Physico-mechanical properties of phosphogypsum and black steel slag as aggregate for bentonite-lime based materials

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ABSTRACT

This study aim to valorizing phosphogypsum (PG) and steel slag (Sc) in geotechnical applications by incorporating them in bentonite (B) stabilized by lime (L). Mineralogical (XRD), spectroscopic (IR-FTIR), geotechnical (Atterberg limits) analyzes were carried out on the raw material. Resistance to axial compression (UCS) was performed on cylindrical specimens prepared for mixtures B-L, B-L-PG, B-L-PG-Sc and cured for 3, 7, 15 and 28 days. The results obtained revealed that the mechanical strength increases with the addition of PG, and reaches its maximum value for a water content equal to 46%. Slag improves the strength of the B-L-PG mixture. The pH and the electrical conductivity of the solutions containing in porosity of the various mixtures decrease over time. The observed decrease is greatest for B-L-PG and B-L-PG-Sc mixtures due to pozzolanic reactions.
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1. Introduction

The recovery of waste generated by growing mining and chemical industrial activities is addressed by researchers from different countries. Phosphogypsum (PG) is an industrial waste produced by the attack of sulfuric acid on natural phosphate. PG contains harmful elements to the ecosystems and human health, in particular heavy metals and radionuclides [1]. In Morocco, the Office Cherifien of Phosphate (OCP) generates more than 15 million tonnes per year of PG in the Jorf Lasfar factory (El Jadida) [2]. This waste is mainly used in the field of civil engineering, particularly as aggregate in cement mortars used for reduce soil permeability [3].

The electric steel is a growth industry worldwide, in particular in the United States, it raised from less than 50% in 2000 to more than 68% in 2018 [4]. This growth is accompanied by a significant increase in slag waste. In Morocco, ArcelorMittal Sonasid Company produces 150,000 tonnes per year of steel slag (Sc) waste. Steel slag can be used as aggregate in concrete, which improves the compressive strength of concrete above the standard values for ordinary Portand cement [5].

Bentonite (B) is well known as good adsorbent for heavy metals [6]. In Morocco, in the Nador region (NE), large deposit of bentonite (Trebia) is available [7] and have recently been successfully tested for improving mechanical strength of hydrated lime based cement [8].

In this study we will test the capability of industrial wastes (PG and Sc) to improve the mechanical properties of bentonite and lime based materials. Geotechnical parameters of the mixtures based on industrial waste-bentonite-lime will be monitored over time. The overall release of ions into distilled water by the stabilized mixtures will be evaluated by measuring the pH and the electrical conductivity.

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2. Materials and methods

2.1. Raw materials and aggregates preparation

Raw bentonite from the Trebia deposit from the Nador area (NE Morocco) was sampled for this study. This bentonite is dioctahedral smectite, with high swelling behavior, high compressibility and poor strength when hydrated [7].

The hydrated lime, $Ca(OH)_2$, used in this study is an industrial material destined to the local Moroccan market (Oujda, Northeast Morocco), it was calcined at 1000 °C at 24H. The PG ($CaSO_4 \cdot 2H_2O$) is a phosphate industry waste from the Cherifien office of Phosphate of Jorf Lasfaar (El Jadida, Morocco). The black slag waste (Sc) is from SONASID electric steelworks produced in the Jorf Lasfar.

Different mixtures of bentonite-lime, bentonite-lime-PG and bentonite-lime-PG-Sc were prepared by mixing 8% of lime, 8% of PG and 8% of Sc by dry weight of bentonite [7,9]. The samples are labeled referring to the main aggregates added to bentonite. Water (46%) was added to the mixture of dry materials to obtain uniform consistency. Cylindrical specimens, with an average weight of 7.6 g and dimensions of 1.6 cm in diameter and 3.2 cm in height were prepared (Fig. 1). The specimen was extracted and placed in airtight polythene bags, which were placed inside a desiccator for curing for 3, 7, 14 and 28 days. For the measurement of pH and conductivity, a B-L and B-L-PG and B-L-PG-Sc specimens cured for 28 days were immersed in 500 mL of distilled water. The specimens were taken out of the desiccator and polythene bag after the desired period of curing and tested for unconfined compressive strength, X-Ray Diffraction (XRD) and Infrared (IR).

3. Results and discussions

3.1. Characterization of the raw material

3.1.1. X-ray diffraction

X-ray diffraction analysis has shown that the bentonite used consists mainly of montmorillonite-Ca characterized by an peak at ~ 15 Å ($Ca_{0.2}(Al, Mg)_2Si_4O_{10}(OH)_2,4H_2O$), montmorillonite-Na ($Na_{0.3}(Al, Mg)_2Si_4O_{10}(OH)_2, 4H_2O$), K-feldspar and Na-feldspar (K, $Na(AlSi_3O_8)$). Raw lime is composed of lime (CaO), periclase (MgO) and calcite ($CaCO_3$). Phosphogypsum consists of gypsum ($CaSO_4, 2H_2O$), hemihydrate ($CaSO_4, ½ H_2O$) and anhydrite ($CaSO_4$). Steel slag is composed of several phases: calcium ferrite ($CaFe_2O_4$), calcium di-silicate ($CaSi_2O_4$), srebrodoskite ($Ca_2Fe_2O_5$) and fayalite (Fe_2SiO_4) (Fig. 2).

3.1.2. Infrared spectroscopy

Infrared spectra of bentonite, phosphogypsum and steel slag show the adsorption band at 3627 cm^{-1} due to the elongation of the OH group of the adsorbed water (Fig. 3). The two peaks observed at 1622 and 1525 cm^{-1} are linked to the vibration of the OH of water adsorbed in the interfoliar space of bentonite and PG hydration water. PG shows a peak at 3390 cm^{-1} attributed to the symmetrical and asymmetrical elongations of the OH bond of the gypsum molecule $CaSO_4 \cdot 2H_2O$ [7]. The band at 669 cm^{-1} is due to the deformation and bending modes of the Si – O bond. The bands at 586 and 518 cm^{-1} are due to the bending vibrations Al – O – Si and Si – O – Si, respectively [10]. The elongation and deformation of the SO_4 group of the PG are observed at 1102 cm^{-1} and 669 cm^{-1} respectively. The strongest band at 992 cm^{-1} was assigned to the asymmetric elongation Si – O – Si, the band at 920 cm^{-1} to the symmetrical elongation Si – O – Si and the band at 518 cm^{-1} to vibrational mode of flexion of Si– O – Si in calcium silicate (Ca_2SiO_4) [11].

3.1.3. Consistency limits

Bentonite has an extremely high plasticity (IP = 72.5), due to the plastic behaviour of montmorillonite and it fine grain-size (Table 1). It contains 60% of fraction less than 80 μm, 33% of fraction less than 63 μm and 14% of fraction less than 4 μm [12].

4. Characterization of the mixtures

4.1. Consistency characteristics

The addition of Steel slug or PG decreases the plasticity index by 10% and 14% respectively. The plasticity index decreases by more than 40% by adding lime to bentonite.

We observe a shift of plasticity index of bentonite when lime, Sc and PG is added. The lowest plasticity index is observed for the mixtures B-L-PG (PI = 31) and B-L-PG-Sc (PI = 26.3). Thus, PG, Sc and lime play a degreasing role allowing to decrease the plasticity of bentonite. The mixtures B-L, B-L-PG and B-L-PG-Sc have the same plasticity as inorganic silts, fine micaceous, diatom sands or silty soils, and elastic soils (Table 1, Fig. 4).

4.2. Variation of pH and electrical conductivity of the mixtures

The addition of lime, PG or slag modify the pH of bentonite in solution which is slightly alkaline ($pH_0 = 8.72$). The addition of PG which contains residual acidity, acidifies the bentonite in solution ($pH_0 = 7.57$). While, the addition of slag increases the alkalinity of the solution containing bentonite ($pH_0 = 10.9$). When lime, a strong base $Ca(OH)_2$, is added the pH becomes strongly alkaline (pH_0 greater than 12) (Table 1).

The variations in pH and electrical conductivity as a function of the curing time in distilled water are given in Fig. 5. The initial average pH of the B-L, B-L-PG and B-L-PG-Sc was close to 12.5
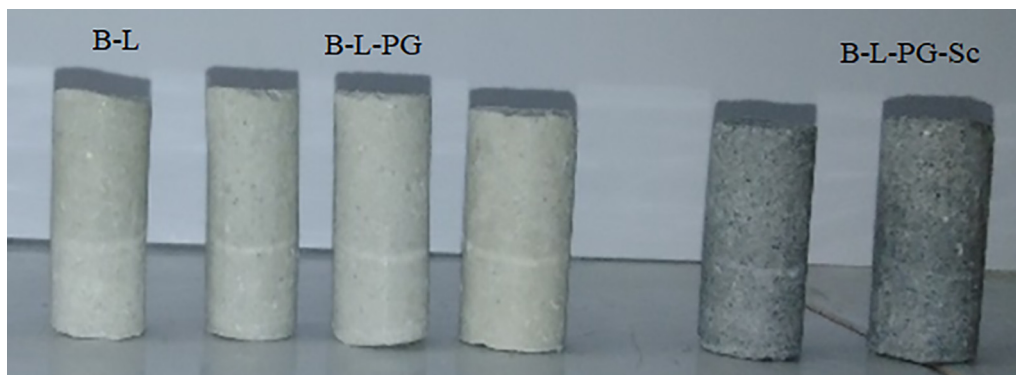

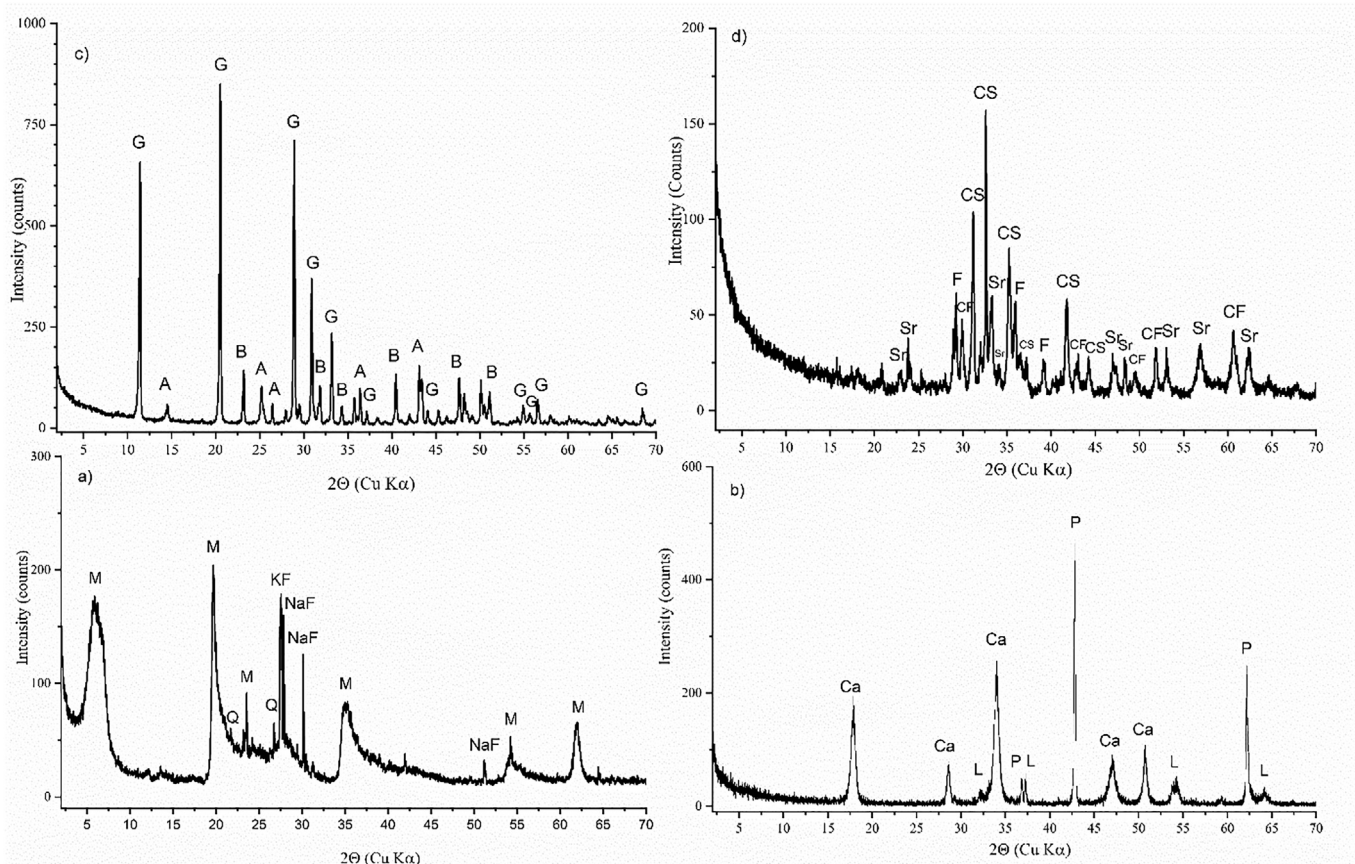**Fig. 1.** The appearance of specimens prepared from the main mixtures.

Fig. 2. XRD spectra of the raw materials : a) Bentonite (M : montmorillonite, KF : K-feldspar, NaF : Na-feldspar, Q : Quartz). b) Lime (L: lime, P: periclase, Ca: calcite. c) Phosphogypsum (G : gypsum, B : hemihydrate, A : anhydrite). d) Steel slug (CF: calcium ferrite, CS: calcium di-silicate, Sr: srebrodoskite, F: fayalite).
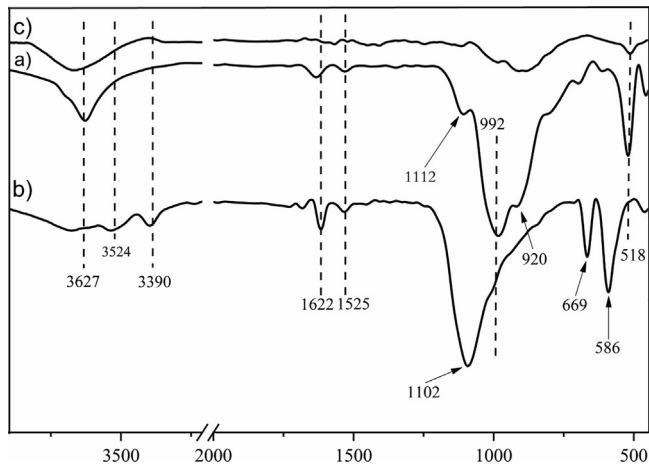

Fig. 3. Infrared spectra of the raw materials: a) Bentonite, b) Phosphogypum, c) Steel slug.

and remained unchanged for the first 3 days of immersion. In this strongly basic conditions pozzolanic reactions, which consume the OH^- ions, are slow [13]. After 3 curing days, a significant decrease in pH for all the mixtures was showed. A marked decrease is showed when PG or PG and Sc is added to bentonite. After 15 curing days, the pH stabilizes for the B-L-PG and B-L-PG-Sc mixtures, but it continues to drop for the B-L mixture. The pozzolanic reactions continue in bentonite mixed with lime. In the presence of PG, the formation of primary ettringite stabilizes the pH [14].

The electrical conductivity (χ) depends on the concentration of ions in very dilute solutions (10^{-2} mol / L), it is expressed in $S.mol^{-1}$ by $\chi = n. [ion^{\pm n}].\Lambda$, with n: valence of the ion, $[ion^{\pm n}]$: the concentration in mol / m^3 and Λ is the ionic molar conductivity expressed in $S.m^2.mol^{-1}$ [15].

We have found that the evolution of the electrical conductivity is identical to that of pH. It decreases sharply as a function of the residence time of the test pieces in an aqueous solution. The decrease is greater for the B-L mixture. The consumption of the ions which take part in the pozzolanic reactions could be the cause

Table 1
Consistency limits and pH values of raw bentonite and the main mixtures.

Samples	B	B-Sc	B-PG	B-L	B-L-PG	B-L-PG-Sc
USCS	CH	CH	CH	MH	MH	MH
Plastic index (%)	72.5	64.8	62.2	42.4	31	26.3
Liquid limit (%)	103	99.4	96.3	81.7	67.4	61
Plastic limit (%)	30.5	34.6	34.1	39.3	36.4	34.7
pH_0	8.72	10.9	7.57	12.6	12.1	12.9
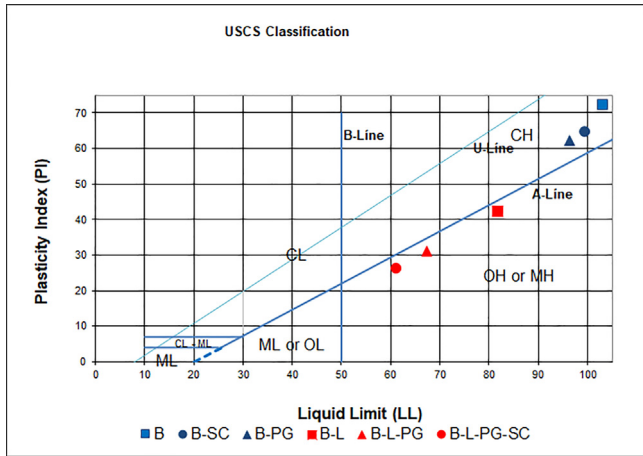
Fig. 4. Plasticity evolution of bentonite with the addition of the lime, PG and Sc aggregates.

Fig. 6. Evolution of mechanical resistance as a function of the mixing water content.

of this reduction. When PG or Sc are added to bentonite, other ions with high ionic molar conductivity are added to the solution.

4.3. Resistance to axial compression and optimal mixing water amount

The resistance to axial compression increases with increasing water content added to the mixtures (Fig. 6). As the amount of water added to the mixtures increases, the mechanical properties after 28 days of setting, are improved for all mixtures. When the bentonite grains become better hydrated, the CSH gel forms quickly and their consolidation progresses favorably [16]. Pozzolanic reactions are activated when the mobility of the ions is favored. With a water / solid ratio = 46%, the mechanical compression takes a maximum value for the different mixtures. We also observe that the addition of PG or PG + Sc decreases the optimal water content, this can be explained by the fact that the addition of PG and PG + Sc decreases the liquid limit of bentonite implying that the transition from the plastic state to the liquid state requires less water compared to the mixture B-L.
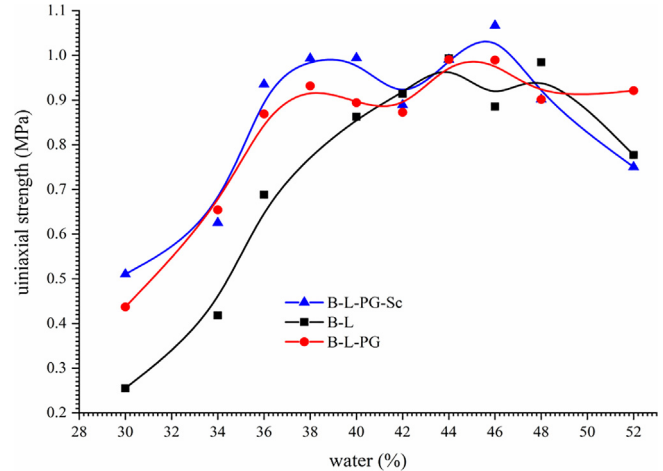
When the quantity of water is added exceed 46%, the ions responsible for setting are drained by gravimetry and the setting of the specimens is not done homogeneously. This heterogeneity in the texture weakens the resistance of the materials to compression. The evolution of the compressive strength increases over time for the different test pieces (Fig. 7). After 28 days, an increase is observed for the BL-PG and BL-PG-Sc mixtures compared to the B-L, which confirms the results of the previous work done for the BL-PG mixture [7,9].

The change in compressive strength is inversely proportional to the change in pH and electrical conductivity (Fig. 6). This inversion is probably due to the fact that the more basic solution in the mortar pores, more bentonite is altered and the formation of the hydrates responsible for setting is more important. After 15 days of hydration, pH and electrical conductivity stabilize, and the evolution of the resistance to compression continues to increase. This can be explained by the fact that the formation of C-S-H gel and other stable hydrated phases responsible for setting consume the ions in solution, particularly the hydroxide ions OH^-. It should be
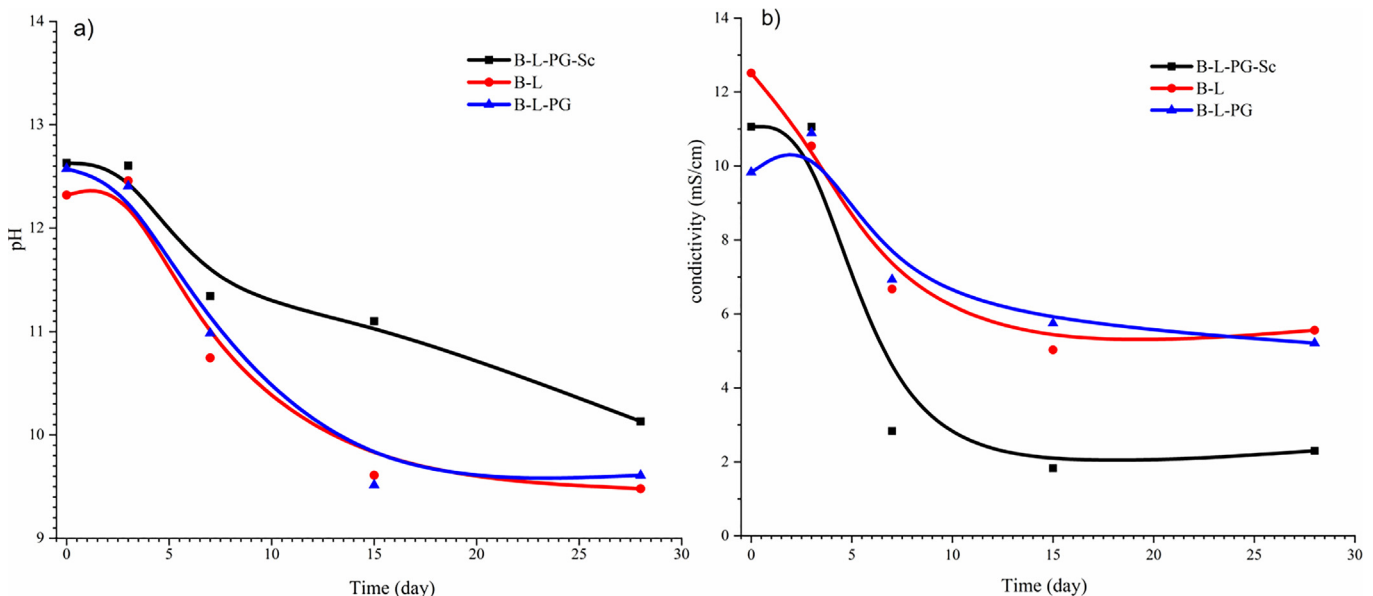

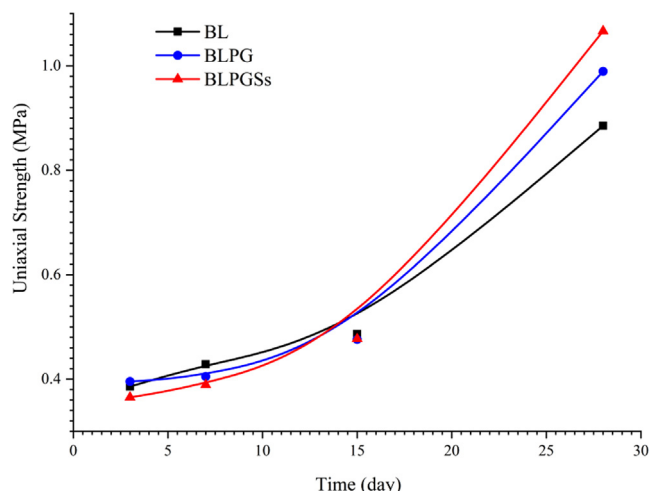Fig. 5. Variation of a) pH and b) conductivity.

Fig. 7. Variation of compressive strength with the curing time.

noted that the higher resistance due to the addition of PG may be associated with the formation of ettringite. The formation of ettringite gives homogeneity to the mixture, which strengthens the mechanical properties [17]. The presence of calcium silicate (Ca_2SiO_4) in the slag would have contributed to the increase in the resistance of the B-L-PG-Sc specimen.

5. Conclusion

The characterization and recovery of solid industrial mining waste comes up against the problem of homogeneity and constitution of raw materials. They generally consist of several phases which show sometimes opposite reactivities. In this study, we investigated the possibility of recovering two solid industrial wastes; phosphogypsum (PG) from the phosphate industry and black steel slag (Sc) produced by the electric steel industry in the field of civil engineering:

The results showed that the addition of 8% PG or Sc slightly influences the plastic limit and the plasticity index of bentonite, and the addition of 8% lime strongly decreases the plastic behavior of bentonite.

Compressive strength is inversely proportional to pH and electrical conductivity. The composition of the solutions in the pores control the mechanical performance of the tested mixtures.

The addition of PG and steel slag increases the compressive strength of the bentonite-lime mixture after 28 days of hydration. The formation of ettringite after the addition of PG gives the homogeneity for the mixtures which reinforces their mechanical properties. The presence of calcium silicate (Ca_2SiO_4), found in Portland cements, in slag increases the compressive strength of the B-L-PG-Sc mixture.

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