

Article

Strength and Microstructure of a Clayey Soil Stabilized with Natural Stone Industry Waste and Lime or Cement

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Abstract: Industrial waste generated by the natural stone industry when working with limestone and dolostone is mainly composed of calcium carbonate and calcium magnesium carbonate. This mineral composition makes soil stabilization a potential use of the natural stone industry waste. However, much research must be carried out to fully understand the aptitude of this waste for soil improvement. In this work, the strength and microstructure of a clayey soil stabilized using limestone powder waste and lime or cement were studied employing the following techniques: unconfined compressive strength tests, mercury intrusion porosimetry, thermogravimetric analysis, X-ray diffraction, and scanning electron microscopy. Moreover, the effects of an aggressive environment were simulated using a sodium sulfate solution. Its effects were investigated from 7 days to 6 months. The results obtained show an increase in the unconfined compressive strength and a more compact structure for the samples with the industrial waste. Therefore, limestone powder waste from the natural stone industry can be used as a ternary element with lime and cement in soil stabilization.

Keywords: soil improvement; industrial limestone waste; by-product; lime; cement



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1. Introduction

Industrial activities generate a large amount of waste that cannot be simply dumped into landfills due to its adverse environmental effects. Waste and industrial by-products must be managed to ensure sustainability and achieve the Sustainable Development Goals adopted by the United Nations. Soil stabilization is one of the potential uses of industrial waste. Soil stabilization is used to improve the geotechnical properties of natural soils when they do not have the acceptable strength or stiffness to be used for embankments or other earth fills. Lime and cement are the most common binders used in soil stabilization. Despite the great properties obtained in binder-treated soils, research on obtaining sustainable materials to be used for soil stabilization has increased significantly in recent years due to the adverse effects on the environment caused by the binder-making process, such as high CO₂ emissions and the use of vast amounts of raw material. For example, the use of ground granulated blast furnace slag has resulted in a reduction of the swelling potential [1] and an increase in the soil shear strength [1–3]. Fly ash has also been studied for soil stabilization with good results, reporting a decrease in plasticity and an increase in soil strength [4–6]. Other industrial by-products, such as waste glass, are also being investigated for soil improvement [7,8]. These sustainable materials can be used as a partial replacement for traditional binders, especially inert by-products. For example, class C fly ash and lime are a good combination for stabilizing silty and sandy soils [9,10]. Horpibulsuk et al. [11] found that the pozzolanic reaction of fly ash was minimal when mixing it with a blended cement-stabilized silty clay. Nevertheless, fly ash was shown to have a positive effect on soil stabilization. Jiang et al. [12] studied the effect of silica fume on the microstructure of a soft soil stabilized with cement. This research concluded that silica fume can reduce the voids in the mixed soil, increasing its strength. However, an excess in the silica fume content

employed can result in the opposite effect. Recycled-glass powder was also studied as an additive to soil stabilization with lime [13]. The results obtained showed an improvement in the microstructure and the mechanical properties of the mixed soil when increasing the glass powder content. Jayanthi and Singh [14] reviewed the utilization of some sustainable materials (fly ash, cement kiln dust, blast furnace slag, rice husk ash, silica fumes, red mud, and textile waste) for soil stabilization, concluding that there was a need for further research to make these materials a practical replacement of the commercial binders. Moreover, solid waste and limestone materials are widely immobilized in cement-based materials [15,16].

Limestone powder is an industrial waste generated from cutting and polishing works by the natural stone industry. This industry is present in many countries worldwide. The global market for the natural stone industry was estimated to be 18 trillion metric tons in the year 2020 and is expected to be about 23 trillion metric tons by 2027 [17]. Due to the large amount of waste generated, efforts are being made to find a constructive use for this limestone powder, transforming the industrial waste into an industrial by-product. Figure 1 shows the temporary landfill for limestone powder waste of a single company in southeastern Spain. Some promising results have been reported when studying natural stone industry waste, which is mainly composed of calcium carbonate, in soil stabilization. Amongst these positive results, a reduction in the Atterberg limits [18–21], a reduction in the free swell index [20–24], and an increase in the strength of mixed soil [20–22,25] can be highlighted. Studies about using this industrial by-product as a ternary element, combined with lime or cement, in soil stabilization are very limited. The results reported by Ahmed et al. [26] showed an increase in the California Bearing Ratio (CBR) of soil when using limestone powder with lime. Similar results were found by Deboucha et al. [27] for marble dust used with ordinary Portland cement for soil stabilization. Due to the lack of other similar studies, some ideas can be extracted from the by-product's chemical nature and the research about other materials with similar composition. In this sense, Ment et al. [28] found that the addition of CaCO_3 nanoparticles in a cement-stabilized soil can improve the compressive strength of the soil due to the nucleation effect and the filling function of these particles. This nucleation effect has been extensively reported when studying cementitious materials such as mortars or concretes [29–31]. The nucleation effect of limestone powder increases with a decrease in the particle size of CaCO_3 or an increase in the amount of CaCO_3 [32]. Wang et al. [31] also concluded that the pore structure of cementitious materials can be refined by incorporating CaCO_3 as a fine limestone powder. In this sense, an improvement in the hydration degree of cement and a denser structure due to its filling effect at an early age was reported by Jiang et al. [33] when limestone powder was used for the preparation of blended cements. Kechagia et al. [34] studied the use of marble dust waste in the production of ternary blended cements, concluding that this by-product could be valorized as a cementitious addition for cement replacement. There have been fewer studies about the use of CaCO_3 with lime. In this sense, Segura et al. [35] studied the influence of recycled limestone filler additions on lime mortars, concluding that a positive impact on the mechanical strength was observed after 56 days due to the nucleation effect. Previous research on limestone powder waste as a ternary element for soil stabilization is very limited and has not covered the strength and microstructure of mixed soil. Former studies have focused on the effect of limestone powder on cement-based materials, but the mineralogy of soils can change this effect. Thus, the study of the microstructure of mixed soil using natural stone industry waste as a ternary additive with lime or cement with different techniques is a novelty in this work.

Sulfates are sometimes present in soils and groundwater due to their geological origin or other causes. It is well known that sulfates can negatively affect lime and cement-stabilized soils [10], resulting in the phenomenon termed sulfate-induced heave [36]. Ettringite, a highly expansive mineral, is formed when the calcium from the binder reacts with soil sulfates in the presence of aluminum compounds in an alkaline environment caused by binder hydration. The harmful effect of sulfates can be modified when using industrial by-products. For example, ground granulated blast furnace slag on lime-stabilized

sulfate-bearing soils reduces the harmful effect of sulfate in soils [37,38]. Then, the use of limestone powder in soil stabilization with calcium-based stabilizers can also affect the durability conditions of the mixed soil. Nevertheless, the effect of an aggressive medium on the microstructure of the soil mixed with limestone powder waste as a ternary element has not been previously investigated. This issue is also a novelty of the present work. Therefore, although the subject is not new, this study represents a considerable increase in the information currently available.



Figure 1. View of a natural stone company's temporary landfill for limestone powder waste in southeastern Spain.

2. Materials and Methods

2.1. Soil

A fine-grained soil of low–medium plasticity was used for this study. The soil consisted of 88% by weight of fines passing through a 0.08 mm sieve, and 100% passing through a 2.0 mm sieve. The amounts of clay (<0.002 mm) and silt particles (0.002–0.06 mm) were 60 and 25%, respectively. The soil had a liquid limit of 44.6 and a plasticity index of 20.8. This soil was classified as CL according to the Unified Classification System (USCS) [39]. The natural moisture content of the soil was 31%. The main mineral composition was obtained by a semiquantitative mineralogical analysis performed using X-ray diffraction, the results of which are shown in Table 1.

Table 1. Soil sample composition by a semiquantitative mineralogical analysis performed using X-ray diffraction.

Property	%
Illite	28.7
Calcite	22.5
Quartz	19.4
Gypsum	7.6
Montmorillonite	5.9
Kaolinite	3.9

2.2. Industrial Waste

The industrial waste used in this study was obtained from a dumpsite of the natural stone industry where polishing and cutting works are performed. The natural rocks used by this industry are mainly limestone and dolostone. Therefore, the powder obtained from

cutting and polishing works is mostly composed of carbonates (CaCO_3 and $\text{CaMg}(\text{CO}_3)_2$). This was confirmed by semiquantitative X-ray diffraction, which confirmed a composition of 67.8% calcite and 26.1% dolomite. The limestone powder consisted of 100% by weight of fines passing through the 0.08 mm sieve. Most of the particles (70%) were silt-sized particles (0.002–0.06 mm), and 30% represented the amount of clay-sized particles (<0.002 mm).

2.3. Lime

A commercial lime classified as CL 90 S was used for this study. This product is a calcic lime with a minimum content of 90% of $\text{CaO}+\text{MgO}$ according to the Spanish/European Standard UNE EN 459-1 [35].

2.4. Cement

A commercial cement classified as CEM IV/B (V) 32.5 N-SR was employed as a hydraulic binder. This is a pozzolanic cement with a supplementary cementing material content (fly ash) making up 36 to 55% of the total binder and is classified as a sulfate-resisting cement according to the Spanish/European Standard UNE EN 197-1 [40]. The loss on ignition of the cement is equal to or less than 5%.

2.5. Sample Preparation

The natural moisture content of the soil was employed for the sample preparation in order to simulate a hypothetical real mixing of the soil, hydraulic binder, and industrial by-product at the field. Firstly, a moisture content of 31% was added to the oven-dried soil. Afterwards, dry limestone powder was added and mixed until a homogeneous mixture was reached. Samples were prepared using 0 and 25% of industrial waste by the total dry weight of the soil. Finally, 9% of the hydraulic binder (lime or cement) was added and combined until a homogeneous mixture was obtained. The time to obtain homogeneous mixtures was set at 5 min based on the observation of the process for the highest percentage of addition. The percentages of industrial waste and commercial binder employed in this research were decided based on previous results, where the unconfined compressive strength was determined for samples made with 3, 6, and 9% commercial binder and 0 to 25% waste. The highest unconfined compressive strength was obtained for 25% waste and 9% commercial binder [41]. In addition to the samples made with distilled water, other samples were made with Na_2SO_4 solution to investigate the effect of sulfate-aggressive water on the stabilized soil. The solution used had a concentration of 3000 mg SO_4^{2-} per liter. This concentration was employed because it is the threshold for considering groundwater as highly aggressive for concrete according to the Spanish Standards [42,43].

The samples were prepared in metal molds 50 mm in diameter and 100 mm in height using standard Proctor compaction energy. The samples were tested at 7 days and at 3 and 6 months to understand the evolution of the mixed soil characteristics over time. The samples were stored in a curing room with a temperature of 20 ± 2 °C and 95% relative humidity until being tested.

A summary of the samples prepared for the study is presented in Table 2.

Table 2. Summary of the samples prepared.

Sample	Binder	Industrial Waste	Sulfate Solution
LM9LP0	Lime 9%	0%	No
LM9LP25	Lime 9%	25%	No
LM9LP0 Sulf	Lime 9%	0%	Na_2SO_4
LM9LP25 Sulf	Lime 9%	25%	Na_2SO_4
CM9LP0	Cement 9%	0%	No
CM9LP25	Cement 9%	25%	No
CM9LP0 Sulf	Cement 9%	0%	Na_2SO_4
CM9LP25 Sulf	Cement 9%	25%	Na_2SO_4

Samples tested at 7 days and at 3 and 6 months.

2.6. Unconfined Compressive Strength (UCS)

Standard Proctor compaction energy was applied to obtain samples 50 mm in diameter and 100 mm in height. The standard UNE 103400 [44] was used for determining the unconfined compressive strength of the samples. UCS is determined as the maximum compressive stress value when the curve normal stress vs. the axial strain shows a peak or as the compressive stress value at an axial strain of 15% if the curve normal stress vs. the axial does not show a peak. The UCS values were determined as the mean value of three samples for each dosage and age.

2.7. pH

The pH of the mixed soil was determined in 1:2.5 soil/water extract. For this procedure, 10 g of the dried soil was added to 25 mL of distilled water and stirred for 10 min. After approximately 30 min, when the solution was clear, electrodes were immersed and the pH value was determined [45].

2.8. Mercury Intrusion Porosimetry

An Autopore IV 9500 from Micrometrics was employed for mercury intrusion porosimetry. Pore diameters between 5 nm and 0.9 mm can be determined using this equipment. Before performing tests, the samples were oven-dried for 48 h at 40 °C.

2.9. Thermogravimetric Analysis (TGA)

DTA-TG tests were performed using GT-DSC2 equipment (Mettler-Toledo, Barcelona, Spain) with a balance accuracy of 0.1 mg. The dynamic heating ramp varied from 30 to 1000 °C, and the heating rate was 10 °C/min.

2.10. X-ray Diffraction

X-ray diffraction was used to characterize changes produced in the mineralogy of the samples over time. A Bruker D8-Advance X-ray diffractometer (Bruker, Billerica, MA, USA) with a high-temperature chamber (up to 900 °C) was used. The generator of the apparatus was an X-Ray Kristalloflex K760-80F (Siemens, Karlsruhe, Germany), power of 3000 W, voltage of 20–60 KV, and current of 5–80 mA provided with a copper anode.

2.11. Scanning Electron Microscopy (SEM)

The observation and study of the mixed soil samples were carried out in a JEOL JSM-840 Scanning Electron Microscope (WEMTech Solutions, Billerica, MA, USA) at 10 to 15 kV accelerating voltages. The samples were made conductive by coating them with gold.

3. Results

3.1. Unconfined Compressive Strength (UCS)

The unconfined compressive strength of the samples is shown in Figure 2. A general trend of strong growth was observed when adding limestone powder to a clayey soil as a ternary element together with lime or cement. Moreover, the samples made with cement had greater values than the samples made with lime at all ages. For the lime samples, the UCS increased from 7 days to 6 months for all samples (with and without limestone powder and using distilled water and the sulfate solution). Therefore, for the lime samples without limestone powder and those made using distilled water, the UCS increased by 249% from 7 days to 3 months and by 303% from 7 days to 6 months. The UCS of the lime samples with limestone powder and those made using distilled water increased by 86% from 7 days to 3 months and by 124% from 7 days to 6 months. Moreover, the UCS was greater for the samples composed of 25% limestone powder than for those without the industrial by-product. This effect can be seen from 7 days to 6 months. The lime samples with limestone powder and made using distilled water had a UCS value 127% greater than the samples without the industrial waste at 7 days, with a reduction in this increase to 21% at 3 months and 26% at 6 months. The samples made with the Na₂SO₄ solution showed

very similar behavior to those made with distilled water. However, the UCS of the samples made with the Na_2SO_4 solution was 5% greater than those made with distilled water for both types of samples (with and without limestone powder) at 6 months.

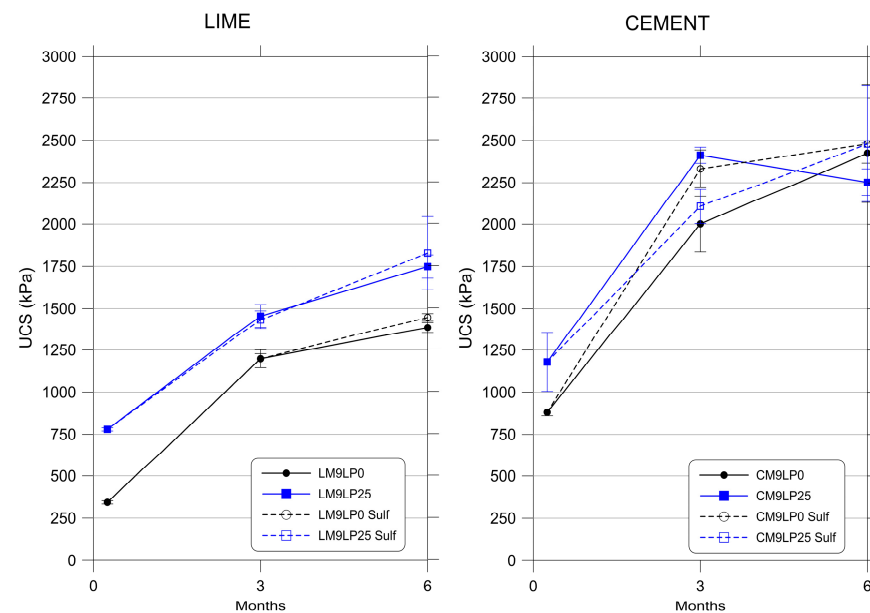


Figure 2. Unconfined compressive strength for lime and cement samples with and without industrial waste at 7 days and at 3 and 6 months.

Regarding the cement samples, the UCS increased from 7 days to 6 months for the samples made without limestone powder and with the industrial waste and sulfate solution. Nevertheless, the UCS of the samples made with limestone powder and those made with distilled water decreased slightly. Therefore, the UCS increased by 127% from 7 days to 3 months and by 175% to 6 months for cement samples without the industrial waste and those made with distilled water, respectively. The UCS of the cement samples with the industrial waste and distilled water increased by 105% from 7 days to 3 months and by 91% from 7 days to 6 months. Concerning the samples made with the Na_2SO_4 solution, the samples without the industrial waste increased their UCS by 165% at 3 months and by 181% at 6 months. Meanwhile, the increase in the UCS of the cement samples with the industrial by-product was smaller, rising by 79 and 110% at 3 and 6 months, respectively. Similar to the lime samples, the UCS values of the cement samples made with the Na_2SO_4 solution were greater than for those made with distilled water.

3.2. pH

The pH results are depicted in Figure 3. The lime samples had a nearly constant value from 7 days to 6 months. This behavior was observed for all lime samples, with and without the industrial waste, and for the samples made with distilled water and for those made using the Na_2SO_4 solution. The pH values recorded for the lime samples were between 12.2 and 12.4.

Regarding the cement samples, the pH values decreased slightly from 7 days to 3 months and rose slightly from 3 to 6 months. The pH changes over time for the cement samples were higher than for the lime samples, varying from 10.8 to 9.9 for samples without the industrial waste with distilled water and to 9.6 for samples without limestone powder made with the sulfate solution. For samples made with the industrial waste, the changes in the pH value were from 10.3 to 9.4 and 10.2 for samples made with distilled water and with the sulfate solution, respectively.

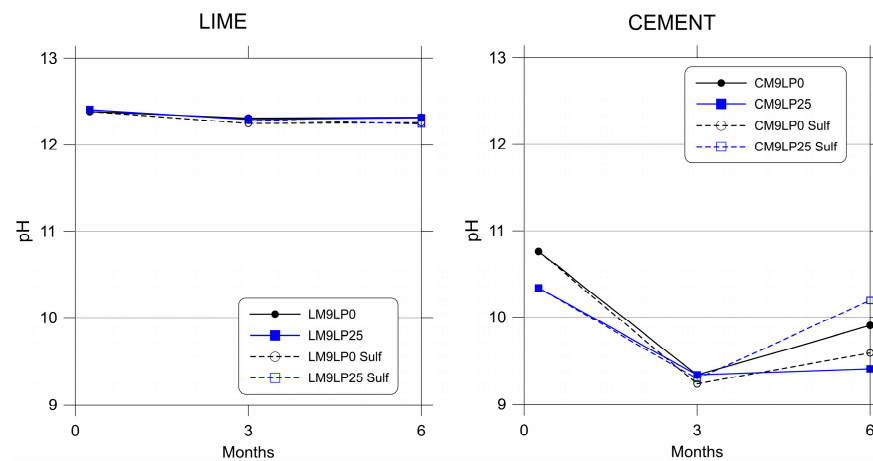


Figure 3. pH for lime and cement samples with and without the industrial waste at 7 days and at 3 and 6 months.

3.3. Mercury Intrusion Porosimetry

The total porosity, the Hg retained at the end of the experiment, and the pore size distribution of the mixed soils are described in this section. The total porosity results are depicted in Figure 4. The samples mixed with the industrial waste had lower values of total porosity than the samples without the waste. This was recorded for all types of samples, with lime or cement and made using distilled water or the sulfate solution. Regarding the changes experienced by the samples over time, a general trend of decreasing total porosity was observed for all samples except the lime samples with the industrial waste made using the Na_2SO_4 solution. From 3 to 6 months, the total porosity slightly increased for all samples made using distilled water, while a decrease was observed for the samples made using the sulfate solution, except for the cement samples with limestone powder, whose total porosity slightly rose.

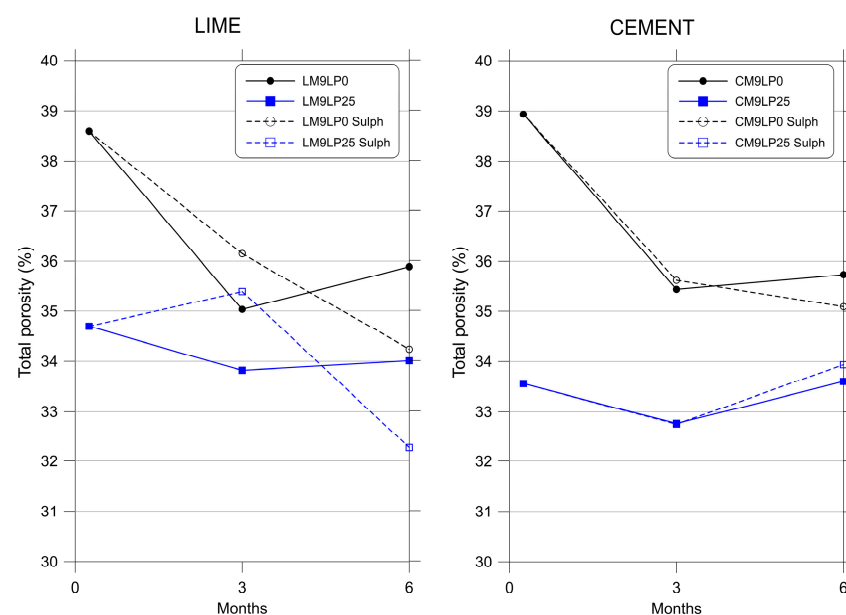


Figure 4. Total porosity of the lime and cement samples with and without the industrial waste at 7 days and at 3 and 6 months.

The pore size distribution of the samples can be observed in Figure 5. An increase in the percentage of pores with a diameter smaller than 100 nm (microstructure refinement)

was observed from 7 days to 3 months for all the specimens. Nevertheless, a decrease in the refinement was recorded from 3 to 6 months for all the samples. This reduction was very clear for the lime samples without the industrial waste. On the contrary, the decrease was not so obvious for the lime samples with the industrial waste. The cement samples showed a small decrease in the microstructure refinement from 3 to 6 months. As for the lime samples, similar refinements were observed for the cement samples without the industrial waste and the samples made using distilled water and the sulfate solution. Nevertheless, the samples made with the Na_2SO_4 solution had a more refined microstructure at 3 months, although similar refinements were observed at 6 months due to a more significant decrease in the microstructure refinement in the samples made using the sulfate solution than in those made using distilled water, whose microstructure did not change significantly from 3 to 6 months.

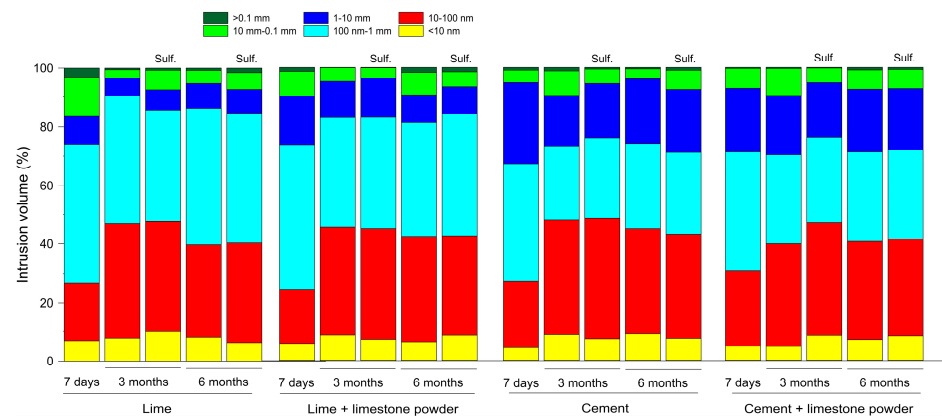


Figure 5. Intrusion volume for lime and cement samples with and without the industrial waste at 7 days and at 3 and 6 months.

Finally, the Hg retained at the end of the experiment was recorded, as this parameter provides information on the possible tortuosity of the pore network [46]. The Hg retained by the cement samples was higher than those retained by the lime samples for all the specimens and at all ages. All the samples had a reduction in the retained Hg from 7 days to 3 months. Nevertheless, from 3 to 6 months, the retained Hg remained broadly constant for all the samples, as shown in Figure 6.

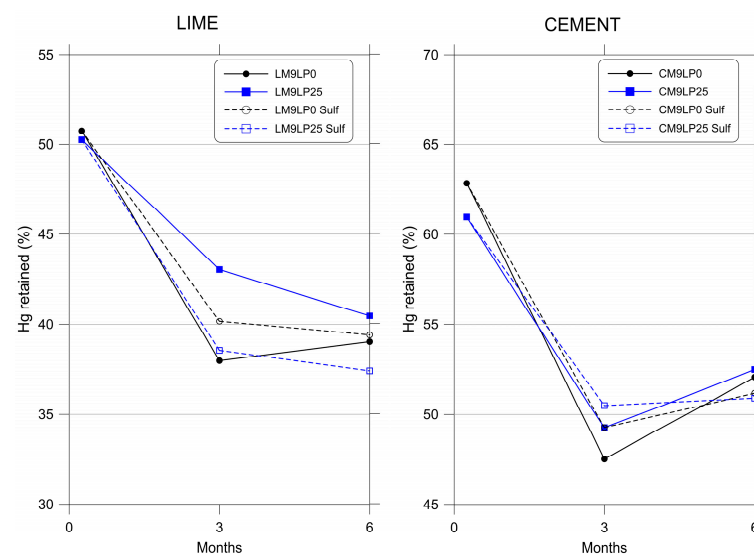


Figure 6. Hg retained for lime and cement samples with and without the industrial waste at 7 days and at 3 and 6 months.

3.4. Thermogravimetric Analysis (TGA)

The TGA results obtained for the lime and cement samples are shown in Tables 3 and 4, respectively. Three regions corresponding to the hydrated compounds were defined as dehydration (dh), ihydroxylation (dx), and decarbonation (dc), with the temperature ranges established by Monteagudo et al. [47]. Dehydration losses include the decomposition of ettringite, as explained by Monteagudo et al. [47]. Very similar behaviors were observed for the lime and the cement samples. The weight loss during the dehydration process was lower for the samples made with the industrial waste. On the contrary, the weight loss during the decarbonation process was much higher for the samples with the industrial waste. This effect can also be seen in the TGA curves presented in Figure 7. No significant difference was observed for the samples made with distilled water or the sulfate solution. Regarding the evolution of the weight loss at different ages, only weight loss during the decarbonation process seemed to show some change over time. The weight loss during the decarbonation process appeared to slightly increase from 7 days to 3 months.

Table 3. Relative values from DTA-TG tests for lime samples.

Binder	Industrial Waste	Sulfate Solution	Curing Age	Weight Loss (%)		
				dh	dx	dc
Lime	No	No	7 days	7.398	1.553	9.832
			3 months	7.346	2.016	10.944
			6 months	7.479	1.974	10.729
	Yes	No	7 days	6.074	1.275	16.364
			3 months	6.457	1.797	17.549
			6 months	6.748	1.903	17.287
	No	Yes	7 days	7.398	1.553	9.832
			3 months	6.727	2.124	12.131
			6 months	7.530	1.739	11.978
	Yes	Yes	7 days	6.074	1.275	16.364
			3 months	5.634	1.903	17.936
			6 months	6.810	1.896	17.052

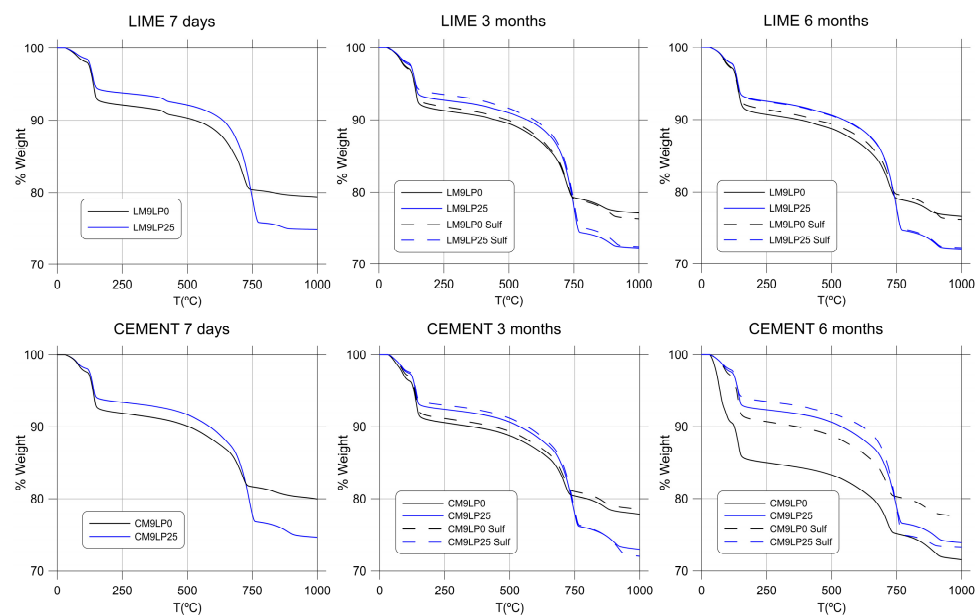


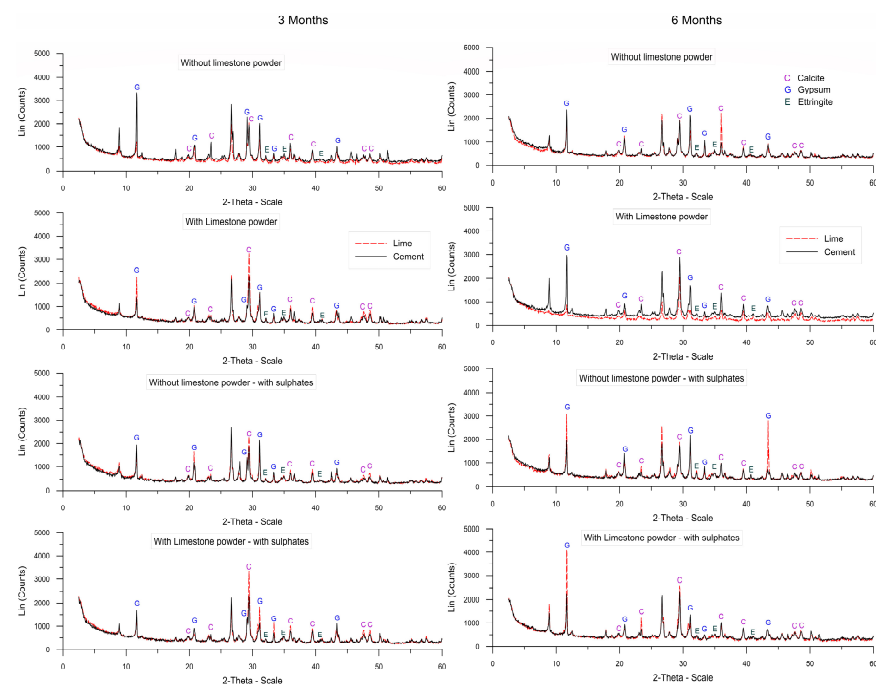
Figure 7. TGA curves at 7 days and at 3 and 6 months.

Table 4. Relative values from DTA-TG tests for cement samples.

Binder	Industrial Waste	Sulfate Solution	Curing Age	Weight Loss (%)		
				dh	dx	dc
Cement	No	No	7 days	6.984	2.089	8.674
			3 months	7.126	2.044	9.594
			6 months	7.030	1.934	10.400
	Yes	No	7 days	5.847	2.187	15.484
			3 months	6.254	2.077	16.262
			6 months	6.481	2.041	15.276
	No	Yes	7 days	6.984	2.089	8.674
			3 months	7.127	2.009	9.485
			6 months	7.673	2.114	9.737
	Yes	Yes	7 days	5.847	2.187	15.484
			3 months	5.897	2.074	17.763
			6 months	5.714	1.610	17.447

3.5. X-ray Diffraction

X-ray diffraction analysis of the samples was performed at 3 and 6 months to characterize the changes that may have occurred in the mixed soil (Figure 8). Changes in the gypsum, calcite, and ettringite were studied to better understand the compounds formed over time in the mixed soil depending on the hydraulic binder employed, the addition of the industrial waste, and the solution used for the sample preparation. The X-ray diffraction analysis showed that more gypsum was generated for the lime samples made using the sulfate solution than for the cement samples made using the same solution. However, more gypsum was detected in the cement samples than in the lime samples when distilled water was used. Moreover, more gypsum was observed in the lime and cement samples made without industrial waste. Regarding the calcite compound, the biggest quantity of calcite was recorded for the lime samples with industrial waste. Concerning the change over time, the amount of gypsum seemed to have increased for the lime samples made using the Na_2SO_4 solution from 3 to 6 months. Additionally, a slight increase in ettringite was observed for the samples without industrial waste at 6 months when those samples were made using the sulfate solution. Lastly, a decrease in the calcite compounds seemed to have occurred from 3 to 6 months in the lime samples made using the sulfate solution.

**Figure 8.** X-ray diffraction analyses of the lime and cement samples at 3 and 6 months.

3.6. Scanning Electron Microscopy (SEM)

The samples made with lime and cement were visualized by SEM at 3 and 6 months. Some of the images recorded are shown in Figures 9 and 10. The lime samples with the industrial waste (Figure 9b,d) presented a more compact structure than that observed in the samples without the industrial by-product (Figure 9a,c). Similarly, the lime samples made using the sulfate solution (Figure 9c,d) presented a closer structure than those samples made using distilled water (Figure 9a,b). Analogous tendencies were observed in the cement samples. However, in this case, the differences appear to be more obvious. Thus, the cement samples with the industrial waste (Figure 10) presented a more compact structure than that observed in the samples without the industrial by-product (Figure 10a,c). Moreover, the cement samples made using the sulfate solution (Figure 10c,d) presented a closer structure than those samples made using distilled water (Figure 10a,b).

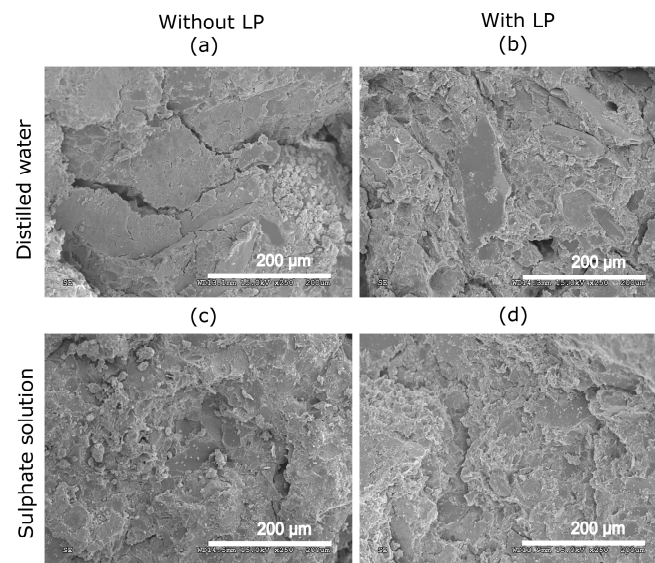


Figure 9. SEM images of lime samples at 6 months (a) without the industrial waste and with distilled water, (b) with the waste and distilled water, (c) without the waste and with the sulfate solution, and (d) with the waste and sulfate solution.

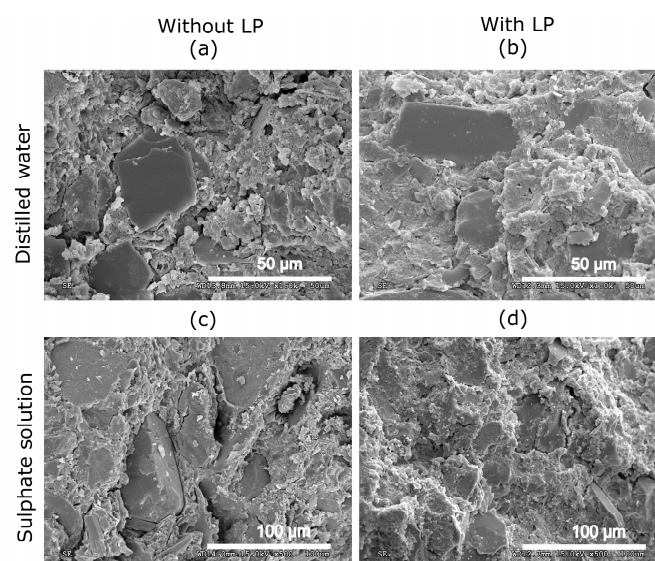


Figure 10. SEM images of cement samples at 6 months (a) without the industrial waste and with distilled water, (b) with the waste and distilled water, (c) without the waste and with the sulfate solution, and (d) with the waste and sulfate solution.

Furthermore, some ettringite crystals were detected in some of the samples, especially in those made with the Na_2SO_4 solution. Nevertheless, the amount and size of the ettringite crystals observed were small in all cases (Figure 11).

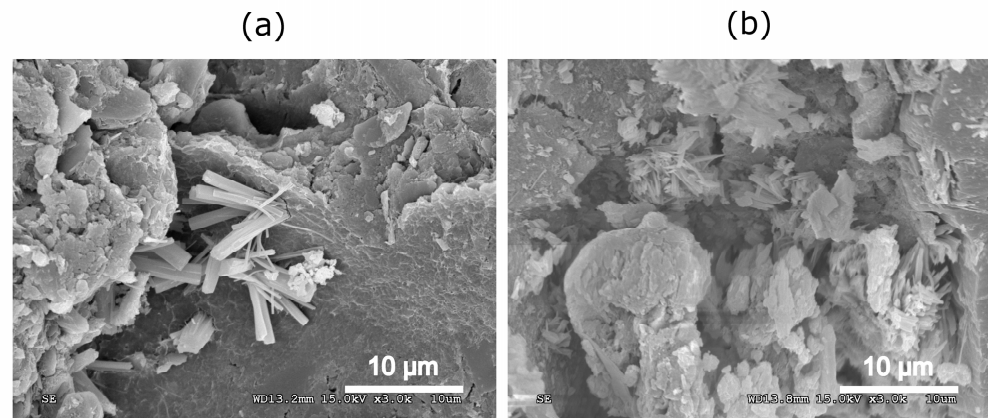


Figure 11. SEM images of ettringite crystals at 6 months in (a) cement samples without the industrial waste and with the sulfate solution and (b) lime samples with the waste and sulfate solution.

4. Discussion

A general trend of increasing strength was observed when adding the industrial waste to a clayey soil as a ternary element together with lime or cement. For the cement samples, the UCS increased by 34% in 7 days when using limestone powder. These results agree with those obtained by Mustafa et al. [48], who reported an increase of about 100% when 20% limestone powder was added to a marly soil with 2.5% ordinary Portland cement. In the study, the UCS obtained with 2.5% cement and 20% limestone powder was greater than that obtained with 7.5% cement but without limestone powder. Thus, this industrial by-product showed a very positive effect on soil stabilization as a partial cement replacement. Similar results were stated by Bazarbekova et al. [49], as the UCS of a silty sand increased by about 18% when 2% of the industrial waste was added to samples with 6% cement. It was also concluded that the combined use of cement and limestone powder in a sulfate-bearing saline soil presented better behavior from a durability point of view. Although studies on using this industrial waste as a ternary element are very limited, considering the calcareous nature of the by-product, it could be said that similar results were obtained by Meng et al. [28], who reported an increase of up to 22.8% when CaCO_3 nanoparticles were added to a clayey soil stabilized with 15% cement. Moreover, Meng et al. [28] also observed a beneficial effect of the calcareous particles when the samples were affected by an aggressive environment, specifically, a marine environment. Nevertheless, in the present work, a general trend for UCS was not clearly observed when using the industrial waste in the cement samples made using the sulfate solution. Regarding the lime samples, an increase in the UCS was certainly observed when adding industrial by-product to the soil samples with lime. Greater values, up to 127%, were recorded compared to the samples without the by-product. These results agree with those obtained by Amira et al. [26]. In that study, the soil strength was measured with the California Bearing Ratio (CBR) test, reporting an increase in the CBR value of 205% when 24% dolomitic limestone powder was added to soil samples with 3% lime. In addition, an increase in the UCS of mixed soils when using this by-product as a standalone stabilizer has been previously reported [20,21,50].

Regarding the microstructure of the mixed soil, the addition of the industrial waste resulted in a decrease in the total porosity of the samples compared to those without the by-product. This result could be expected from the UCS values, as higher results were observed for samples containing the by-product. Similar results were found in another study when using fly ash as a partial cement replacement, where a reduction in the total porosity was found from 0 to 28 days, remaining approximately constant from this age to 3 months [11].

Similarly, Meng et al. [28] concluded that the addition of CaCO_3 nanoparticles made the soil more compact by the nucleation effect and by filling voids, promoting the generation of cement hydration products. In that study, a beneficial effect on the durability was also stated when nanoparticles were added to the soil in a marine environment. This was also observed in the SEM images. Ibrahim et al. [50] also reported a decrease in the void ratio of a clayey soil improved using limestone powder. In the present study, the evolution of the total porosity showed a general decrease from 7 days to 3 months, remaining broadly constant from 3 to 6 months. The observed decrease was attributed to the reactions between the clay and the cement particles, similar to the pozzolanic reactions that, in the cement samples, resulted in the growth of cementitious products filling the pores. These pozzolanic reactions filling the pores agree with the formation of pores of a smaller diameter and a decrease in the percentage of the bigger pores observed for up to 3 months. It is worth noting that the pH of the samples remained approximately constant over time, so the pozzolanic reaction was not limited because of this factor. No previous results have been reported using cement and limestone powder waste. Nevertheless, Horpibulsuk et al. [4] reported a reduction in the pores smaller than $0.1\ \mu\text{m}$ up to 7 days for a cement-stabilized silty clay. After 7 days, the volume of pores larger than $0.1\ \mu\text{m}$ decreased and the volume of smaller pores increased.

The thermogravimetric analysis showed a clear increase in weight loss during the decarbonation process for the samples with the industrial waste. These results agree with previous results obtained for an expansive soil amended with marble dust [20]. Similar results were observed using X-ray diffraction analysis, where the biggest quantity of calcite was recorded for the lime samples with the industrial waste. This observation was also made by Al-Mukhtar et al. [51] for a lime-treated expansive soil, with the calcite crystals formation (CaCO_3) attributed to the carbonation reaction between the lime, $\text{Ca}(\text{OH})_2$, and the carbon dioxide, CO_2 , existing in the air. However, only lime and natural soil were used in that case. Therefore, in the present study, the effect of the presence of the industrial waste also had to be considered. This result reinforces the idea of nucleation on the surface of the industrial by-product particles. On the contrary, slightly lower values of portlandite seem to be found in the samples with the industrial waste in the TGA analysis. A general trend of slightly increasing $\text{Ca}(\text{OH})_2$ was found when the duration increased, which is in agreement with the results of a previous study using fly ash as a cement partial replacement [11]. The reduction of dehydroxylation over time for the cement samples can be related with the decrease in the total porosity observed in the mercury intrusion porosimetry results. This reduction was attributed to the reaction of the portlandite with the clay minerals filling the pores. This reduction was not observed in the lime samples because the calcium hydroxide was released for a longer time. Moreover, the lime samples showed slightly greater values of weight loss at the dehydroxylation stage than the cement samples. This could be because lime produces $\text{Ca}(\text{OH})_2$, and also because, according to Al-Mukhtar et al. [51], the lime treatment of soils strongly modifies the hydroxylation band in the TGA analysis. No previous results for comparison have been found using limestone powder waste in soil stabilization using this technique.

The increase in the amount of gypsum over time observed by the X-ray diffraction analysis when the samples were made using a sulfate solution could explain the lower values of total porosity obtained by mercury intrusion porosimetry and the more compact structures of these samples observed in the SEM images. In the same way, the SEM images show a more compact structure in the samples with the industrial waste than in the samples without the by-product. This observation agrees with the total porosity and the microstructure refinement observed using mercury intrusion porosimetry for the industrial waste samples. This more compact structure could be due to the nucleation effect of the by-product, as previously reported when using other by-products as a partial binder replacement [4].

Regarding the samples made using the Na_2SO_4 solution, no harmful effect was found in these samples compared to those made using distilled water. A more compact structure

was observed in the SEM images, and lower values of total porosity were recorded for these samples. Moreover, the UCS values recorded were slightly greater for these samples at 6 months. These results could be due to the concentration of the sulfate solution used for the present study, 3000 mg SO_4^{2-} per liter, is the threshold for considering groundwater as highly aggressive for concrete according to the Spanish Standards. In this regard, Harries et al. [52] stated that sulfate concentrations below 7000 ppm can generally be treated with lime. On the other hand, a sulfate-resistant cement was used to make the cement samples, and this would explain the good behavior of these samples made with the sulfate solution. As the soil contained 7.6% of gypsum, the effect of the sulfates contained in the soil must be added to the effect of the sulfate solution. This could explain the little difference observed between the samples made using distilled water and those made using the sulfate solution. Moreover, it is known that sodium sulfate is an activator for other by-products used as stabilizers, such as ground granulated blast furnace slag (GGBS) and fly ash [53,54], so it could also play a role with the industrial by-product that, with the experimental design used, has not been observed. Finally, the CaCO_3 of the industrial waste could have stabilized the ettringite by reacting with the aluminate phase in the cement, as it was stated by Wang et al. for limestone powder in cement-based materials [31].

5. Conclusions

The unconfined compressive strength and the microstructure of a clayey soil stabilized with lime or cement and industrial waste from the natural stone industry were studied. The experimental results show a general positive effect of using this by-product as a ternary element in soil stabilization. The main conclusions drawn from this study can be summarized as follows:

- A clear positive effect was observed on the unconfined compressive strength of the stabilized soil when adding limestone powder as a ternary element together with lime or cement.
- The strengthening effect of the limestone powder waste was higher when using lime as a commercial binder.
- The addition of limestone powder resulted in a more compact structure with lower values of total porosity.
- Limestone powder waste can be used for soil stabilization in a sulfate aggressive medium, as no harmful effect was observed when samples with cement or lime, with or without limestone powder, were made with a sulfate solution of 3000 mg SO_4^{2-} per liter up to the maximum age studied (6 months).
- Limestone powder waste from the natural stone industry enhanced the stabilization effect of lime and cement for soil stabilization.

Future lines of research in this field include an increase in the percentage of industrial waste employed for soil stabilization, studying the influence of the type of soil on the results obtained and the construction of full-scale embankment models to study the real behavior of the mixing soil.

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