMENTAL PROGRAM

The experimental program was conducted in two steps. The first one addressed the investigation of the use of low contents of Portland cement in order to promote strength improvements. The second step was directed to study mineralogical compounds formation in the process of soil modification in short and long term.

2.1 Materials

A lateritic fine-grained soil was used in this study. Table 1 presents the summary of geotechnical properties of soil. The material consists of a residual gneiss soil, pedologically classified as red-yellow latosol soil, which commonly appears in the B horizon of soft slopes and is classified as silty sand clay. X-ray diffraction data showed the presence of kaolinite, goethite and gibbsite as the main minerals (Figure 3a). Table 2 introduces chemical soil properties.

Commercial chemically pure powdered Portland cement (PC II-E-32) was used throughout the study.

Table 1. Geotechnical properties of soil

Properties		Standard method
Clay (%)	66	
Silt (%)	6	NBR 7181/84
Sand (%)	28	
Liquid limit (%)	70	NBR 6459/84
Plasticity index (%)	29	
Specific gravidity	2.73	NBR 6508/84
Maximum dry unit weight (kN/m^3)	14.9	NBR 7182/84
Optmum water content (%)	27.9	

Table 2. Chemical properties of soil

Properties	
pH	6.76
ZPC	6.02
CEC (cmol$_c$/dm^3)	1.25
BS (%)	80

2.2 Methods

Contents of 1, 2 and 3% of Portland cement in weight were mixed to dry soil samples, adding subsequently the water contents in order to reach the optimum water content. The homogeneous mixtures samples were put into plastic bags before of the samples compaction. UCS tests specimens were molded at the optimum water content and maximum dry unit weight of intermediate Proctor test of each mixture; then, the mixtures was cured during 7 and 28 days before the UCS tests performance.

2.2.1 Mechanical behavior parameters

UCS tests were carried out according to ASTM D2166/98 in cylindrical specimens with 10 cm diameter and 12.7 cm height, molded at the optimum compaction parameters of soil and mixtures. Specimens were cured during 7 and 28 days. Acceptance criteria of specimens were the range of $\pm$ 0.30 kN/m^3 for maximum dry unit weight, and $\pm$ 0.5% for optimum water content. Soil and mixtures results were obtained from the average value of the failure stresses of three specimens, adopting the acceptance criteria of UCS average value $\pm$ 10% for each specimen.

2.2.2 Amorphous mineralogical analysis

Minerals of silica, alumina, calcium and iron were identified in amorphous phase by a sequential attack with three extractors, namely: barium chloride ($BaCl_2$); ammonium oxalate; and sodium hydroxide (NaOH). The extractor barium chloride is widely used in order to obtain exchangeable cations in clay minerals. The ammonium oxalate is indicated to determine iron in amorphous forms (Schwertmann 1973). The sodium hydroxide acts increasing substantially the pH of soil solution destabilizing the equilibrium conditions of silica and alumina minerals, weakening even more no formed structures, which allows the quantification of amorphous elements of silica and alumina.

The samples used in the mineralogical evaluations were removed from post-failure UCS specimens after 7 and 28 days of curing times. Portions of the specimens were prepared by breaking, sieving through 2 mm sieve, oven-drying at 105°C and separated in plastic bags. The sequential attack procedure was used as follows:

- stage 1- extraction of the soluble and changeable components with barium chloride: 1.0 g of soil sample smaller than 2 mm was weighed and placed in centrifuge tubes (capacity of 30 ml); then, 20 ml of $BaCl_2$ (0.5 mol/L) were added and agitated it for 2 hours in a mechanical agitator;
- stage 2 – determination of the soluble minerals in ammonium oxalate: the centrifuge tubes containing the samples of the previous extraction were involved in aluminum foil to prevent light penetration (since the reaction

must occur in the dark); then, it was added 10 mL of the "Reagent TAM" solution (ammonium oxalate 0.2 mol/L plus oxalic acid 0.2 mol/L at pH 3.0), and the tubes were immediately closed; later, the set of tubes was placed in a horizontal agitator (so that they were parallel to the direction of the movement) and agitated for two hours; and

- stage 3 – amorphous determination: 40 ml of NaOH 0.5 mol/L were added to the samples of the centrifuge tubes, and heated in water-bath at 90°C for 15 minutes.

After each stage of the extraction, the samples were centrifuged and the supernatant was retained for later determination of the concentration of the cations calcium (Ca^{2+}), Iron (Fe^{2+}), silicium (Si^{4+}) and aluminium (Al^{3+}), using a plasma emission spectrometer, Perkin Elmer, model 3300 TV, from Federal University of Viçosa – Minas Gerais.

2.2.3 X-ray diffractometry behavior (XRD)

Mineralogical characterizations of crystalline form were carried out using XRD analysis. Mixtures samples used in this analysis were extracted from post-failure UCS test specimens after 7 and 28 days of curing times, and prepared by breaking, sieving through the 2 mm sieve, and oven-drying at 105°C. Clay-silt (diameter ≤ 0.05 mm) and sand (0.05 < diameter ≤ 2 mm) fractions were separated by sedimentation. The XRD analyses were conducted using an X-ray diffractometer (Rigaku company) from the Department of Soils at the Federal University of Viçosa. All samples were irradiated using Cobalt laminas (Co-kα) and scanning intervals ranging from 4° to 50° 2θ. The sand fraction samples were molded in excavated glass lamina without mineral orientation, and the clay-silt fraction samples were installed in flat glass lamina with mineral orientation (Gibbs 1965).

3 RESULTS AND DISCUSSIONS

3.1 Mechanical behavior

Figure 1 shows results from UCS data at failure for soil modified with cement after 7 and 28 days of curing times. Soil modification with cement increased substantially the UCS for both curing times with contents of 2 and 3% of stabilizer. Strength values after 28 days of cure were higher than for 7 days. Figure 2 illustrates the increment in strength caused by modification with 1, 2 and 3% of cement after 7 and 28 days of curing. The increase rates were determined in relation to the untreated soil strength. Addition of 1, 2 and 3% of cement caused increments of 26, 166 and 233% in the UCS strength. For specimens cured during 28 days, the addiction of 1, 2 and 3% of cement promoted increments of 35, 218 and 255%, respectively. Therefore, the use of low contents of cement showed to be effective in the soil strength improvement.
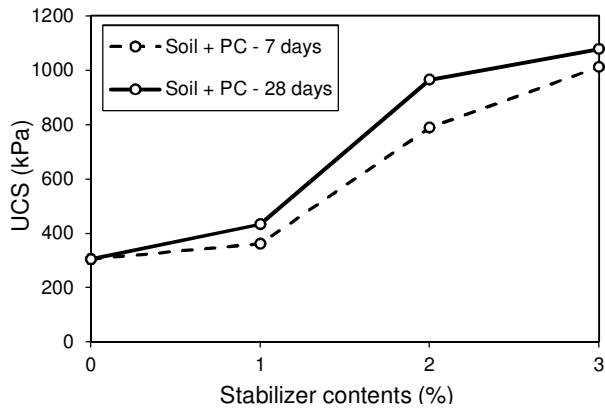
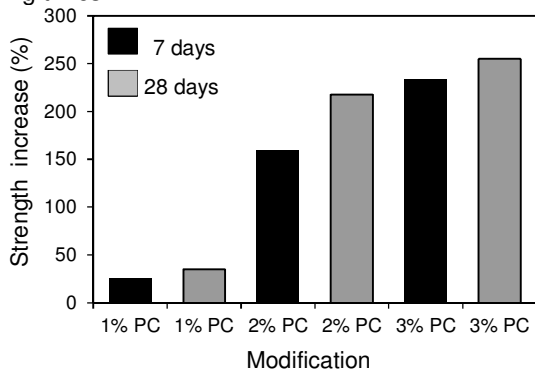Figure 1. UCS of cement mixtures, after 7 and 28 days of curing times.

Figure 2. Strength increases of mixtures after 7 and 28 days of curing.

3.2 Amorphous analysis

Figures 3 to 6 present the minerals of silica, alumina, calcium, and iron in amorphous phase of cement mixtures formed after 7 and 28 days of curing time.

Concentration of Silica amorphous measured using the oxalate extractors increased at very high rates with cement addition for specimens after curing times of 7 and 28 days. Additionally, no alterations of the concentration of silica were observed between 7 and 28 days of curing times. Silica amorphous minerals extracted by sodium hydroxide shows that the concentration increased until 2% of cement after 7 days of curing time, and 1% for 28 days. However, decreases of concentration are evident after 28 days, mainly with contents of 2 and 3%. Probably, part of the silica in amorphous state processed to the crystallization. Herrin and Mitchell (1961) report that the product of these reactions is a silicate and calcium aluminate gel, which tends to cement the soil particles, similarly to the way produced by the hydration of the Portland cement.

Curves of alumina amorphous are presented in Figure 4. An interesting aspect is the reduction of alumina concentration in specimens with curing time of 28 days, in comparison with curing time of 7 days, when extracted with the sodium hydroxide solution. In fact, the reductions occurred in mixtures with 2 and 3% of

cement. Specifically the application of 1% of cement, increases in the concentration of alumina is evident. Therefore, crystallization of gels formed or hydration cement reactions occurred during 28 days of curing time for 2 and 3% of cement.

Figure 5 presents concentrations of calcium compounds. Reduction of the calcium concentration occurred from 7 to 28 days of curing time as noticed with silica and alumina compounds. The concentration of calcium observed in Figure 5a consists of exchangeable cations retained by the surface of the clay minerals. The reduction of concentration observed after 28 days suggests the formation of a new minerals with calcium in their composition.

Figure 6 shows the iron compounds concentrations. Clearly, the curves of calcium and iron presented similar tendencies what suggest an association of minerals. Furthermore, both minerals concentration reduced from 7 to 28 days.
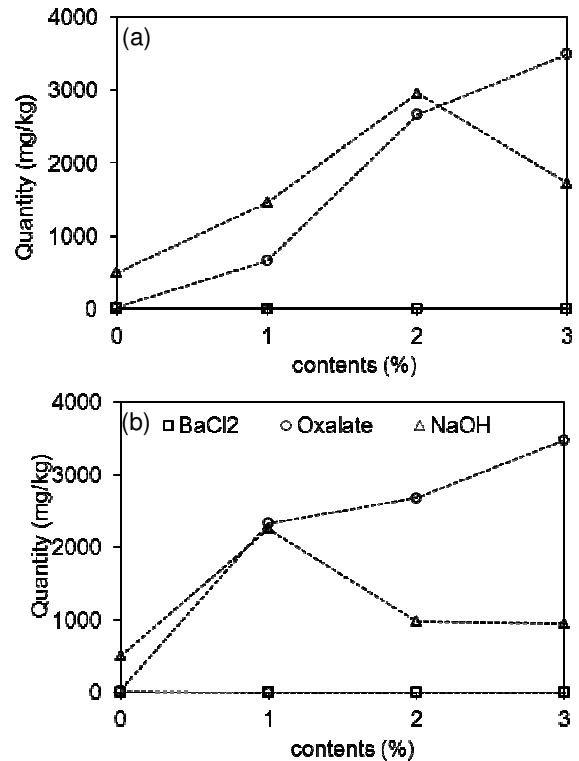

Figure 3. Silica amorphous concentration in cement mixtures, for the curing period of 7 (a) and 28 days (b).
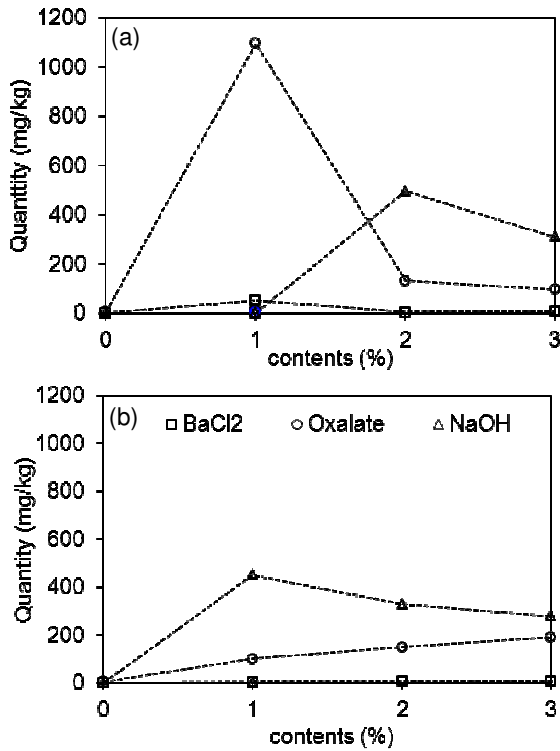
Figure 4. Alumina amorphous concentration in cement mixtures, for the curing period of 7 (a) and 28 days (b).
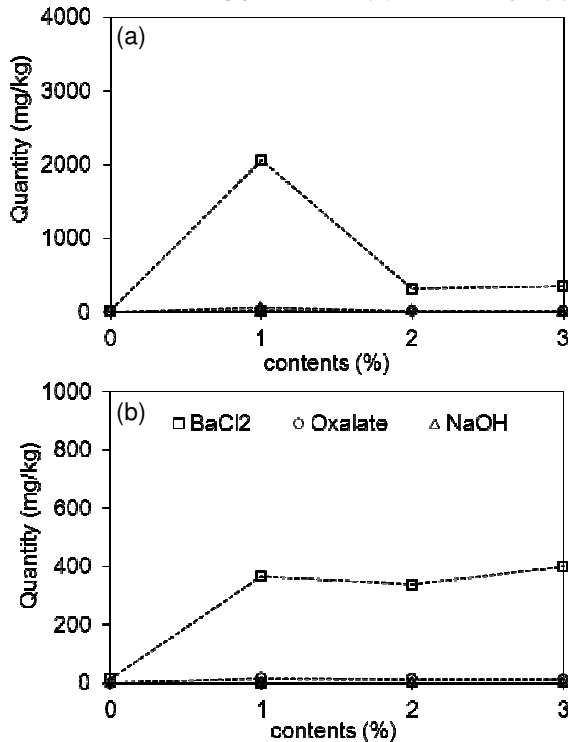

Figure 5. Calcium amorphous concentration in cement mixtures, for the curing period of 7 (a) and 28 days (b).
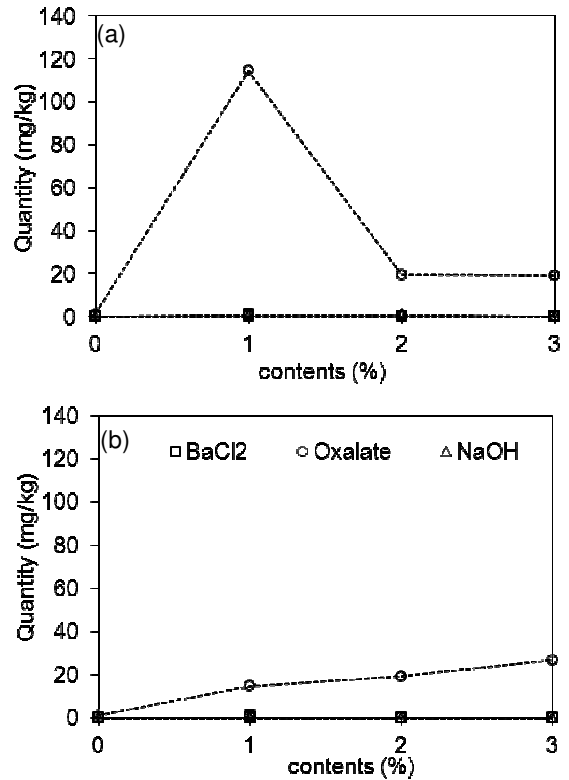

Figure 6. Iron amorphous concentration in cement mixtures, for the curing period of 7 (a) and 28 days (b).

3.3 XRD analysis

Figure 7 presents XRD analysis results of finer fractions (silte and clay) and granular fractions (sand) of mixtures, after 7 days of curing time. Results show that the use of 1 and 2% of cement were not efficient to change the soil mineralogy in short time. New minerals were not observed in the clay-silt and sand fractions after 7 days of curing times. On the other hand, addiction of 3% of cement favored the formation of Calcium silicate, identified as Rankinite, after 7 days of curing time.
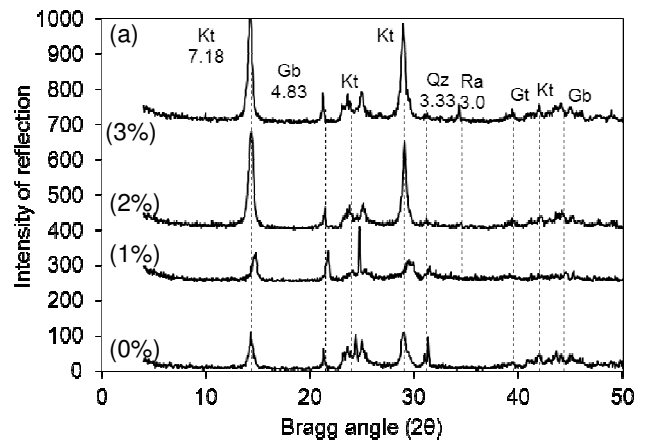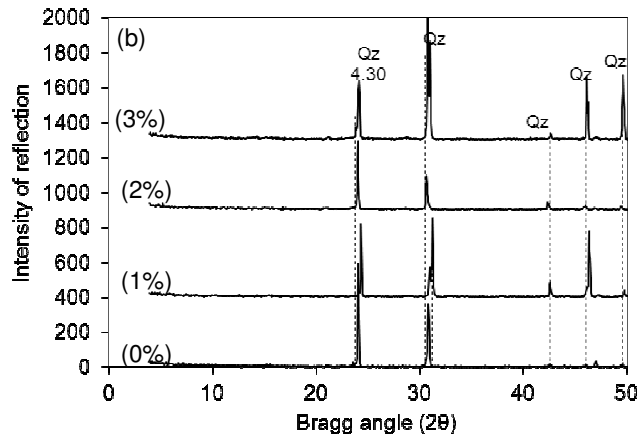
Figure 7. XRD data of finer and granular fractions of soil and mixtures after 7 days of curing time.

Figure 8. XRD data of finer and granular fractions of soil and mixtures after 28 days of curing time.

The XRD analysis data for samples cured during 28 days is showed in Figure 8. It is clearly observed the crystallization of minerals of Calcium Silicate (Rankinite) in the finer fraction of mixtures in all modifications suggested in this work. In addition, a new mineral formation is evident in the granular fraction (Grossular) modified with 2% of cement. Therefore, the curing time of 28 days is sufficient for the occurrence of the crystallization of the gels formed in short time.
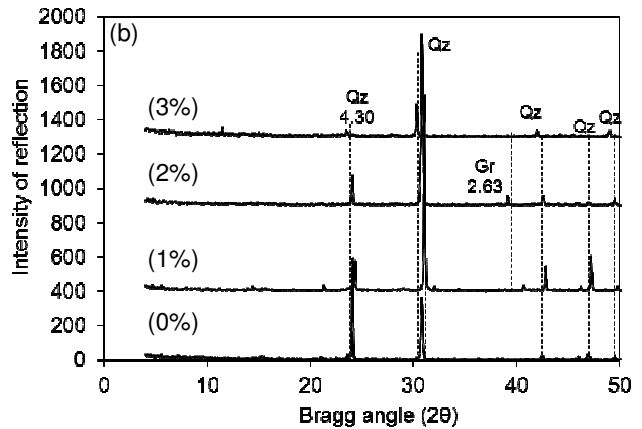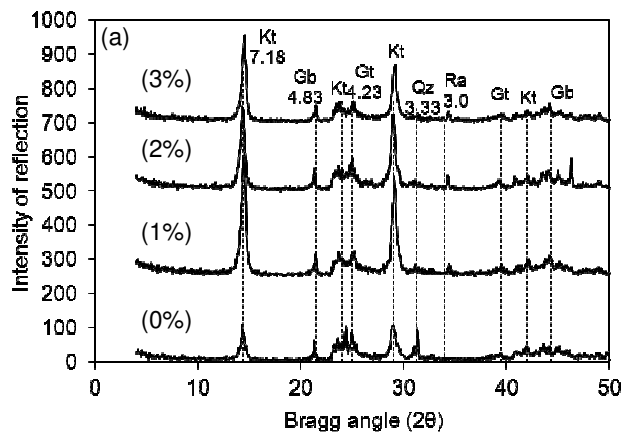

3.4 Final Discussions

The process of modification can be an efficient and economical solution for subgrade and base of pavement referring to this residual soil. However, the modification just passes to be efficient with modification up to 2% of cement, when effective strength improvements were noted even after 7 days of curing time. Higher concentrations of amorphous minerals are observed after 7 days of sample rests possibly representing the initial steps of modification process. Hence, the hydration reactions were sufficient to formation of new minerals gels. Additionally, the gels formed may be responsible for the strength improvement occurred in specimens cured during 7 days. The highest strength values observed in the modification with 3% of cement was associated with the formation of the new crystallized mineral observed in the XRD analysis (Figure 7). In fact, the reduction of silica and alumina amorphous and observation of a new mineral of Calcium silicate can sustain the soil improvement.

Evidently, the process of modification was more defined after 28 days of curing time. Reductions of concentration of silica, alumina and calcium were clearly noted in Figures 3b, 4b and 5b, showing the end of the crystallization process. Furthermore, the formation of calcium silicates in mixtures with 1, 2 and 3% of cement can sustain the hypothesis. Therefore, the effective increases of strength after 28 days can be associated with the mineralogical alterations.

4   CONCLUSIONS

Results supports that cement modification can be an efficient and economical technique for flexible pavement design. In addition, mineralogical aspects can be related to the strength improvement, as follows:

- Cement modification enhanced the soil strength with contents of 2 and 3% even after relative short term (7 days); however, higher values

were observed after a long term of curing time (28 days).

- Large concentration of amorphous minerals of silica, alumina, calcium and iron were verified after 7 days of curing time. Thereafter, the concentration reduced significantly after 28 days, suggesting the crystallization of the gels formed.
- New minerals formation were observed in the XRD analysis in samples with 3% of cement and 7days of curing times, and 1, 2 and 3% of cement after 28 days of curing times. Furthermore, the highest strength increases were associated with the mineral alterations.

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