

Article

Comparison of Two Sulfate-Bearing Soils Stabilized with Reactive Magnesia-Activated Ground Granulated Blast Furnace Slag: Swelling, Strength, and Mechanism

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Abstract: Sulfate-bearing soils, which causes many engineering problems, e.g., cracking, collapse, and pavement layer settlement, are often encountered in the construction of pavements. Ground granulated blast furnace slag (GGBS)-magnesia (MgO) has been regarded as an effective curing agent in the treatment of sulfate-bearing soil containing gypsum. However, field sulfate-bearing soils usually include other forms of sulfates, such as sodium sulfate (Na_2SO_4) and magnesium sulfate (MgSO_4). Currently, few studies have investigated the effect of the type of sulfate on the properties of sulfate-bearing soil stabilized with GGBS-MgO. In this study, GGBS-MgO was used to treat Ca-sulfate-soil and Mg-sulfate-soil. Swelling, unconfined compressive strength (UCS), X-ray diffraction (XRD), and scanning electron microscopy (SEM) tests were employed to investigate the properties of the stabilized soils. The results showed that when suitable GGBS:MgO ratios were achieved, the swelling of the two types of sulfate-bearing soils could be well suppressed. However, the trend that the swelling varied with the decrease in the GGBS:MgO ratios was opposite between the two soils. The UCS of Mg-sulfate-soils was much lower than that of the Ca-sulfate-soils after the stabilization of GGBS-MgO irrespective of the curing or soaking stage. CSH significantly occurred in Ca-sulfated soils treated by GGBS-MgO. Ettringite was not observed in the soil with GGBS-MgO = 9:1 but was observed in 6:4. Compared to Ca-sulfate-soils, MSH and less CSH were formed in Mg-sulfate-soils stabilized with GGBS-MgO, which caused the lower strength of the stabilized Mg-sulfate-soils. No ettringite was formed in such soils. Hence, the sulfate type contained in the soils had a significant effect on the swelling and strength properties of sulfate-bearing soils with GGBS-MgO, and so the sulfate needs to be identified before the soil's stabilization.

Keywords: GGBS-MgO; Ca-sulfate-soil; Mg-sulfate-soil; swelling; strength; ettringite



Citation: Li, W.; Li, R.; Chen, Y.; Xiao, H. Comparison of Two Sulfate-Bearing Soils Stabilized with Reactive Magnesia-Activated Ground Granulated Blast Furnace Slag: Swelling, Strength, and Mechanism. *Buildings* **2023**, *13*, 230. <https://doi.org/10.3390/buildings13010230>

Academic Editors: Siqi Lin, Xifeng Yan, Binglin Lai, Qingfei Gao and Suraparb Keawsawasvong

Received: 4 December 2022

Revised: 23 December 2022

Accepted: 3 January 2023

Published: 13 January 2023



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1. Introduction

As a problematic soil, sulfate-bearing soil is widely distributed over the world, covering an area of more than 1 billion hectares [1]. Enormous sulfate-bearing soils exist in China, the United Kingdom, and the United States [2–5]. Sulfate is usually present in this soil in the form of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), sodium sulfate (Na_2SO_4), potassium sulfate (K_2SO_4), and magnesium sulfate (MgSO_4). Sulfate-bearing soils, which cause many engineering problems, such as cracking, collapse, and pavement layer settlement, are often encountered in the construction of pavements [6–8]. A 3.5 km (2.2 mi) section of a road in Georgia had unexpected transverse bumps within 6 months after its construction, which was caused by the ettringite formed from cement soil eroded by sulfate. This was also a potential problem in pavement engineering containing sulfate [9]. Therefore, such soils need to be stabilized before they are used in civil engineering. بردان کتی

Calcium-based curing agents, such as cement and lime, have been widely used to treat sulfate-bearing soils. Studies by [4,10–14] showed that the sulfate contained in the soil

reacted with the calcium from the calcium-based curing agent and alumina (from soil and agent) to form ettringite, which will cause an expansion. This ettringite-induced expansion has a negative impact on the subgrade of the road and the soil's foundation [15]. For calcium-based curing agents curing sulfate-bearing soil, Adeleke et al.'s [8] research results showed that the sulfate concentration had a significant impact on the soil's properties after curing. When the sulfate concentration was 10%, the sample expansion rate was at the maximum. Ehwailat et al. [16] made further research on a 10% sulfate concentration, and the research results were mutually verified with predecessors. When the lime content was 20% for curing sulfate-bearing soil, the maximum swelling rate of the sample reached 22.22%. Hence, ground granulated blast furnace slag (GGBS), a by-product of the iron and steel industry, has emerged as a binder of sulfate-bearing soils [17–22] to address the above-mentioned problems. Gokul et al. [23] used GGBS and sodium hydroxide to improve the stability of clay. When the content of the GGBS was 24%, the maximum strength was 4.062 MPa at 28 days under the appropriate ratio. When GGBS was used to partially replace cement, the swelling of the cement was effectively restrained compared with that of cement alone [24]. However, the production of cement will consume an enormous amount of energy and emit lots of CO₂, resulting in the loss of energy and serious environmental problems [19]. The GGBS needs to be activated by alkali to provide the binding force for soils [25]. As an alkali activator, lime has been used for many years to activate GGBS. This is because lime accelerates the hydration of GGBS to form calcium silicate hydrate (CSH) gel, which effectively improves the strength and swelling properties of soils [3,26–29]. When lime-GGBS was used to solidify sulfate-bearing soil, the extension of the drying and curing time can effectively reduce the vertical swelling and crack of the sample. Long time curing will produce more cementitious products, so it can improve the swelling resistance of the sample [29]. However, like cement, lime will damage the environment during the calcination and production. For example, the production of one ton of lime emits about 0.95 tons of CO₂ and consumes about 3200 MJ of energy [30]. Moreover, lime-GGBS can also induce the formation of ettringite and result in the expansion of soils when it was used to treat sulfate-bearing soils due to the introduction of calcium ion sourced from lime [19,31,32].

Recently, it has been proved that magnesia (MgO) had the ability to activate GGBS, and the strength of the soil was greatly improved by MgO-activated GGBS [18,19,33–35]. Li et al. [18] showed that when GGBS was excited by highly active magnesium oxide, the 7 days strength of solidified Ca-sulfate-soil reached its height at 1.9 MPa. This result was consistent with the study conducted by Yi et al. [33]. Seco et al. [36] used magnesium oxide-rich substances and GGBS to stabilize the natural sulfate-bearing soil. The highest strength generally occurred in 14 days and reached 13.4 MPa. Furthermore, Li et al. [18] and Seco et al. [36] showed that MgO-activated GGBS (GGBS-MgO) could better suppress the swelling of gypseous soil (denoted as Ca-sulfate-soil) than cement, and no significant ettringite was formed in the stabilized soil. When GGBS-MgO-stabilized clay was soaked in Na₂SO₄ solution, its durability was stronger than that of cement stabilized clay [31]. Wu et al. [37] showed that when the dry wet cycle exceeds four times, the clay stabilized by GGBS-MgO showed lower E_{50} than that stabilized by cement. As for permeability, when the content of curing agent was 10%, the optimal ratio of GGBS to MgO was 9:1 [38].

The above results indicate that GGBS-MgO is a promising curing agent for stabilizing sulfate-bearing soils. It is worth noting that most of previous studies were on the stabilization of soils containing gypsum (denoted as Ca-sulfate-soils) [3,16,18,39,40], and few scholars paid attention to the impact of the type of sulfate-bearing soils (e.g., soils containing MgSO₄ or Na₂SO₄) on the properties of stabilized soils. Studies by [31] found that GGBS-MgO-stabilized soils did not present ettringite, but exhibited different engineering performance when being attacked by external Na₂SO₄ and MgSO₄ solutions. For example, the stabilized soil specimen flaked off after eroded by the external MgSO₄ solution, whereas did not show this change eroded by Na₂SO₄ the solution. This result indicated that GGBS-MgO-stabilized soils may have different engineering properties when subjected

to an internal CaSO_4 , MgSO_4 , or Na_2SO_4 attack. The internal sulfate attack means the sulfate is a part of soils, i.e., sulfate-bearing soil. Hence, to clarify this issue, this study investigated the strength and swelling properties of Ca-sulfate-soil and Mg-sulfate-soil (i.e., soil containing MgSO_4) stabilized with GGBS-MgO by using the unconfined compression strength (UCS) test and swelling test. X-ray diffraction (XRD) and a scanning electron microscope (SEM) were used to study the mineralogical and micro-structural properties of the stabilized soils associated with exploring the stabilization mechanism.

2. Materials and Methods

2.1. Test Material

The white powder kaolin used in this study was purchased from Guangzhou Chuangke New Material Technology Co., Ltd. The plastic limit, liquid limit, and plasticity index of kaolin were 34.95%, 54.08%, and 19.13%, respectively. The maximum dry density of kaolin was 1.36 g/cm^3 , and the optimal moisture content was 32%. The sulfate-bearing soils used in this study were divided into two types. One type was made of kaolin and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), called Ca-sulfate-soil, and the other one was made of kaolin with magnesium sulfate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), called Mg-sulfate-soil. In both sulfate-bearing soils, the sulfate concentration was set as 20,000 ppm, which belongs to the high sulfate content in civil engineering [3,4,17,39,41].

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ were purchased from Wuhan Xianglong building materials Co., Ltd. and Shanxi Nanfeng Group Chemical Co., Ltd., respectively. GGBS was obtained from Henan Yuanheng Environmental Protection Engineering Co., Ltd. MgO was provided by the Hebei Zhuyan alloy material Co., Ltd. Ordinary Portland cement, type 42.5, was obtained from Dengfeng Zhonglian dengdian Cement Co., Ltd. The chemical composition of the soil and curing agents used in the tests were analyzed by X-ray fluorescence spectroscopy and the results are shown in Table 1.

Table 1. Oxide composition and percentage content of main materials.

Composition	CaO	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃	SO ₃	TiO ₂	K ₂ O	Others
Kaolin	ND	53.90	43.24	ND	0.89	0.08	1.36	0.19	0.34
MgO	5.62	10.23	6.34	76.72	ND	0.55	ND	ND	0.54
GGBS	42.22	31.33	14.82	6.83	ND	2.31	0.79	ND	1.70
Cement	59.39	20.66	5.60	3.87	3.23	4.99	ND	0.10	2.16
Gypsum	58.39	8.32	2.61	5.21	0.72	23.70	ND	0.55	0.50
M	1.21	14.64	7.73	20.09	0.22	55.11	0.07	0.30	0.63

Note: ND—not detected; M— $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

2.2. Test Methods

2.2.1. Mixing and Sample Compaction

Following a previous experimental design [17,18], the content of the curing agent was determined as 10% by the weight of dry soil, and the ratio of GGBS:MgO was 9:1, 8:2, 7:3, and 6:4. The dry material was uniformly blended for 8 min, and then the required amount of water was added and further blended for another 20 min. A splitting mold with a size of $\Phi 50 \text{ mm} \times 100 \text{ mm}$ was utilized to accommodate the compacted specimen. Each specimen was compacted in three layers, and each layer was compacted for 30 blows. The surface of the first and second layers was scraped to avoid layering before the next layer was compacted. The compaction was conducted by using a hammer of 0.51 kg that fell freely along a steel rod at a height of 270 mm. After compaction, the specimen was demolded by a jack. The demolded specimen was sealed with a plastic film and then cured at room temperature for the required curing ages. The unit compaction work was 606.73 kJ/m^3 , which was close to 605.60 kJ/m^3 of the standard Proctor test [42].

Figures 1 and 2 show the compaction curves of Ca (and Mg)-sulfate-soils with and without curing agents, which reflect the relationship between the water content and dry

density for each soil. In Figure 1, the optimal moisture content of the Ca-sulfate-soil with GGBS-MgO was significantly higher than that of the untreated soil (i.e., 31%). Its optimal moisture content raised and then stabilized with the increased MgO content. The optimal moisture content was 32% for the soil with GGBS:MgO = 9:1, 34% for GGBS:MgO = 8:2, 7:3 and 6:4, and 36% for the cement-treated soil. Figure 2 shows that the optimal moisture content of Mg-sulfate-soil also increased and then remained stable with the increase in the MgO content. The GGBS-MgO-treated soil required a higher moisture content (28–30%) than the untreated soil (26%) to reach the maximum dry density, while the cement-treated soil had a higher optimal moisture content of 34%. The specimens for the swelling and UCS tests were prepared at their respective optimal moisture content.

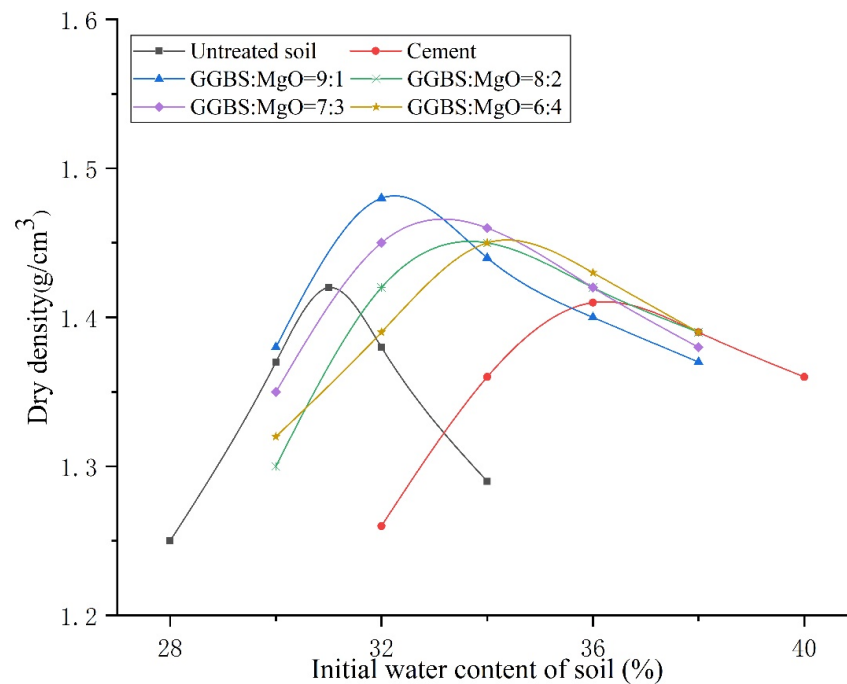


Figure 1. Compaction curves of Ca-sulfate-soil with and without curing agents.

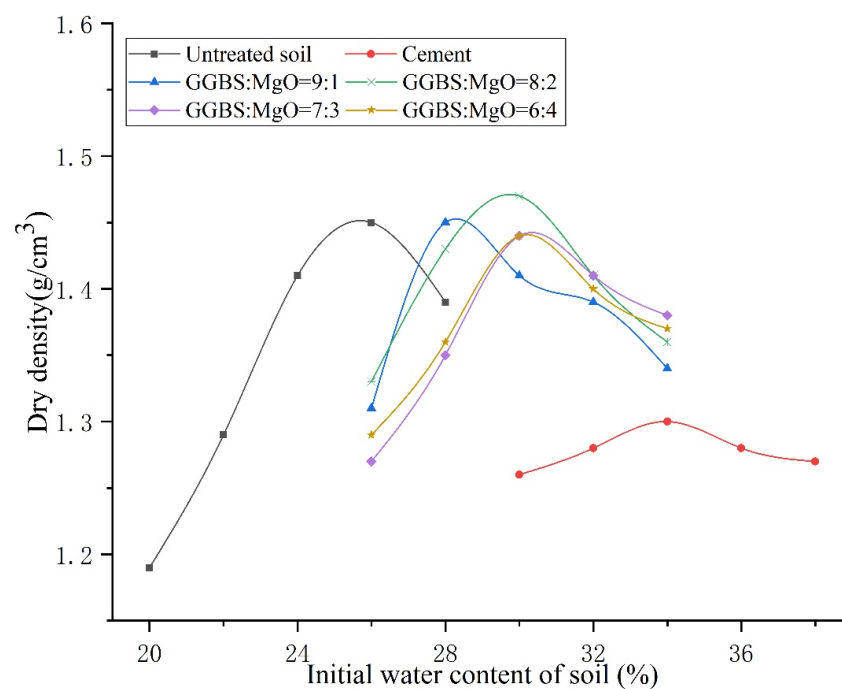


Figure 2. Compaction curves of Mg-sulfate-soil with and without curing agents.

2.2.2. Experimental Studies

Similar to previous studies [17,18,43], the swelling test used in this study was a 3-dimensional swelling test, and only vertical swelling was recorded. After the specimen was made, it was sealed and cured for 7 days, and the swelling of the specimen was recorded during the curing process. After 7 days of curing, the specimen was immersed in water for the swelling test. The recording interval on the first day was 15, 30, 60, 75, 180, 360, and 720 min, and then 1440 min until the swelling was stable for three consecutive days. However, if the swelling finished less than 28 days after the specimen was soaked in water, the test would end on the 28th day. The schematic for the device of the swelling test was shown in Figure 3. The specimen was placed in a beaker with a flat bottom, and a porous stone was placed on the top of the specimen. The tap water was used for the swelling test, which was added into the beaker until the water level reached half of the height of the porous stone.

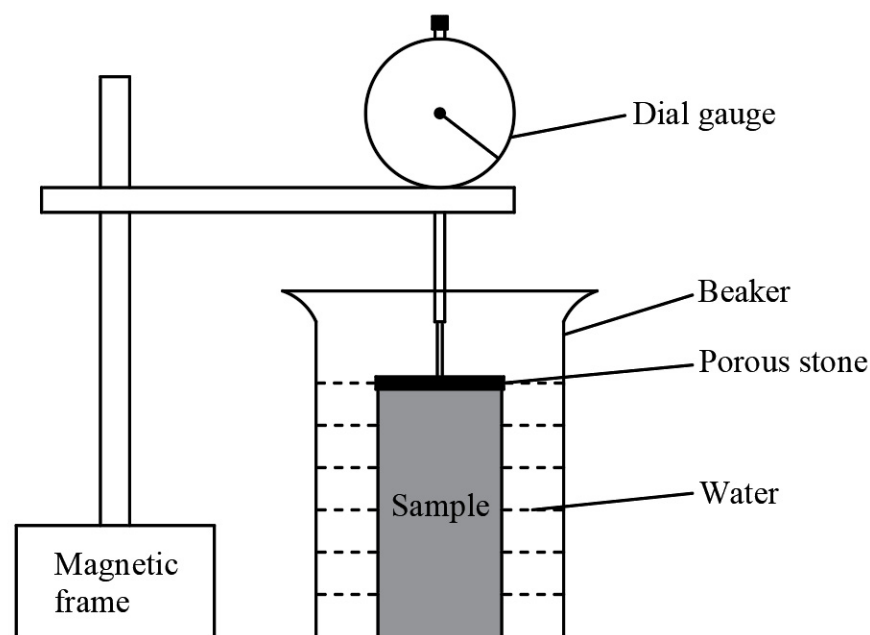


Figure 3. Schematic for the swelling test.

After the swelling test, the UCS test was carried out on the soaked specimen. For the specimens not used in the swelling test, they were subjected to the UCS test after being cured to the required curing ages (i.e., 7 and 28 days of curing). A universal testing machine was used for the UCS test. The maximum load was 20 kN and the loading rate of the device was 1 mm/min, determined according to [44]. The UCS test was conducted in replicate, and the variation between the two replicates was between 4% and 20%, which was regarded as an effective result. The crushed specimens after the UCS test were collected and put into the YTLG-12C vacuum freeze dryer, produced by Shanghai Yetuo Technology Co., Ltd., for drying. The dried samples were further processed for mineralogical and micro-structural tests. Parts of the dry samples were used for the SEM test and some were ground to pass through a 0.075 mm sieve for the XRD test. The XRD test was performed by using a Dutch Empyrean X-ray diffractometer, running at 45 kV, 40 mA. The SEM test was conducted by using the Hitachi SU8010 high-resolution field emission scanning electron microscope, to investigate the surface morphology of the samples.

3. Results and Discussion

3.1. Vertical Swelling

Figure 4 shows the swelling of the Ca-sulfate-soil with curing agents. The treated soils shrank during the curing period. When in contact with water, the soils treated with cement

and GGBS:MgO = 9:1, 8:2, and 7:3 swelled immediately and their swelling percentages tended to be stable in the first week. However, the swelling of the soil treated with 6:4 increased significantly and became stable after 8 weeks. The soil with cement presented a swelling percentage of 1.30%, which was between the percentages of the soils with GGBS-MgO. For the soils treated with GGBS-MgO, the swelling percentage increased with the decrease in the ratio of GGBS-MgO from 9:1 to 6:4. The swelling percentage of the soil reached a maximum value of 14.30% with GGBS:MgO = 6:4. The ratio of the soils with 9:1 and 8:2 had a swelling percentage of ~0.15%, less than 1.30% of cement-treated soil. Therefore, with suitable GGBS:MgO ratios (e.g., 9:1 and 8:2), the binder of GGBS-MgO could better suppress the swelling than cement for the Ca-sulfate-soil. These results were in agreement with the study of [18], who found that the swelling percentage increased with the decreased GGBS-MgO ratio when highly reactive MgO was used.

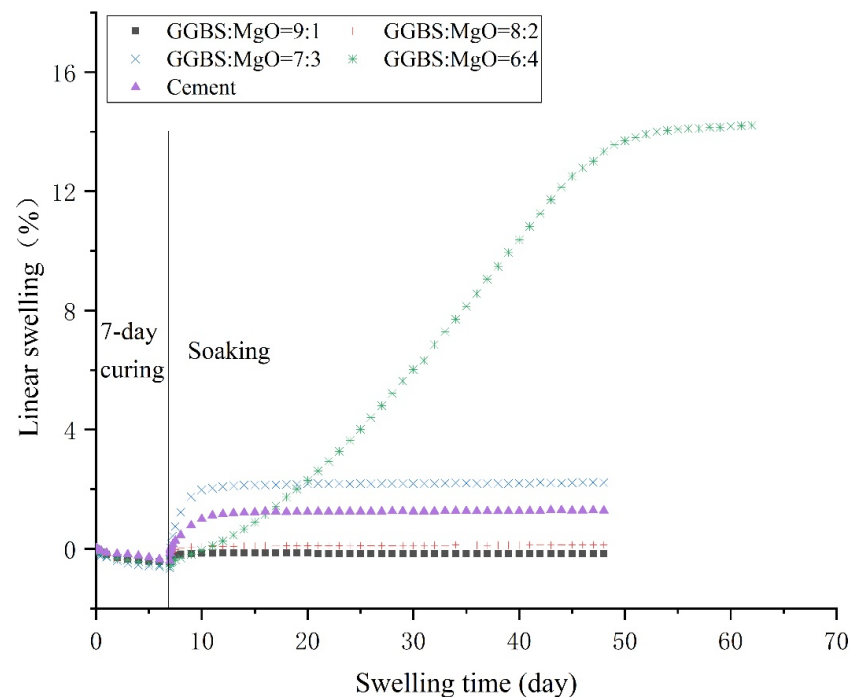


Figure 4. Vertical swelling percentages of Ca-sulfate-soil treated with cement and GGBS-MgO.

Figure 5 gives the swelling of Mg-sulfate-soil with GGBS-MgO and cement. During curing, each treated soil also shrank. In the soaking stage, it generally took a longer time for the treated soils to reach a stable swelling compared to those treated Ca-sulfate-soils. The swelling percentages of the soils with GGBS:MgO = 9:1, 7:3, and 6:4 tended to be stable in 4 weeks, while those of the soils with GGBS:MgO = 8:2 and cement stabilized in 8 weeks. In terms of the final swelling percentage, the cement-treated Mg-sulfate-soils had a value of 5.39%, much higher than that of the Ca-sulfate-soils with cement (1.30%). With the stabilization of GGBS-MgO, the Mg-sulfate-soil had a different trend with the Ca-sulfate-soil. The swelling percentage increased with the increased GGBS-MgO ratio and produced a maximum value of 5.13% at GGBS:MgO = 9:1, while a minimum value of 0.02% at GGBS:MgO = 6:4.

Similar to Ca-sulfate-soil, Mg-sulfate-soil treated with cement showed a higher swelling percentage than the soil treated with GGBS-MgO, which indicated that GGBS-MgO had a better capability to resist swelling than cement for the Mg-sulfate-soil at a proper GGBS:MgO ratio.

A comparison between stabilized Ca-sulfate-soils and Mg-sulfate-soils illustrated that as long as suitable GGBS:MgO ratios were achieved, the swelling of the two types of sulfate-bearing soils could be suppressed to the largest extent, e.g., 9:1 for Ca-sulfate-soils and 6:4 for Mg-sulfate-soils. However, the trend that the swelling varied with the GGBS:MgO

ratios was the opposite; that is, the lowest swelling occurred at GGBS:MgO = 9:1 for Ca-sulfate-soils while it occurred at 6:4 for Mg-sulfate-soils. These two types of soils showed significantly different swelling percentages in the presence of cement. A lower swelling of 1.30% was observed for Ca-sulfate-soil, while 5.39% occurred for Mg-sulfate-soils.

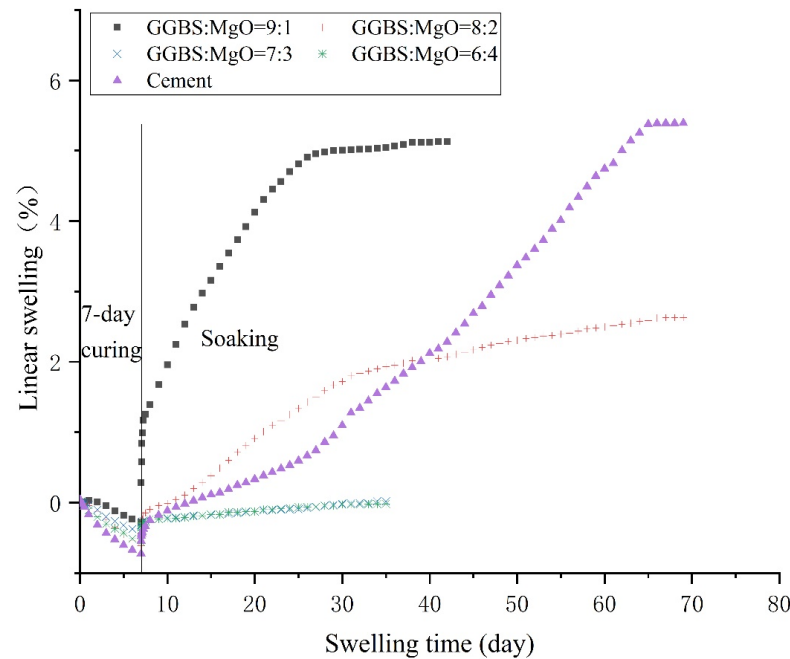


Figure 5. Vertical swelling percentages of Mg-sulfate-soil treated with cement and GGBS-MgO.

3.2. UCS Results

Figure 6 shows the UCS of the treated Ca-sulfate-soils at different curing and soaking stages. The curing stage referred to the 7 and 28 days curing without soaking and after soaking referred to the end of the swelling test. Some specimens collapsed after the swelling test and could not be used for the UCS test, so the UCS after soaking was recorded as 0.

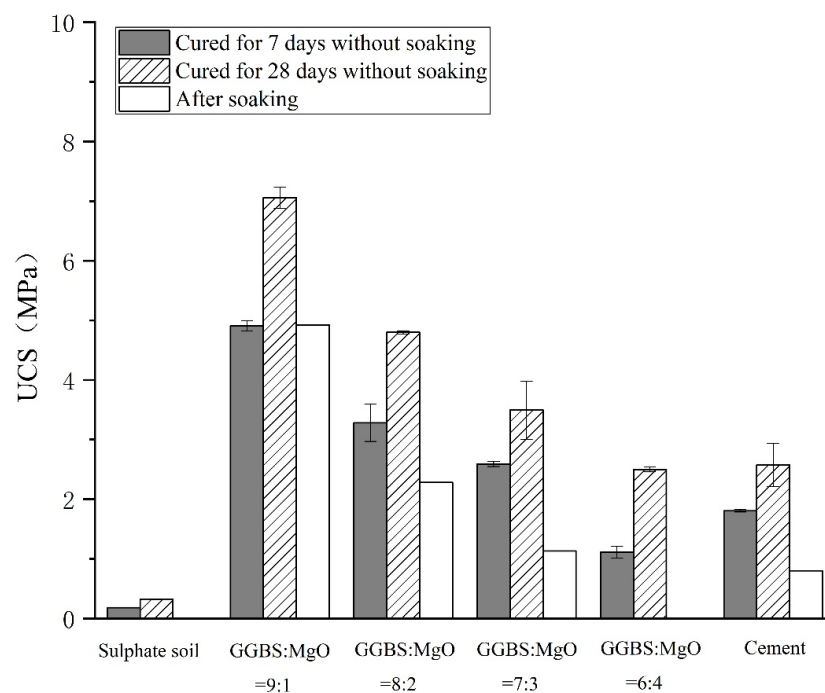


Figure 6. UCS of treated Ca-sulfate-soil at different curing and soaking stages.

The strength of the untreated Ca-sulfate-soil was only 0.18 MPa; when the curing age increased, the strength increased to 0.33 MPa. This may be because the calcium ion in gypsum will consume some water with the increase in time, which will make the sample harder and thus improve the strength. Additionally, the strength was significantly improved after the addition of the curing agents. As for the specimen without soaking, the 7 and 28 days UCS reached the highest of 4.91 and 7.06 MPa, respectively, at GGBS:MgO = 9:1, and then reduced with the decrease in the GGBS-MgO ratio. This was in line with the result mentioned by [33] that over a high MgO content had a negative impact on the strength performance of soils with GGBS-MgO. Both GGBS-MgO and cement-treated soils showed a significant increase in UCS at 28 days curing compared to 7 days of curing. However, the soils treated with GGBS:MgO = 9:1, 8:2, and 7:3 always had a higher UCS than those treated with cement at different curing and soaking stages (7, 28 days curing, or after soaking).

After soaking, the Ca-sulfate-soils with GGBS:MgO = 9:1, 8:2, and 7:3 all had higher UCS than the cement-treated soil (0.8 MPa). The highest UCS was achieved at GGBS:MgO = 9:1 which reached 4.92 MPa, while the GGBS:MgO = 6:4 treatment lost its load-bearing capacity, and thus was recorded as 0. Therefore, this result illustrated that the binder of GGBS-MgO, with proper GGBS:MgO ratios (e.g., 9:1 to 7:3), could more effectively improve the strength than cement for the Ca-sulfate-soil.

Figure 7 provides the UCS of the treated Mg-sulfate-soils at different curing and soaking stages. Without soaking, both 7 and 28 days UCS decreased from the ratio of GGBS:MgO = 9:1 to 8:2 and then increased with the decreased ratio of GGBS-MgO. Such UCS (with a range of 0.24–0.85 MPa) were lower than those (0.85 and 1.21 MPa) of the cement-treated soils at the corresponding curing age. After soaking, the UCS of all of the treated Mg-sulfate-soils significantly decreased, to a range of 0–0.22 MPa, and cement-treated soil still had the highest UCS among all of the treated soils. This illustrated that for Mg-sulfate-soil, GGBS-MgO was less effective than cement in improving the strength.

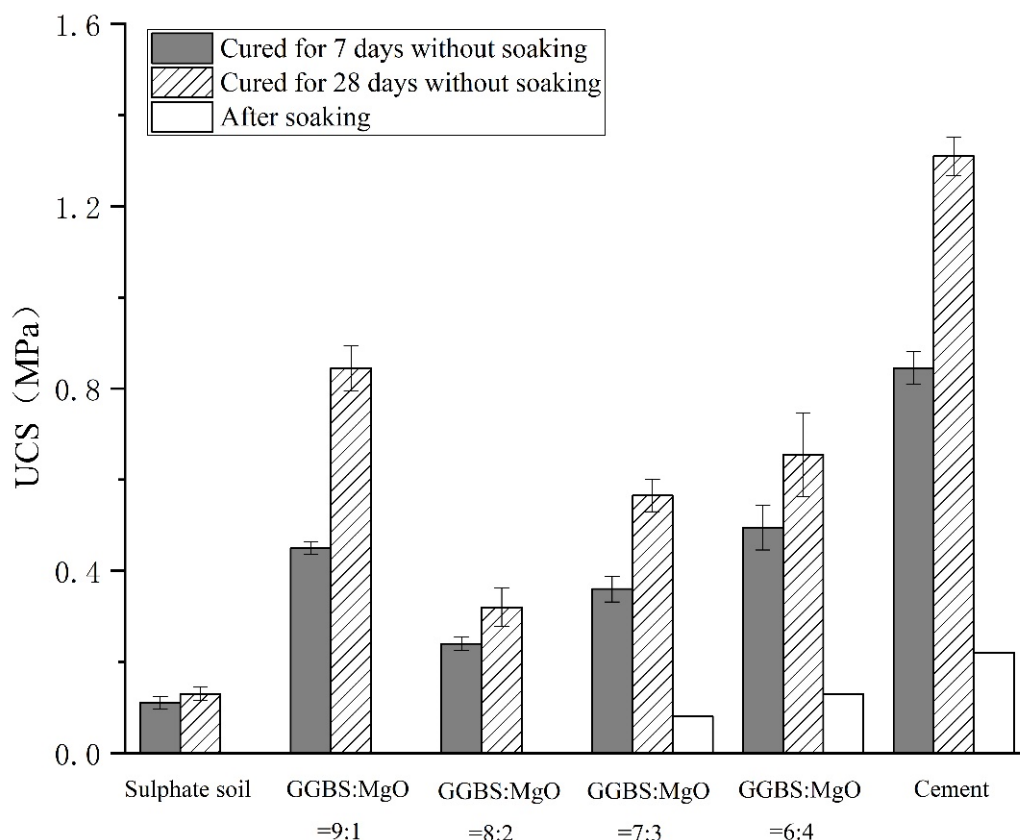


Figure 7. UCS of treated Mg-sulfate-soil at different curing and soaking stages.

In general, the UCS of Mg-sulfate-soils was much lower than that of the Ca-sulfate-soils after the stabilization of GGBS-MgO and cement. With the treatment of GGBS-MgO, the strength of the Ca-sulfate-soil ranged from 1.11 to 7.06 MPa after 7 and 28 days of curing, while the strength of Mg-sulfate-soil only ranged from 0.24 to 0.85 MPa. For GGBS-MgO-treated sulfate-bearing soil, the highest after-soaking strength of the Ca-sulfate-soil could reach 4.92 MPa, which was much higher than that of the Mg-sulfate-soil (only 0.13 MPa). The cement-treated Ca-sulfate-soils had a UCS of 1.51, 2.58, and 0.80 MPa at 7 and 28 days of curing, and after soaking, respectively, while the lower UCS of 0.85, 1.21, and 0.22 MPa occurred for cement-treated Mg-sulfate-soils at the corresponding stages. This result shows that the type of sulfate-bearing soil had a significant effect on the strength of the soils stabilized with GGBS-MgO or cement. It seemed that the introduction of Ca^{2+} contained in the soils facilitated the strength enhancement of the stabilized sulfate-bearing soils.

3.3. XRD and SEM

Figure 8 shows the XRD results of pure kaolin, as well as Ca-sulfate-soils treated with GGBS:MgO = 9:1, 6:4, and cement after soaking. The XRD pattern of pure kaolin was provided for a comparison. The kaolinite and quartz that occurred in all soils were from kaolin. CSH, detected at ~ 30 degrees in all treated soils, was mainly responsible for the development of strength [17,18,34]. Ettringite was not confidently detected in the soil treated with GGBS:MgO = 9:1, but it was presented in the soil with 6:4, shown as a weak peak at 9.2° and 23° . The presence of ettringite in the cement-treated soil could not have been surely identified as the peaks for CSH, and ettringite might overlap at 23° . It is notable that magnesium silicate hydrate (MSH) was formed in the soil stabilized with the GGBS:MgO = 6:4 due to the fact that there was sufficient Mg involved in the production of MSH in this soil [31,45,46].

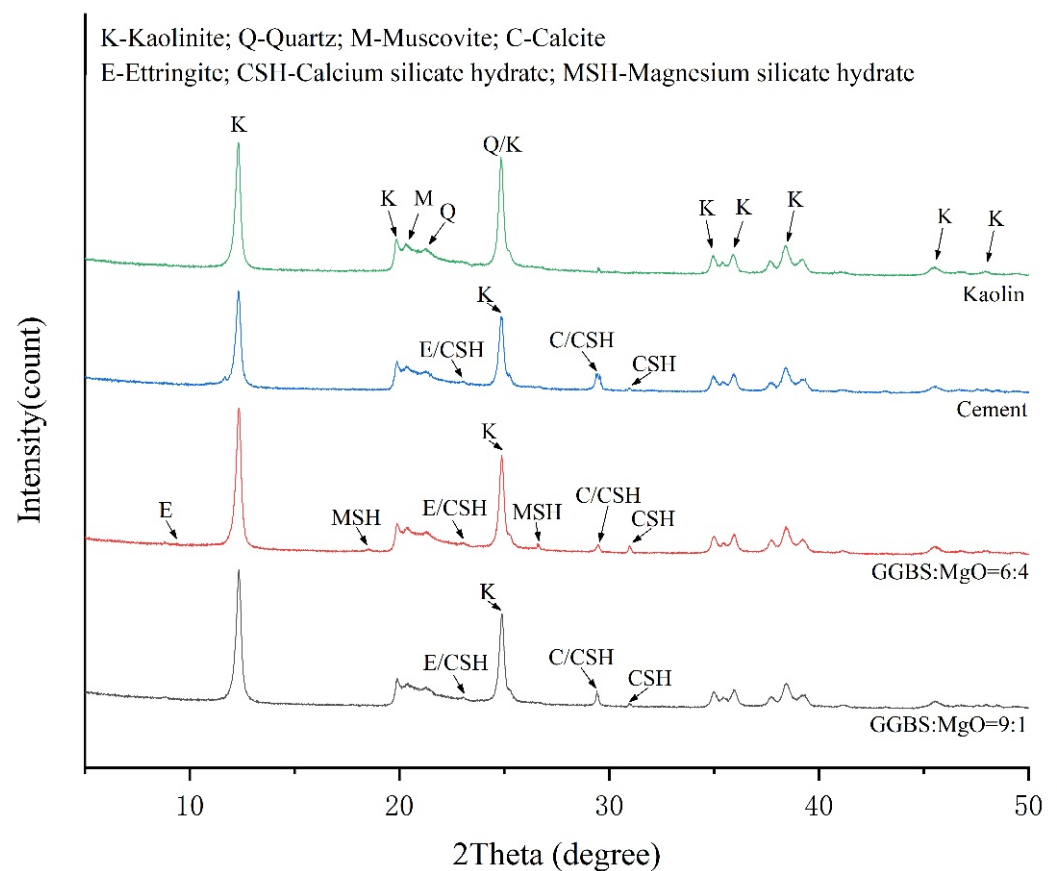


Figure 8. XRD patterns of kaolin and Ca-sulfate-soils treated with cement, GGBS:MgO = 6:4, and 9:1 after soaking.

Figure 9 presents the XRD results of the Mg-sulfate-soils treated with GGBS:MgO = 9:1, 6:4, and cement after soaking. All treated soils had a peak of CSH at ~ 30 degrees, which was a source of strength. Ettringite was found in the cement-treated soil, but not in the GGBS-MgO-treated soil. MSH was produced in the soils with GGBS:MgO = 9:1 and 6:4. This was probably attributed to that excessive Mg^{2+} hydrolyzed from MgSO_4 and MgO , which reacted with some OH^- to form $\text{Mg}(\text{OH})_2$, which further reached with amorphous SiO_2 to form MSH, which was a gel with limited cementation properties [46,47]. Additionally, lower CSH peaks, indicating less CSH, appeared at 30° and 32° for Mg-sulfate-soils after GGBS-MgO and a cement treatment, compared to the Ca-sulfate-soils. Less CSH and the formation of MSH caused the lower strength of the stabilized Mg-sulfate-soils than that of the stabilized Ca-sulfate-soils.

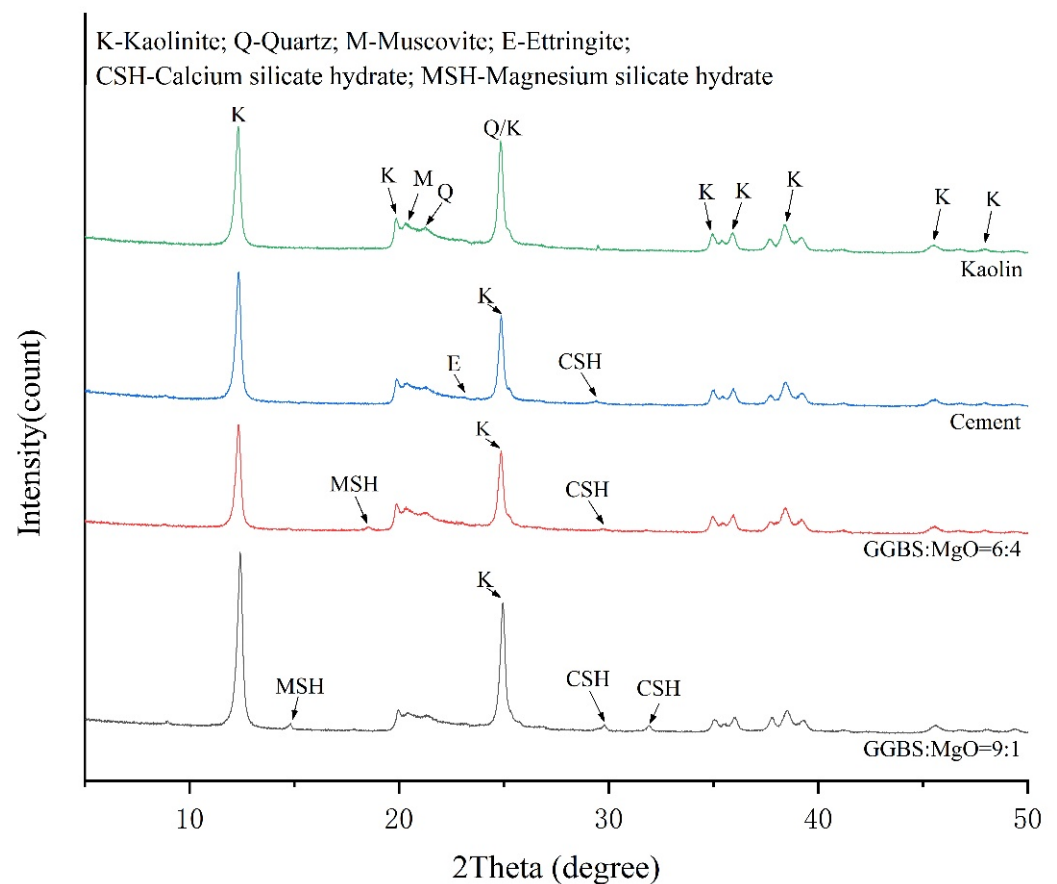


Figure 9. XRD patterns of kaolin and Mg-sulfate-soils treated with cement, GGBS:MgO = 6:4, and 9:1 after soaking.

The SEM test was conducted on the same samples used in the XRD test. Each sample was examined thoroughly by the SEM machine to seek ettringite, and the representative images were presented as shown in Figure 10. Figure 10a–f shows the SEM photos of the Ca-sulfate-soils and Mg-sulfate-soils, respectively. No significant ettringite was observed in the Ca-sulfate-soil with GGBS:MgO = 9:1 (Figure 10a), while significant ettringite was found in the soil treated with GGBS:MgO = 6:4 and cement (Figure 10b,c). Regarding the Mg-sulfate-soils, no ettringite was found after the stabilization of GGBS-MgO (Figure 10d,e). Nevertheless, ettringite was formed in the cement-treated soil, as seen in Figure 10f. These observations confirmed the results observed by XRD.

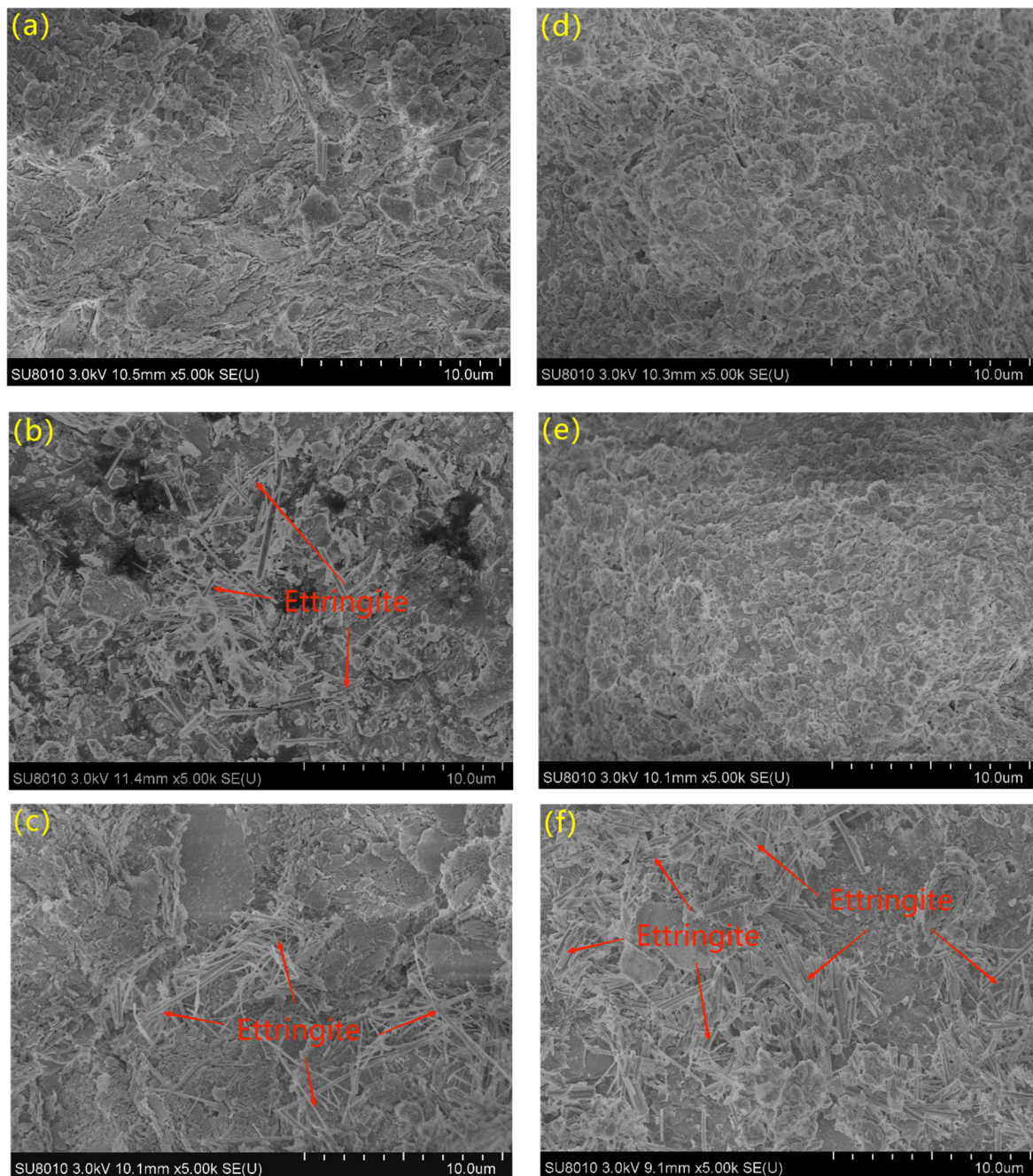


Figure 10. SEM photos of treated soils after soaking: Ca-sulfate-soil treated by (a) GGBS:MgO = 9:1; (b) GGBS:MgO = 6:4, (c) cement; Mg-sulfate-soil treated by (d) GGBS:MgO = 9:1; (e) GGBS:MgO = 6:4; (f) cement.

4. Discussion of Mechanism

The above results indicated that the type of sulfate-bearing soils had a significant effect on the swelling, strength, mineralogical, and micro-structural properties of the soils stabilized with GGBS-MgO. If suitable GGBS:MgO ratios were achieved, the swelling of both sulfate-bearing soils could be decreased to a low level. However, the trend that the swelling varied with the decrease in the GGBS:MgO ratios was opposite; that is, the least swelling occurred at GGBS:MgO = 9:1 for Ca-sulfate-soils, while it occurred at 6:4 for Mg-sulfate-soils. The UCS of the Mg-sulfate-soils was much lower than that of the Ca-sulfate-soils after the stabilization of GGBS-MgO, irrespective of the curing or soaking

stage. It was inferred that the cations (e.g., Ca^{2+} and Mg^{2+}) sourced from sulfate-bearing soils caused the difference in the properties of the stabilized soils.

Ca^{2+} hydrolyzed from Ca-sulfate-soils facilitated the occurrence of CSH and led to the formation of ettringite, particularly when excessive MgO was used for the GGBS activation, as shown in Figures 8 and 10. CSH was formed significantly and no ettringite was detectable in the soil with 9:1. This result indicated that most Ca^{2+} contributed to the synthesis of CSH, causing the enhancement in the strength of the Ca-sulfate-soils treated with GGBS:MgO = 9:1. CSH was detected in all stabilized soils, and it had been confirmed that CSH was the main binding product of GGBS-MgO [34,48]. With the decrease in the GGBS:MgO ratio (meaning the increase in the MgO content), MSH and a small amount of ettringite occurred, as shown in Figure 11a,b. This might be attributed to the competition between Mg^{2+} and Ca^{2+} in binding silicate hydrate. MgO was firstly supplied for the GGBS activation to form silicate hydrate [30], which would combine Mg^{2+} or Ca^{2+} to synthesize MSH or CSH, respectively. As Ca^{2+} was more readily replaced by Mg^{2+} , MSH would be more likely to be produced at low GGBS:MgO ratios (e.g., 6:4) [47,49], and hence free Ca^{2+} was left in the Ca-sulfate-soils with 6:4. Some Ca^{2+} would participate in the formation of CSH after Mg^{2+} was completely consumed, and other Ca^{2+} would go to the synthesis of ettringite. Hence, when the GGBS:MgO ratio decreased to 6:4, MSH, CSH, and ettringite were all identified in its XRD result (Figure 8). The binding capacity of MSH was weaker than that of CSH [50,51], and a small amount of MSH was distributed between CSH [47], which weakened the anti-swelling property of the stable soil. The trace of ettringite can be clearly seen from Figure 10, which was the cause of the cement soil swelling. When lime-GGBS was used, ettringite will also be produced in stabilized soil [3,17,31,52].

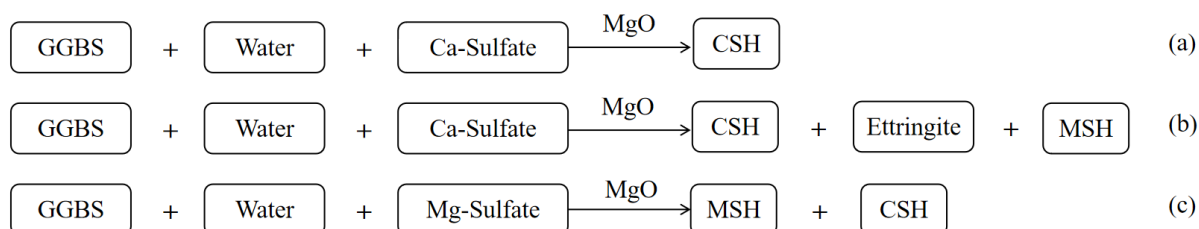


Figure 11. Schematic of mechanism for (a) and (b) GGBS-MgO-treated Ca-sulfate-soils, (c) GGBS-MgO-treated Mg-sulfate-soils.

As for Mg-sulfate-soils, Mg^{2+} occurred in a large amount because the hydrolysis of MgSO_4 contained in the soils. With the addition of GGBS-MgO, MgO would also be used for the GGBS activation to form silicate hydrate. Likewise, due to the competition of Mg^{2+} and Ca^{2+} , silicate hydrate would more easily bind Mg^{2+} in comparison to Ca^{2+} , resulting in most silicate hydrate being consumed for the formation of MSH instead of CSH and ettringite, as shown in Figure 11c. Hence, MSH and less CSH, formed in the soils stabilized with GGBS-MgO, caused a lower strength of the stabilized Mg-sulfate-soils than that of the stabilized Ca-sulfate-soils (Figures 6 and 7). As MSH existed in stabilized Mg-sulfate-soils in a dominant role, which had a dominant effect on the strength and swelling of the soil, more MSH formed in the stabilized soils with a higher MgO content (e.g., 6:4) would have a higher strength in comparison to those with a lower MgO content (e.g., 9:1 to 7:3), despite the limited cementation capability that MSH had. Considering that insignificant ettringite was formed in such soils, the swelling should be induced by the water absorption of the soil particles. Therefore, a higher soil strength meant a higher capability of resisting water absorption-induced swelling, which was the reason why the Mg-sulfate-soil with 6:4 had the lowest swelling.

5. Conclusions

As long as suitable GGBS:MgO ratios were achieved, the swelling of the two types of sulfate-bearing soils could be suppressed to the largest extent, e.g., 9:1 for Ca-sulfate-

soils and 6:4 for Mg-sulfate-soils. However, the trend that the swelling varied with the decrease in the GGBS:MgO ratios was opposite; that is, the lowest swelling occurred at GGBS:MgO = 9:1 for Ca-sulfate-soils, while it occurred at 6:4 for Mg-sulfate-soils. In contrast, these two types of soils showed significantly different swelling percentages in the presence of cement. A lower swelling of 1.30% was observed for Ca-sulfate-soil, while 5.39% occurred for Mg-sulfate-soils. The UCS of the Mg-sulfate-soils was much lower than that of the Ca-sulfate-soils after the stabilization of GGBS-MgO, irrespective of the curing or soaking stage.

CSH significantly occurred in the Ca-sulfate-soils treated by GGBS-MgO. Ettringite was not observed in the soil with GGBS-MgO = 9:1, but it was observed when excessive MgO was used, i.e., at 6:4. Therefore, the ettringite-induced swelling developed for the ratio from 8:2 to 6:4 and caused the reduction in the strength. Compared to the stabilized Ca-sulfate-soils, MSH and less CSH were formed in the Mg-sulfate-soils stabilized with GGBS-MgO, which caused the reduction in the strength of the stabilized Mg-sulfate-soils. No ettringite was formed in such soils, so the swelling should be induced by the water absorption of the soil particles. Mg-sulfate-soils with a higher strength (e.g., 6:4) had a higher capability to resist water absorption-induced swelling.

It was deduced that the cations (e.g., Ca^{2+} and Mg^{2+}) sourced from sulfate-bearing soils, competing to bind silicate hydrate, caused the difference in the swelling and strength properties of the stabilized soils with GGBS-MgO.

Author Contributions: W.L.: conceptualization, methodology, and writing—review and editing. R.L.: writing—original draft, writing—review and editing, and investigation. Y.C.: data curation and investigation. H.X.: funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This study was funded by the Hubei University of Technology [Grant No. 430100319], Hubei, China and the Innovation Group Project of Hubei Science and Technology Department [Grant No. 2020CFA046] and Outstanding Young and Middleaged Science and Technology Innovation Team of colleges and universities in Hubei Province [Grant No. T2022010].

Data Availability Statement: If readers require the data from this article, please contact the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Lv, Q.; Jiang, L.; Ma, B.; Zhao, B.; Huo, Z. A study on the effect of the salt content on the solidification of sulfate saline soil solidified with an alkali-activated geopolymer. *Constr. Build. Mater.* **2018**, *176*, 68–74. [\[CrossRef\]](#)
2. Zhang, W.; Junze, M. LianTang, Experimental study on shear strength characteristics of sulfate saline soil in Ningxia region under long-term freeze-thaw cycles. *Cold Reg. Sci. Technol.* **2019**, *160*, 48–57. [\[CrossRef\]](#)
3. Wild, S.; Kinuthia, J.M.; Jones, G.I. Suppression of swelling associated with ettringite formation in lime stabilized sulphate bearing clay soils by partial substitution of lime with ground granulated blastfurnace slag. *Eng. Geol.* **1999**, *51*, 257–277. [\[CrossRef\]](#)
4. Puppala, A.J.; Griffin, J.A.; Hoyos, L.R. Studies on Sulfate-Resistant Cement Stabilization Methods to Address Sulfate-Induced Soil Heave. *J. Geotech. Geoenviron. Eng.* **2004**, *130*, 391–402. [\[CrossRef\]](#)
5. Zhao, N.; Wang, S.; Wang, C.; Quan, X.; Yan, Q.; Binbin, L. Study on the durability of engineered cementitious composites (ECCs) containing high-volume fly ash and bentonite against the combined attack of sulfate and freezing-thawing (F-T). *Constr. Build. Mater.* **2020**, *233*, 117313. [\[CrossRef\]](#)
6. Aldaood, A.; Bouasker, M.; Al-Mukhtar, M. Mechanical Behavior of Gypseous Soil Treated with Lime. *Geotech. Geol. Eng.* **2021**, *39*, 719–733. [\[CrossRef\]](#)
7. Kalıpcılar, İ.; Mardani, A.; Sezer, A.; Sezer, G.; Altun, S. Sustainability of cement-stabilised clay: Sulfate resistance. *Eng. Sustain.* **2018**, *171*, 254–274. [\[CrossRef\]](#)
8. Adeleke, B.; Kinuthia, J.; Oti, J. Strength and Swell Performance of High-Sulphate Kaolinite Clay Soil. *Sustainability* **2020**, *12*, 10164. [\[CrossRef\]](#)
9. Rollings, R.; Burkes, J.; Rollings, M. Sulfate Attack on Cement-Stabilized Sand. *J. Geotech. Geoenviron. Eng.* **1999**, *125*, 364–372. [\[CrossRef\]](#)
10. Harris, J.; Sebesta, S.; Scullion, T. Hydrated Lime Stabilization of Sulfate-Bearing Vertisols in Texas. *Transp. Res. Rec.* **2004**, *1868*, 31–39. [\[CrossRef\]](#)
11. Hunter, D. Lime-Induced Heave in Sulfate-Bearing Clay Soils. *J. Geotech. Eng.* **1988**, *114*, 150–167. [\[CrossRef\]](#)

12. Mitchell, J. Practical Problems from Surprising Soil Behavior. *J. Geotech. Eng.* **1986**, *112*, 255–289. [\[CrossRef\]](#)
13. Kampala, A.; Jitsangiam, P.; Pimraksa, K.; Chindaprasirt, P. An investigation of sulfate effects on compaction characteristics and strength development of cement-treated sulfate bearing clay subgrade. *Road Mater. Pavement Des.* **2020**, *22*, 2396–2409. [\[CrossRef\]](#)
14. Wang, P.; Ye, Y.; Zhang, Q.; Liu, J.; Yao, J. Investigation on the sulfate attack-induced heave of a ballastless track railway subgrade. *Transp. Geotech.* **2020**, *23*, 100316. [\[CrossRef\]](#)
15. Kota, P.; Hazlett, D.; Perrin, L. Sulfate-Bearing Soils: Problems with Calcium-Based Stabilizers. *Transp. Res. Rec.* **1996**, *1546*, 62–69. [\[CrossRef\]](#)
16. Ehwailat, K.; Mohamad Ismail, M.A.; Ezreig, A. Novel Approach for Suppression of Ettringite Formation in Sulfate-Bearing Soil Using Blends of Nano-Magnesium Oxide, Ground Granulated Blast-Furnace Slag and Rice Husk Ash. *Appl. Sci.* **2021**, *11*, 6618. [\[CrossRef\]](#)
17. Li, W.; Yi, Y.; Puppala, A.J. Utilization of carbide slag-activated ground granulated blastfurnace slag to treat gypseous soil. *Soils Found.* **2019**, *59*, 1496–1507. [\[CrossRef\]](#)
18. Li, W.; Yi, Y.; Puppala, A.J. Suppressing Ettringite-Induced Swelling of Gypseous Soil by Using Magnesia-Activated Ground Granulated Blast-Furnace Slag. *J. Geotech. Geoenviron. Eng.* **2020**, *146*, 06020008. [\[CrossRef\]](#)
19. Yi, Y.; Zheng, X.; Liu, S.; Al-Tabbaa, A. Comparison of reactive magnesia- and carbide slag-activated ground granulated blastfurnace slag and Portland cement for stabilisation of a natural soil. *Appl. Clay Sci.* **2015**, *111*, 21–26. [\[CrossRef\]](#)
20. Jegandan, S.; Al-Tabbaa, A.; Liska, M.; Osman, A. Sustainable binders for soil stabilisation. *Proc. Ice—Ground Improv.* **2010**, *163*, 53–61. [\[CrossRef\]](#)
21. Islam, S.; Haque, A.; Wilson, S. Effects of Curing Environment on the Strength and Mineralogy of Lime-GGBS-Treated Acid Sulphate Soils. *J. Mater. Civ. Eng.* **2014**, *26*, 1003–1008. [\[CrossRef\]](#)
22. Adeleke, B.; Kinuthia, J.; Oti, J. Impacts of MgO waste:GGBS formulations on the performance of a stabilised natural high sulphate bearing soil. *Constr. Build. Mater.* **2022**, *315*, 125745. [\[CrossRef\]](#)
23. Gokul, V.; Steffi, D.A.; Kaviya, R.; Harni, C.V.; Dharani, S.M.A. Alkali activation of clayey soil using GGBS and NaOH. *Mater. Today Proc.* **2020**, *43*, 1707–1713. [\[CrossRef\]](#)
24. Eyo, E.U.; Abbey, S.J.; Ngambi, S.; Ganjian, E.; Coakley, E. Incorporation of a nanotechnology-based product in cementitious binders for sustainable mitigation of sulphate-induced heaving of stabilised soils. *Eng. Sci. Technol. Int. J.* **2020**, *24*, 436–448. [\[CrossRef\]](#)
25. Rahmat, N.; Kinuthia, J. Sustainable soil stabilisation with blastfurnace slag—A review. *Proc. Ice—Constr. Mater.* **2010**, *163*, 157–165. [\[CrossRef\]](#)
26. Wild, S.; Kinuthia, J.; Robinson, R.; Humphries, I. Effects of Ground Granulated Blast Furnace Slag (GGBS) on the Strength and Swelling Properties of Lime-Stabilized Kaolinite in the Presence of Sulphates. *Clay Miner.* **1996**, *31*, 423–433. [\[CrossRef\]](#)
27. Çelik, E.; Nalbantoglu, Z. Effects of ground granulated blastfurnace slag (GGBS) on the swelling properties of lime-stabilized sulfate-bearing soils. *Eng. Geol.* **2013**, *163*, 20–25. [\[CrossRef\]](#)
28. Gupta, S.; Seehra, S.S. Studies on lime-granulated blast furnace slag as an alternate binder to cement. *Highw. Res. Bull. (New Delhi)* **1989**, *38*, 81–97.
29. Li, W.; Yi, Y.; Puppala, A. Effects of curing environment and period on performance of lime-GGBS-treated gypseous soil. *Transp. Geotech.* **2022**, *37*, 100848. [\[CrossRef\]](#)
30. Yi, Y.; Liska, M.; Jin, F.; Al-Tabbaa, A. Mechanism of reactive magnesia-ground granulated blastfurnace slag (GGBS) soil stabilisation. *Can. Geotech. J.* **2016**, *53*, 773–782. [\[CrossRef\]](#)
31. Yi, Y.; Li, C.; Liu, S.; Jin, F. Magnesium sulfate attack on clays stabilised by carbide slag- and magnesia-ground granulated blast furnace slag. *Géotechnique Lett.* **2015**, *5*, 306–312. [\[CrossRef\]](#)
32. Yi, Y.; Li, C.; Liu, S. Alkali-Activated Ground-Granulated Blast Furnace Slag for Stabilization of Marine Soft Clay. *J. Mater. Civ. Eng.* **2015**, *27*, 04014146. [\[CrossRef\]](#)
33. Yi, Y.; Gu, L.; Liu, S.; Jin, F. Magnesia reactivity on activating efficacy for ground granulated blastfurnace slag for soft clay stabilisation. *Appl. Clay Sci.* **2016**, *126*, 57–62. [\[CrossRef\]](#)
34. Yi, Y.; Liska, M.; Al-Tabbaa, A. Properties and microstructure of GGBS–magnesia pastes. *Adv. Cem. Res.* **2014**, *26*, 114–122. [\[CrossRef\]](#)
35. Behnood, A. Soil and clay stabilization with calcium- and non-calcium-based additives: A state-of-the-art review of challenges, approaches and techniques. *Transp. Geotech.* **2018**, *17*, 14–32. [\[CrossRef\]](#)
36. Seco, A.; Miqueleiz, L.; Prieto, E.; Marcelino, S.; García, B.; Urmeneta, P. Sulfate soils stabilization with magnesium-based binders. *Appl. Clay Sci.* **2016**, *135*, 457–464. [\[CrossRef\]](#)
37. Du, Y.-J.; Bo, Y.-L.; Jin, F.; Liu, C.-Y. Durability of reactive magnesia-activated slag-stabilized low plasticity clay subjected to drying–wetting cycle. *Eur. J. Environ. Civ. Eng.* **2016**, *20*, 215–230. [\[CrossRef\]](#)
38. Yi, Y.; Liska, M.; Al-Tabbaa, A. Properties of Two Model Soils Stabilized with Different Blends and Contents of GGBS, MgO, Lime, and PC. *J. Mater. Civ. Eng.* **2014**, *26*, 267–274. [\[CrossRef\]](#)
39. Cheshomi, A.; Eshaghi, A.; Hassanpour, J. Effect of lime and fly ash on swelling percentage and Atterberg limits of sulfate-bearing clay. *Appl. Clay Sci.* **2017**, *135*, 190–198. [\[CrossRef\]](#)
40. Seco, A.; Castillo, J.M.; Espuelas, S.; Marcelino-Sádaba, S.; García, B. Sulphate soil stabilisation with magnesium binders for road subgrade construction. *Int. J. Pavement Eng.* **2020**, *23*, 1840–1850. [\[CrossRef\]](#)

41. Little, D.N.; Nair, S.; Herbert, B. Addressing sulfate-induced heave in lime treated soils. *J. Geotech. Geoenviron.* **2009**, *136*, 110–118. [[CrossRef](#)]
42. ASTM D698-12e2; Standard Test Methods for Laboratory Compaction Characteristics of Soil Using Standard Effort. ASTM International: West Conshohocken, PA, USA, 2012.
43. Wild, S.; Kinuthia, J. Effects of Some Metal Sulfates on the Strength and Swelling Properties of Lime-Stabilised Kaolinite. *Int. J. Pavement Eng.* **2001**, *2*, 103–120. [[CrossRef](#)]
44. ASTM D1633; Standard Method for Compressive Strength of Molded Soil-Cement Cylinders. ASTM International: West Conshohocken, PA, USA, 2017.
45. Abdalqader, A.; Jin, F.; Al-Tabbaa, A. Characterisation of reactive magnesia and sodium carbonate-activated fly ash/slag paste blends. *Constr. Build. Mater.* **2015**, *93*, 506–513. [[CrossRef](#)]
46. Zhang, T.; Vandeperre, L.J.; Cheeseman, C.R. Formation of magnesium silicate hydrate (M-S-H) cement pastes using sodium hexametaphosphate. *Cem. Concr. Res.* **2014**, *65*, 8–14. [[CrossRef](#)]
47. Xing, H.; Yang, X.; Xu, C.; Ye, G. Strength characteristics and mechanisms of salt-rich soil–cement. *Eng. Geol.* **2009**, *103*, 33–38. [[CrossRef](#)]
48. Jin, F.; Gu, K.; Abdollahzadeh, A.; Al-Tabbaa, A. Effects of Different Reactive MgOs on the Hydration of MgO-Activated GGBS Paste. *J. Mater. Civ. Eng.* **2015**, *27*, B4014001. [[CrossRef](#)]
49. Dehwah, H. Effect of Sulfate Concentration and Associated Cation Type on Concrete Deterioration and Morphological Change in Cement Hydrates. *Constr. Build. Mater.* **2007**, *21*, 29–39. [[CrossRef](#)]
50. Santhanam, M.; Cohen, M.; Olek, J. Sulfate attack research—Whither now? *Cem. Concr. Res.* **2001**, *31*, 845–851. [[CrossRef](#)]
51. Hekal, E.; Kishar, E.; Mostafa, H. Magnesium sulfate attack on hardened blended cement pastes under different circumstances. *Cem. Concr. Res.* **2002**, *32*, 1421–1427. [[CrossRef](#)]
52. Yi, Y.; Li, C.; Liu, S.; Al-Tabbaa, A. Resistance of MgO–GGBS and CS–GGBS stabilised marine soft clays to sodium sulfate attack. *Géotechnique* **2014**, *64*, 673–679. [[CrossRef](#)]

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